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"Only when we are brave enough to explore the darkness will we discover the infinite power of our light."

— Brené Brown

To my family, to Jeanette.

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When reporting on scientific methods and results, "we" is often used regardless of who actually sat in the lab or had the initial idea. I believe this does justice to all the people involved in the process leading a researcher all the way from education to publication. I now know from experience that it does "take a village to raise a [scientific] child", not to mention two.

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Abstract

Semiconductor materials have given rise to today's digital technology and consumer electronics. They have revolutionized data communication and storage. Sensors extend our senses and our capacity to probe the universe. Photovoltaic energy is one of the most available and affordable renewable energies. Widespread adoption is closely linked to the ability to process semiconductor materials and integrate them in devices industrially. Where flexibility and large surfaces are required, such as in smart textiles and distributed sensing, multifunctional fibers have a key role to play. Thermal drawing, the process which enabled global production of optical fibers, is ideally suited for the integration of multiple materials and functionalities in elongated structures in a scalable manner.

However, to extend the realm of accessible semiconductor architectures by thermal drawing, indepth understanding of the phenomena at play during heating and scaling down is required, such as the interplay between capillary forces and viscosity. Chapter 1 presents the challenges related to the processing and miniaturization of thin chalcogenide glass films and wires, namely capillary break-up and glass microstructure. By reaching micro- and nanoscale dimensions, photodetection sensitivity and response time can be improved by orders of magnitude. Fiber preform consolidation and drawing challenges are discussed. Strategies to overcome limitations are proposed. In Chapter 2, we report a scalable process to generate encapsulated flexible nanowire arrays with high aspect ratios and excellent tunable size and periodicity. Our strategy is to control nanowire self-assembly into 2D and 3D architectures via the filamentation of a textured thin film under anisotropic stretching. This is achieved by coupling soft lithography, glancing angle deposition, and thermal drawing to obtain well-ordered meters-long nanowires with diameters down to 50 nm. We demonstrate that the nanowire diameter and period of the array can be decoupled and manipulated independently. We propose a filamentation criterion and perform numerical simulations implementing destabilizing long-range Van der Waals interactions. Applied to high-index chalcogenide glasses, we show that this decoupling allows for tuning diffraction. In Chapter 3 we extend this work by harnessing Mie resonances and demonstrate the possibility to fabricate macroscopic meta-grating superstructures for nanophotonic applications. Lithographic processes are used on a fiber preform to benefit from both the resolution offered by clean room tools and the scaling inherent to thermal drawing. A 1D metalens design is simulated and constructed. Fabrication constraints are accounted for, which feeds back into optimizing the focusing efficiency. An application to microfluidic index sensing is proposed.

Next, we consider optoelectric architectures. In Chapter 4, we show contacting schemes for these fiber semiconducting architectures. This requires engineering of the rheological properties of electrodes for good shape retention at the temperatures necessary for chalcogenide glass drawing. Nanocomposites based on carbon nanoparticle fillers in a polymer matrix have the potential to fill this role. However, there is a trade-off between viscous and conducting properties, also impacting the possibility to obtain transparency with carbon nanotubes at small film thickness. An architecture preventing short circuits is proposed. Based on our understanding of the piezoresistive and capacitive behaviour of these nanocomposites, an application to in situ monitoring of the fabrication of resin composites is showed. As the multifunctional fiber sensor remains embedded in the fabricated part, decoupled temperature and strain sensing is demonstrated. In Chapter 5, we discuss geometries and solutions for the scalable integration of a semiconductor junction, necessary for photovoltaics and sensitive photodetection. A ZnSe/Se heterojunction is characterized and an architecture for high geometric control is obtained based on solid Zn co-feeding. Combined to the

highly viscous semi-transparent nanocomposites presented in the previous chapter, all building blocks are lined up for the realization of an in-fiber planar photodiode.

<u>Keywords</u>: Thermal drawing, Multimaterial fibers, Micro- and nanofabrication, Composites, Nanowire, Heterojunction, Electrode, Semiconductor, Optics, Photodiode, Metasurface

Résumé

Les matériaux semiconducteurs ont donné naissance aux technologies digitales modernes et à l'électronique grand public. Ils ont révolutionné la transmission et la sauvegarde de données. Les capteurs prolongent nos sens et notre capacité à sonder l'univers. L'énergie photovoltaïque est une des énergies renouvelables les plus accessibles. L'adoption massive de ces technologies dépend étroitement de la possibilité de façonner les matériaux semiconducteurs et de les intégrer industriellement dans dispositifs fonctionnels. Lorsque flexibilité et grandes surfaces sont de mises, comme dans les textiles intelligents et pour une distribution distribuée, les fibres multifonctionnelles ont un rôle clé à jouer. L'étirage à chaud, le procédé qui a permis la production mondiale de fibres optiques, est idéalement positionné pour l'intégration de multiples matériaux et fonctionnalités dans des structures allongées à grande échelle.

Toutefois, pour étendre la gamme des architectures semiconductrices accessibles par étirage à chaud, une compréhension profonde des phénomènes en jeu pendant le chauffage et le rétrécissement est requise, notamment du couplage entre forces capillaires et viscosité. Le Chapitre 1 présente les enjeux relatifs à la mise en forme et la miniaturisation de films fins et de fils de verres de chalcogénure, comme leur rupture capillaire et leur microstructure. En atteignant des dimensions micro- voire nanoscopique, la sensibilité de photodétection et le temps de réponse peuvent varier en ordres de grandeurs. La consolidation et l'étirage de la préforme de fibre sont considérées. Des stratégies pour en dépasser les limitations sont proposées. Dans le Chapitre 2, nous rendons compte d'un procédé de fabrication évolutif pour générer des réseaux de nanofils encapsulés flexibles avec de forts rapports d'aspect et un excellent contrôle de leurs taille et périodicité. Notre stratégie est de contrôler la formation spontanée des nanofils en architectures 2D et 3D via la filamentation d'un film fin texturé sous traction. Nous y parvenons en combinant lithographie souple, déposition de biais et étirage à chaud pour obtenir des mètres de nanofils ordonnés de diamètres allant jusqu'à 50 nm. Nous démontrons que le diamètre et la période du réseau peuvent être découplés et variés indépendamment. Nous proposons un critère de filamentation et des simulations implémentant des forces déstabilisantes de Van der Waals à longue distance. Appliqué aux verres de chalcogénure, nous montrons que ce découplage permet d'ajuster la diffraction. Dans le Chapitre 3, nous étendons ce travail afin d'exploiter des résonnances de Mie et démontrons la possibilité de fabriquer des superstructures macroscopiques en méta-réseaux pour des applications photoniques. Des procédés lithographiques sont employés sur une préforme de fibre pour bénéficier de la résolution des outils de salle blanche ainsi que l'effet d'échelle inhérent à l'étirage à chaud. Une méta-lentille 1D est simulée et conçue. Les contraintes de fabrication sont prises en compte, ce qui nourrit l'optimisation de l'efficacité de focalisation. Une application microfluidique en détection d'indice de réfraction est proposée.

Nous considérons ensuite des architecture optoélectroniques. Dans le Chapitre 4, nous montrons des mises en contact pour ces architectures de fibres semiconductrices. Cela requière l'ingénierie des propriétés rhéologiques des électrodes pour une bonne rétention des géométries aux températures requises pour l'étirage des verres de chalcogénure. Des nanocomposites à base de particules de carbone dans une matrice de polymère ont le potentiel pour répondre à ce besoin. Toutefois, il y a un nécessaire compromis entre viscosité et conductivité, impactant aussi la possibilité d'obtenir une transparence avec des nanotubes de carbones à faibles épaisseurs de film. Une architecture prévenant les courts-circuits est proposée. Basé sur notre compréhension du comportement piézorésistif et capacitif de ces nanocomposites, une application pour le suivi in situ de la fabrication de composites de résine est mise en avant. Le capteur à fibre multifonctionelle

reste dans la pièce fabriquée et le découplage des mesures thermiques et de déformation est démontré. Dans le Chapitre 5, nous traitons des géométries et solutions pour l'intégration à grande échelle d'une jonction semiconductrice, nécessaire pour la photovoltaïque et la photodétection sensible. Une hétérojonction ZnSe/Se est caractérisée et une architecture pour le fort maintien des géométries est obtenue, basée sur co-fibrage de Zn solide. Combiné aux composites visqueux semitransparents présentés au chapitre précédent, toutes les briques élémentaires pour la réalisation d'une photodiode planaire dans une fibre sont réunis.

<u>Mots clés</u> : Etirage à chaud, Fibres multimatériaux, Micro- et Nanofabrication, Composites, Nanofils, Hétérojonction, Electrodes, Semiconducteur, Optique, Photodiode, Métasurface.

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List of abbreviations

AR	Aspect ratio			
AST	Arsenic Selenium Tellurium glass			
ChG	Chalcogenide glass			
cPC	Conductive Polycarbonate			
CB-PC	Carbon Black Polycarbonate			
cPE	Conductive Polyethylene			
CB-PE	Carbon Black Polyethylene			
CNT	Carbon nanotubes			
DR	Draw ratio			
DSC	Differential Scanning Calorimetry			
EDX	Energy Dispersive X-ray			
FWHM	Full Width at Half Maximum			
HRTEM	High Resolution TEM			
IR	Infrared			
ITO	Indium Tin Oxide			
MG	Metallic Glass			
NMP	N-Methyl-2-Pyrrolidone			
NW	Nanowire			
PC	Polycarbonate			
PDMS	Polydimethylsiloxane			
PE	Polyethylene			
PEI	Polyetherimide			
PMMA	Poly(methyl metacrylate)			
PSU	Polysulfone			
SAED	Selective Area Electron Diffraction			
SEM	Scanning Electron Microscopy			
TEM	Transmission Electron Microscopy			
Тg	Glass transition Temperature			
TTT	Time Temperature Transformation			
VdW	Van der Waals			
XRD	X-ray Diffraction			

0. Introduction

Optoelectronics

In 1782, as he reported his findings on electricity to the Royal Society of London, Alessandro Volta observed that a separate class of materials acted unreliably in between conducting metals and insulating dielectrics [1]. Equipped with a gold leaf electrometer, early version of a Voltmeter, he first coined the term "semicoibente" (semi-insulating), later translated to English as "semiconductor" to describe such materials which released their charge "unreliably" upon contact. Although scientists of the 19th century such as Humphry Devy, Michael Faraday and Edmond Becquerel discovered resistivity dependence to temperature and light [2], it was only in the first decades of the 20th century that Koenigsberger tried to explain the role of temperature by an electron dissociation theory [3], which would later give rise to the understanding of band gaps, characteristic of semiconductors. Their dependence on external stimuli was the materials science breakthrough needed for logic and sensing, which led to revolutions in the way we expand our senses through CCD cameras [4], LED lighting [5], microphones and miniaturized speakers, store our memory [6], and probe the universe [7]. From the discovery of a diode-like behaviour in metalsemiconductor contacts [8] to the invention of the blue LED [5], twelve Nobel prizes were awarded for discoveries and inventions related to semiconductor physics [9]. Nowadays, all electrical communication and consumer devices stem from the technologies derived from these findings. Enabled by the adoption of advanced characterisation methods such as electron microscopy, diffractive and spectroscopy techniques, the field of optoelectronics is still in full expansion. Recent trends include materials discovery by improved simulation capabilities and the fabrication of nanostructures from which new quantum physical properties emerge such as heterostructures, 2D materials, nanowires and quantum dots. As this thesis will show, research in semiconductor physics sits at the interface between seemingly separate fields such as materials science, physics of band structure and carrier transport, chemistry and surface science.

Thermal drawing: a scalable fabrication method for elongated flexible optoelectronic structures

Optical fibres are ideal guides for photons. They have revolutionized communication technologies, high-power laser beam delivery and sensing applications. The industrial process that has allowed to generate hundreds of kilometres of optical fibre in a day, making it cost effective enough to develop international networks for data transmission, is thermal drawing. From an easy to manufacture macroscopic preform, this process allows a drastic reduction in scale by heating and stretching in a dedicated furnace, generating at low-cost long lengths of thin fibre. By conservation of volume, the length generated scales with the square of the reduction in width. For a scaling factor 100, termed "draw ratio" DR, a one meter-long preform yields a 10 km-long fiber. Not only can it be used for conventional cylindrical optical fibers, but also for more complex geometries, integrating multiple materials at the same time, giving rise to a new class of "multimaterial" fibers. Metals, semiconductors and insulators, the building blocks of optoelectronic devices, can be assembled simultaneously in complex architectures, as illustrated in Figure 0.1a. In particular, chalcogenides are glassy semiconductors (e.g. based on selenium or sulphur) with viscosities in the range of 10^3 to 10^7 Pa.s compatible with fibre drawing. They exhibit band gaps in the 1-3 eV range and high refractive

indices (n \approx 3). Figure 0.1b reviews the different materials which have been reported to be compatible with the thermal drawing process, and the associated phases they can be processed in. As the cross section can be tuned at will for a variety of applications, these fibres have significant potential for technologies requiring flexible, portable and large area functionalization, leading to applications in distributed sensing [10], communication [11], actuation [12], thermal regulation [13] and energy harvesting [14], to name a few.



Figure 0.1 – Architectures, materials and phases in the thermal drawing toolkit. a) Example of the assembly process for a metal-semiconductor-insulator multimaterial fiber thermally drawn. 1: semiconducting chalcogenide film; 2: metal busbars; 3: nanocomposite electrodes; 4: insulating cladding with a hollow core for microfluidic sensing. Adapted from [15]. b) Materials available to thermal drawing. "Discrete IC embedding" is a based on the method in [11].

The ability to use the thermal drawing process to integrate high quality semiconducting materials and junctions within flexible fibers has the potential to reconcile large-area flexible waveguides and advanced optoelectronic devices. Indeed, the combination of several materials in a fibre can deliver the functionalities associated with metal-semiconductor-insulator devices [16], which can be weaved into smart fabric [17], placed regularly to cover an area or span a long length, or inserted with minimum invasion [18], [19], at the scale and cost traditionally associated with optical fibres. Based on a thorough understanding of the interplay between surface tension and viscosity of the materials at play, combined with control over their microstructure, this process offers a versatile platform for translating the macroscopic architecture in the preform to the micro - or even nanoscale. In turn, such dimensions allow a drastic increase in optical and electronic performance, by reaching subwavelength semiconductor architectures and efficient charge extraction. To reach the full potential of fibre microelectronics and photonics, one not only needs to be able to draw semiconductors, but also achieve a junction for photogeneration of charge carriers. Designing a photodiode involves most building blocks of optoelectronic devices: a transparent cladding and electrode, enhanced optical absorption in the active material, charge separation and extraction. Thermal drawing has the potential to drive costs down by miniaturizing, integrating, synthesizing and encapsulating all constituents of the device in a single fibre drawing step.

Design process

To address this challenge, we propose the following design process, summarized in Figure 0.2. We start from materials selections, based on the desired optoelectronic properties, which usually stem from chemical composition. Both light-matter interaction and conduction are highly dependant on atomic electronic structures and molecular bonds. This leads us to choose materials which have adequate refractive indices, absorption edges, bandgaps, Fermi levels or polymeric molecular weight, for instance. Then, we filter those compatible with our fabrication process, based on their rheological behaviour, sensitivity to thermal treatments, and phase stability. This step requires an indepth understanding of the materials' microstructure. Advanced characterization and modelling are of the essence. Next, these building blocks with distinct properties can be assembled into a device. Here engineering of the assembled architecture is critical to its performance. When geometries are nanoscopic, new properties can emerge from localized modes of the electromagnetic field. In multimaterial fibers, multiple functionalities can be combined in a single device. However, it is only their placement in a relevant use case which makes the application effective. Embedded, weaved or knitted into smart textile and other functionalized substrates, multifunctional fibers may solve real world-problems and give rise to a new generation of tools with distributed functionality.

	Design step:	Functionality from:	Properties from:
8	Materials selection	Composition	Chemical Electrical Optical
\bigcirc	Fabrication Processing	Microstructure	Phase Rheology Filler dispersion
R	Device	Architecture	Core Film Nanowire
	Application	Placement	Sensor Actuator Connector

Figure 0.2 - Design and assembly process, from materials to application.

Outline of the thesis

This thesis is divided in five parts:

Chapter 1 introduces semiconductor architectures, the motivation for miniaturization and potential contacting geometries. Next, fabrication challenges are discussed: different preform consolidation strategies are presented, and a trade-off regarding the role of composition and crystallization for the glassy semiconductor is suggested. We show that there are degrees of freedom when drawing: allowing to reduce reflow and crystallization, or to the contrary, enhance capillary break-up and chemical reactions. A model for film stability under anisotropic stretching is introduced, justifying the usage of semiconducting wire arrays as a stable scalable geometry.

In chapter 2, building on this understanding of capillary break-up, a process for controlling film dewetting dynamically during drawing is proposed, based on glancing angle deposition on a templated preform. Highly regular large-scale nanowire (NW) arrays are obtained. In collaboration with Complex fluids Lab (Fudan University), instability growth is modelled using linear theory, leading us to propose a criterion for templated filamentation. We validate this analysis by iteratively scaled Computational Fluid Dynamics simulations implementing a body force calculated from intermolecular forces. By varying the deposition angle, the templated break-up criterion is validated experimentally. The versatility of achievable geometries is then discussed, such as the possibility to tune independently NW diameter and array period. Based on this control, applications in diffraction gratings and 1D metasurfaces are suggested.

Chapter 3 expands the span of array periods and diameters achievable within a single array by combining photolithography with thermal drawing. A one-dimensional metalens is designed,

constructed and simulated based on Mie resonance in chalcogenide NWs. The lift-off fabrication process is optimized within aspect ratio constraints. Although the dispersity in NW diameters may hamper focusing efficiency, an application for index sensing based on extraordinary reflection is showed, promising the realization of a microfluidic sensing device.

Chapter 4 focuses on the electrodes required for contacting semiconductor structures. In the first part, we expose the limitations of state-of-the-art nanocomposite materials considering for relative to our requirements and propose a better suited blend. Fabrication via melt-extrusion and via the solution route are shown to yield different filler dispersions, and thus different processability, conduction and transparency. Two fabrication methods for a preform architecture using an insulating spacer are shown to contact chalcogenide NW arrays without short-circuits. The second part of this same chapter considers an application for the electrodes themselves. Their resistive and capacitive properties are harnessed to make distributed sensors for resin transfer moulding. Several strategies are demonstrated to decouple temperature and strain measurements in the resulting functionalized parts.

In Chapter 5, in-fiber semiconductor junctions are discussed. We first review reported attempts at obtaining junctions in fibers and expose their limitations in terms of active surface, rheological behaviour and inter-electrode distance. Fabrication of a ZnSe/Se heterojunction is considered. ZnSe synthesis in fiber is achieved and characterised using TEM and EDX. SnSe synthesis is also considered. Finally, a fiber architecture for drawing at high viscosity based on co-feeding of a solid Zn wire is demonstrated and electrically characterised.

1. Processing challenges for semiconductor thermal drawing

Many strategies have been reported for the fabrication of semiconducting structures in fibers. However, to harness the full scalability of thermal drawing, this thesis focuses on fully drawable semiconductor architecture. Thus, micro- and nanoscale geometries can directly be processed and embedded in kilometre-long fibers produced continuously at high throughput. For some applications, flexibility and distributed sensing are desired, such as in smart functional textile. It is also possible to cut the fiber into multiple sections, with very low marginal costs per unit of length or surface. To achieve this objective, we focus on low temperature thermal drawing, where many materials are available, and for which techniques for polymer processing, such as coating, moulding and 3D printing, provide ample freedom in fiber architectures and properties. Additionally, at such processing temperatures, degradation, atomic diffusion and oxidation are reduced.

We will first describe the geometrical requirements for performant devices, before facing the constraints pertaining to the fabrication process. Finally, we suggest a strategy for fully drawable nanostructures, explored and demonstrated throughout the rest of the thesis.

Film thickness

The trend of the past decades in electronics and optics has been that of miniaturization, as a higher density of devices provides more power, functionality and portability. For functional fibers to follow a similar trend to "Moore's law" for transistors [20], limiting factors to the ultimate achievable feature sizes for optoelectronic fibers need to be understood and overcome.

Let us first consider this importance of the semiconductor film thickness, a critical parameter to achieve high photodetection sensitivity. Let *s* be the sensitivity of a photodetecting device:

$$s = \frac{I_{ph} - I_{dark}}{I_N}$$
 Eq. 1.1

where I_{ph} is the average current under a given illumination, I_{dark} is the average current without illumination, and $I_N = \sigma_{I_{dark}}$ the standard deviation of the dark current fluctuations. Sorin et al [21] showed that at small penetration depths δ (e.g. 150 nm corresponding to an incident wavelength λ = 674 nm) the thin film geometry illustrated on Figure 1.1a shows an order of magnitude higher sensitivity than its bulk counterpart. This is qualitatively explained by dark current fluctuations in the bulk in the core geometry which are much larger than in the thin film configuration, for similar photogenerated currents $I_{ph} - I_{dark}$ (penetration depth $\delta \ll d$).



Figure 1.1 – Sensitivity comparison for a thin film with thickness t and diameter d and a solid core of same diameter. a) Cross-section of the geometries considered, the illumination plane and the connection scheme. b) Sensitivity s for two different thin film thicknesses t and a solid core of identical diameters, against penetration depth δ , itself given in the inset as a function of the incident wavelength λ . Adapted from ref [21].

This study further explained that for the connection scheme considered, as $I_{ph} - I_{dark} \propto 1 - e^{-\frac{1}{\delta}}$ and $I_N \propto \sqrt{t}$, we get:

$$s \propto \frac{1 - e^{-\frac{t}{\delta}}}{\sqrt{t}}$$
 Eq. 1.2

For a given λ , or corresponding δ , the thickness $t_{s,max}$ for which $s = s_{max}$ is maximal can be calculated. For instance, for $\delta(\lambda = 674 \text{ nm}) = 150 \text{ nm}$, $t_{s,max}(\delta = 150 \text{ nm}) = 240 \text{ nm}$ [21]. Thus, for a given wavelength λ , the film thickness can be optimized to maximize sensitivity. This scaling trend is independent of the photoconducting material considered. Additionally, if we solve s_{max} for any $t_{s,max}(\delta)$, we get $s_{max} \propto 1/\sqrt{t_{s,max}} \propto 1/\sqrt{\delta}$. That is to say that the highest sensitivity at small wavelengths is obtained for small thicknesses. Yan et al. also showed increased photoresponsivity for smaller electrode spacing [18]. It is thus desirable to discuss what ultimately limits film thickness to small values, discussed in Chapter 2. When used in a photovoltaic context for electrical power generation, a semiconducting film's thickness is a compromise between charge generation (optical absorption maximized by large thicknesses) and charge extraction (series resistance) [22], [23]. A technoeconomic optimization, however, may encourage decreasing materials costs, i.e. small thicknesses [24].

Wire diameter

Yaman et al. [25] also explored the benefits of scaling down chalcogenide wires to the nanoscale. A preform was prepared with a photoconducting semiconductor core (Se) and drawn into a fiber. Multiple fiber sections were stacked into a new preform and drawn again. A third "stack-and-draw" step was preformed, leading to an array of thousands of nanowires (NWs). Figure 1.2a illustrates this process of successive redrawing. After crystallizing the wires and connecting them at both ends (Figure 1.2b), they showed an exponential increase in the gain I_{ph}/I_{dark} after each drawing step

(Figure 1.2c). The authors attributed this scaling trend in gain to the high optical density of selenium (i.e. a better match between the penetration depth δ and wire diameter), increased surface-area-to-volume ratio and scattering in the polymer matrix. Also note a reduction in switching time τ . Unfortunately, they did not account for I_N to conclude about sensitivity s, but the strong increase in gain is still a testament to the benefits of scaling geometries down, despite the amount of material per fiber being lower at each step (10 times less photoactive surface at step 3 than step 1).

Note that in the two previous state-of-the-art fully drawable photoconducting in-fiber geometries (Figure 1.2d and e), connections to the film/wire were made at extremities. For a given applied bias, the electric field gradient would be one or two orders of magnitude higher if the film/wire could be connected perpendicularly (Figure 1.2f and g). We will discuss the requirements and potential strategies for achieving such geometries in Chapter 4 and 5.



Figure 1.2 – Scaling down geometries and contacting schemes. a) Two successive stack-and-draw steps from a semiconductor core. b) At each drawing step, wires are crystallized and connected. Under illumination, the current *I* is measured for a given bias *V*. c) When light is turned on, the photocurrent gain I/I_0 shows an order of magnitude increase at each drawing step, for reduced switching times. Adapted from ref [25]. d) In the first example of the chapter, films are connected across their width. e) In the second example, wires are connected across their length (at either ends). f) Planar geometry. g) Wires connected along their length, resulting in an order of magnitude higher electric field.

Glass composition and semiconductor film stability

In the first case presented in this chapter, the addition of 40% As to the chalcogenide glass composition enabled much higher viscosity (Figure 1.3a) and higher stability to crystallization [26], so that the film could be thermally drawn with its cladding in a metastable supercooled amorphous state above its T_g . Qualitatively, the "dwell time" $\tau_{dwelling}$ spent at low viscosity in the drawing furnace should remain lower than the instability time scale τ . The fiber cladding should be appropriately chosen so that its viscoelasticity is compatible with thermal drawing [17]. Given this

processing temperature, the glassy semiconductor should have a comparable or lower viscosity, or it will not flow with the cladding, resulting in a solid inclusion hampering drawing. Figure 1.3b and Figure 1.3c show such problematic cases, where crystallized Se films were drawn at a temperature too low for the latter to melt and flow within the polymer. In the first case, the Se film was broken up by shear-induced strain; in the second, a thicker Se film could not be broken up by shear and came down as one large solid inclusion in the polymer cladding. Figure 1.3d shows potentially suitable cladding-film couples for co-drawing, if $\tau < \tau_{dwelling}$ (in the shell configuration of ref [27]).

Glasses with much higher photoconducting properties could be employed [28]–[30], at the cost of lower viscosities during drawing [8], [14]–[18]. Pure Se for example, crystallizes easily (Figure 1.3e) upon annealing, showing higher light absorption, responsivity, sensitivity, and response speed [18], [36]. Polycrystallinity results in lower electron mobility (scattering at grain boundaries and dislocations), but for optimal electronic properties, laser [36]–[39] and sonochemical [18] post-drawing crystallization schemes have been proposed. Note that the same can be obtained for Si or Ge molten cores in silica fibers by laser techniques [40]–[44] and by controlling the cooling rate [45].



Figure 1.3 – Chalcogenide glass processability. a) Viscosity dependance on temperature, for three common chalcogenide glasses, adapted from ref [27]. b) Drawing of a crystallized Se film in PSU. c) Drawing of a Se film in PC. d) Potentially suitable material couples based on their viscosity, adapted from ref [27]. e) Optical micrograph in transmission of a 5 μ m Se layer crystallized at 200°C for 20 min.

At low viscosity, capillary break-up of thin films is a major issue when processing fibers. Figure 1.4a shows how holes nucleate and grow in a 5 μ m selenium film heated above its T_g ($T_{g,Se}$ = 40°C) at temperatures required for drawing. Achieving advanced geometries such as thin films or micro/nanowires requires a good understanding of capillary forces and related instabilities. Reports of this phenomenon in fibers demonstrated that because of initial imperfections in the film, thickness fluctuations, or "instabilities", grow during drawing until the film breaks-up into smaller elements [46]. These dynamics are governed by intermolecular forces at film interfaces and

enhanced by low viscosity. However, since the film is stretched in the drawing axis, we will now show that longitudinal instabilities grow slowly compared to transverse ones, resulting in a break-up of the film into long filaments [47], as shown on Figure 1.4b. The filaments, or wires, on the other hand, present a stable cross-sectional shape (in 2D, the circle minimizes surface tension) which can be exploited to achieve nanoscale semiconductor architecture in fibers with optimal optoelectronic properties.



Figure 1.4 – Capillary instabilities in thin films. a) Optical transmission micrograph of the nucleation and growth of holes when annealing at 170°C for 20 mn a 5 μ m Se film deposited and encapsulated in PC. b) Optical transmission micrograph of a rectangular fiber showing Se filaments in a PSU cladding.

Stability of wires: Anisotropic perturbation growth

Let us consider a film thickness fluctuation, with a wavenumber k, a growth rate ω_k , and an initial amplitude perturbation a_0 , its amplitude a growing with time t as a continuous function: $a(t)=a_0 \exp(\omega_k t)$. The stretching-induced *anisotropy* entails modified wavenumbers and thus growth rates for instabilities parallel and perpendicular to the stretching direction [47]. The wavenumber k(t) of a given perturbation now depends on time, and so does its growth rate $\omega_k(t)$. Let K = kH be an dimensionless wavenumber to account for downscaling of the film thickness H throughout fiber drawing [48], [49]. By considering the equivalent one-dimensional "fiber limit" case for volume conservation [50], we get [47]:

$$k_{\parallel}(t) = \frac{k_{\parallel}(t=0)}{DR(t)^2}$$
(1.)

$$k_{\perp}(t) = k_{\perp}(t=0) DR(t)$$

One can then express dimensionless wavenumbers perpendicular (K_{\perp}) and parallel (K_{\parallel}) to the fiber axis:

$$K_{\parallel}(t) = \frac{k_{\parallel}(t=0)}{DR(t)^2} \frac{H(t=0)}{DR(t)} = \frac{K_{\parallel}(t=0)}{DR(t)^3}$$
(1.

(1.

(1.

$$K_{\perp}(t) = k_{\perp}(t=0) DR(t) \frac{H(t=0)}{DR(t)} = K_{\perp}(t=0) \text{ (independent of DR)}$$

$$6)$$

These two equations denote a distinct evolution along and perpendicular to stretching. Along the longitudinal direction, as DR(t) increases with drawing time, the wavenumber of a given

perturbation is continuously reduced, which disfavours the growth of instabilities. We now show why a reduction in all K_{\parallel} by stretching leads to a decrease in the *amplitude* growth, compared to the transverse case.

Let us consider that all wavenumbers are initially present in infinitesimal amplitudes. At any given time t of drawing, there is a wavenumber $K_{\perp,max}(t)$ (resp. $K_{\parallel,max}(t)$) for which the growth rate $\omega_{K_{\perp,max}}(t)$ (resp. $\omega_{K_{\parallel,max}}(t)$) is maximal. In the transverse case, since $K_{\perp}(t) = K_{\perp}(t=0)$, there is a single $K_{\perp,max}$ for all times t. Therefore, $a_{\perp}(t) = a_0 \exp(\omega_{K_{\perp}}t)$ is maximal for this wavenumber $K_{\perp,max}$:

$$a_{\perp,max}(t) = a_0 \exp\left(\omega_{K_{\perp,max}}t\right)$$
⁷⁾

However, in the longitudinal case, a_{\parallel} for a given perturbation $K_{\parallel}(t) = \frac{K_{\parallel}(t=0)}{DR(t)^3}$ (i.e. given by the initial perturbation $K_{\parallel}(t=0)$) must be calculated over the draw: $a_{\parallel}(t) = a_0 \exp(\Omega_{K_{\parallel}}(t)t)$ where $\Omega_{K_{\parallel}}(t) = \frac{1}{t} \int_0^t \omega_{K_{\parallel}}(\tau) d\tau$ is the total (integrated) growth rate through thermal drawing. As opposed to the transverse case, maximal amplitude must therefore be calculated over all initial instabilities $a_{\parallel,max}(t) = \max_{K_{\parallel}(t=0)} \left(a_0 \exp\left(\Omega_{K_{\parallel}(t=0)}(t)t\right)\right) = \max_{K_{\parallel}(t=0)} \left[a_0 \exp\left(\int_0^t \omega_{K_{\parallel}(t=0)}(\tau) d\tau\right)\right]$, and since at all times $\tau : \omega_{K_{\parallel}(t=0)}(\tau) \le \omega_{K_{\parallel,max}}(\tau)$, longitudinal amplitude growth is suboptimal:

$$a_{\parallel,max}(t) \le a_0 \exp\left(\omega_{K_{\parallel,max}}t\right) \tag{8}$$

Compared to Rayleigh-Plateau's non-stretched case [48], [51], drawing therefore dampens the fastest growing instability in the longitudinal direction.

Consolidation

This leads us to propose architectures which rely on the stability of viscous wires during anisotropic stretching. By contrast, any thermal treatment above the chalcogenide glass' T_g without stretching, required for example for the fabrication of the preform, should be avoided. Preliminary experiments sought to find strategies for minimizing annealing of the semiconductor structure during encapsulation and consolidation of the preform cladding. By consolidation, we mean sealing of the preform in polymer cladding, usually by annealing so that different parts of the assembled cladding merge and adhere by polymer chain interpenetration (diffusive adhesion). This is typically achieved in a consolidation oven or in a hot press by annealing 20 to 30 °C above the cladding's T_g . Four strategies were proposed to obtain preform sealing while minimizing annealing: dip-coating, dynamic consolidation, multi-material consolidation and solvent consolidation.

Dip-coating the cladding material onto the semiconductor structure ensures intimate conformity and encapsulation of geometrical features. This protects them from mechanical damage when assembling the preform, provides a higher surrounding viscosity than air or vacuum to prevent reflow, and may reduce interfacial tension [52]. Hot pressing a polymer film or plate onto the semiconductor structure may achieve the same result, but with less control; it is unclear whether the cladding will flow intimately into all gaps as the polymer solution does, and the mechanical pressure may distort or damage the said structure. Figure 1.5a shows an SEM picture of a Se film deposited on a square PSU substrate, onto which approximately 15 μ m PSU was dip-coated from a chloroform solution. This solution is to be preferred when an encapsulation of a few tens of μ m is

(1.

(1.

sufficient at the preform level. When thicker claddings are required, one of the following consolidation strategies are best.

The idea behind "dynamic consolidation" is to consolidate the preform thermally but to avoid heating the fiber core to a temperature where the semiconductor viscosity is lowered and capillary break-up may occur, by only heating preform edges rapidly. The temperature does not have time to uniformize in the whole preform. This is helped by first cooling the preform in liquid nitrogen, to ensure a high thermal gradient between the preform edge and the core. Figure 1.5b shows a rectangular PSU preform whose edges are being heated to 300°C, while the core remains cold after liquid nitrogen cooling, evidenced by condensated water droplets. The Se film in the core remains continuous. This is an elegant strategy but with low reproducibility: as the preform is manually immersed in liquid nitrogen and placed in the hot press, the timing of each step may vary slightly and lead to different results. The edges of the preform are heated well above the cladding's T_g and may reflow/melt more than desired; any features on the outer layer of the preform would be lost. For some applications, this method may also induce some undesired internal stress (high thermal gradients).

Different parts of a polymer preform can also be assembled with minimal heating by using an intermediate polymer film of lower T_g . This film needs to be drawable and have some adherence to the cladding material. Since the latter remains highly viscous during this low temperature consolidation, adherence is limited to dispersive adhesion (Van Des Waals forces) from the intermediate film coming into intimate contact with the preform parts, which is much weaker than diffusive adhesion. In the case of internal stress (drawing furnace-induced temperature gradient) or external stress (wire feeding), the preform may delaminate. A successful example is given in Figure 1.5c for two PSU plates consolidated at a temperature 30°C lower (than for PSU alone) with an intermediate CB-PC film (in black), showing successful drawing. This multi-material consolidation would be greatly improved if chemical bonding could be obtained, such as when silanes are used for PDMS bonding.

Finally, diffusive consolidation can be obtained without any heating by dissolving slightly the preform parts where joining is required. There are two drawbacks to this method: (i) it is not easy to control where the solvent is infiltrated/deposited because of capillary action; (ii) some solvent tends to get trapped inside the sealed preform, which results in disruptive bubbles when drawing. Provided the preform is placed in vacuum for the residual solvent to diffuse out prior to drawing, this strategy yields diffusive adherence with the lowest annealing possible. Figure 1.5d shows two PSU plates adhering to each other after infiltrating a drop of chloroform at the interface between them.



Figure 1.5 – Consolidation strategies to avoid isotropic annealing of semiconductor structures. a) SEM picture of a Se film deposited on a square substrate, dip-coated. Scale bar: 10 μ m. b) Dynamic thermal consolidation c) Multimaterial consolidation. d) Solvent-assisted diffusive consolidation.

Drawing degrees of freedom

The final processing step after consolidation is thermal drawing. We here describe the constraints on temperature and the drawing speed to prevent rupture, which leaves some freedom in the drawing parameters to minimize shape reflow or glass crystallization.

As the preform is heated in the draw furnace and stretched by a drawing force F, neck-down occurs where the viscosity is decreased. The drawing furnace is open to ambient air at both ends for preform insertion/feed (at V_{feed}) and fiber pulling/drawing (at V_{draw}), so the temperature profile inside it is far from uniform. It is best approximated by a parabolic temperature profile given by:

$$T(z) = T_{max} - az^{2} = T_{max} - \frac{(T_{max} - T_{g})z^{2}}{\left(\frac{L}{2}\right)^{2}}$$
 Eq. 1.9

Where T_{max} is the maximum temperature inside the oven (z = 0), T_g is the glass transition temperature of the polymer cladding, L is the length of the hot zone, typically 20 cm. All parameters are described and illustrated in Figure 1.6a. *a* (or *L*), $T_{max,PEI}$ and the corresponding viscosity η , following an Arrhenius law, were measured experimentally [53]: $a \approx 14300 \ ^{\circ}C/m^2$; $T_{max,PEI} = 245 \pm 5 \ ^{\circ}C$; $\eta(T) = \exp(\frac{22819}{T} - 29.381)$ with *T* in K.

One can then use conservation of mass flow, force balancing and a stress-shear relationship in the z direction given by Trouton law:

$$\begin{cases} v(z)R(z)^2 = constant & \text{Eq. 1.10} \\ F = \sigma_{zz}\pi R(z)^2 \\ \sigma_{zz} = 3\eta(z)\frac{\partial v(z)}{\partial z} \end{cases}$$

Where v is the velocity, F is the pulling force, R the fiber radius, assuming a circular cross section. Solving for z the partial differential equation in v, we get:

$$v(z) = \exp\left(\ln V_{feed} + \frac{\int_{-\frac{L}{2}}^{z} \frac{dZ}{\eta(Z)}}{\int_{-\frac{L}{2}}^{\frac{L}{2}} \frac{dZ}{\eta(Z)}} \ln \frac{V_{draw}}{V_{feed}}\right)$$
Eq. 1.11

In the Lagrangian description, this velocity profile in *z* tells us how fast a slice travels down the neckdown region. Knowing the dynamics of isothermal reflow from Laplace Pressure [53] and crystallization from a TTT diagram [54], one can integrate through the drawing furnace respectively a reflow factor for a given shape or the fraction of time to crystallization.

Moreover, we can now optimize over the drawing parameters. If, for instance, we want to minimize reflow, we might want to reduce temperature as much as possible, to keep viscosity high and increase the reflow time scale. At best, σ_{zz} should remain lower than rupture stress $\sigma_{rupture}$. σ_{zz} is maximal when the radius R is minimal, at $z = \frac{L}{2}$, so from Eq. 1.10 and Eq. 1.11 we get the constraint:

$$\sigma_{rupture} = \sigma_{zz} \left(z = \frac{L}{2} \right) = \frac{3 \ln(V_{draw}/V_{feed})}{\int_{-\frac{L}{2}}^{\frac{L}{2}} \frac{1}{\eta(z)} dz} v(z = \frac{L}{2}) = \frac{3 \ln(V_{draw}/V_{feed})}{\int_{-\frac{L}{2}}^{\frac{L}{2}} \frac{1}{\eta(z)} dz} V_{draw}$$
Eq. 1.12

Given the target scale reduction $DR = \sqrt{\frac{V_{draw}}{V_{feed}}}$, we have a variance of only 1 to vary V_{feed} , V_{draw} and the viscosity profile. If for example, we want to draw faster, we increase V_{feed} and consequently V_{draw} and η are given by:

$$V_{draw} = DR^2 V_{feed}$$
 Eq. 1.13

$$\int_{-\frac{L}{2}}^{\frac{L}{2}} \frac{1}{\eta(z)} dz = \frac{3\ln(DR^2)}{\sigma_{\text{rupture}}} V_{draw}$$
 Eq. 1.14

 η being a direct function of T, itself given by T_{max} and a.

Let us assume a standard drawing condition where $V_{feed,std} = 1 \text{ mm/mn}$ and $T_{max,std}$ has been measured. Since $\sigma_{rupture}$ is a constant given by the cladding material properties, if a is given by L, we can now compute the required increase $\Delta T_{max} = T_{max} - T_{max,std}$ corresponding to an increase $\Delta V_{feed} = V_{feed} - V_{feed,std}$, as plotted in Figure 1.6c. Let us call $k = \frac{\Delta T_{max}}{\Delta V_{feed}}$, Figure 1.6d shows that depending on the value of k, we can choose a non-standard V_{feed} to minimize the reflow factor f_{Re} , defined as [53]:

$$f_{Re} = 1 - \frac{h\left(z = \frac{L}{2}\right)}{h\left(z = -\frac{L}{2}\right)/DR}$$
 Eq. 1.15

where h is the height of a sinusoidal pattern with period λ imprinted on the polymer surface (Figure 1.6b). We ran the simulation in Figure 1.6d for PC, using semi-empirical values: $\eta(T) = \eta_0 \exp[\alpha(\frac{1}{T} - \frac{1}{T_0})]$, with $\eta_0 = 209365$ Pa.s, $\alpha = 22493$ K⁻¹ and $T_0 = 200$ °C, period $\lambda = 10$ µm, interfacial tension $\gamma = 10^{-3}$ N.m⁻¹, $T_{max} = 190$ °C, a = 14300 °C/m² and DR = 20. $f_{Re} = 1$ means complete flattening of the square structure, and $f_{Re} = 0$ means the structure is perfectly preserved. This factor accounts for the scaling by DR of the initial feature height. Literature on thermal drawing shows indeed varying feed speeds [55]. The present model provides an explanation for the reasons behind these empirical choices.

Similarly, we could minimize reflow and crystallization over the temperature profile width (a and T_{max}), all things being equal, by using more or less heating zones of the furnace. Conversely, we could maximize capillary break-up and chemical synthesis during drawing by optimizing over these degrees of freedom at the lowest viscosity possible. This time, the constraint would translate into not falling under its own weight. At all times and positions, we should keep:

$$\sigma_{zz}\pi R(z)^2 > m(z)g \qquad \qquad \text{Eq. 1.16}$$

where m(z) is the mass of the fiber under position z. Under this constraint, we can again optimize over the temperature profile or the drawing speed.



Figure 1.6 – Model for the prediction of a sinusoidal pattern reflow during thermal drawing. a) Thermal drawing parameters. b) Reflow of a sinusoidal surface pattern on polymer. c) Simulated plot of three hypothetical parabolic temperature profiles necessary to maintain a constant maximum drawing stress at three different feed speeds, for PC. d) Simulated plot of the reflow factor for varying feed speeds, for three different linear dependencies k of the maximum temperature to the feed speed ($k = \frac{\Delta T_{max}}{\Delta V_{feed}}$). For any dependency, reflow can be minimized with respect to the standard situation by adapting the feed speed.

Conclusion

For a fully drawable semiconductor architecture to the micro- or nanoscale, processing challenges need to be addressed. The motivation for semiconductor film sensitivity and thickness optimization was presented, as well as the benefit of achieving nanowire arrays for increased photodetection gain. We then highlighted the trade-off in chalcogenide glass composition and microstructure between optoelectronic properties and processability. Next, we exposed why under stretching, longitudinal instabilities in film thickness are dampened with respect to transverse ones, leading potentially to the break-up of fluid thin films into stable NW arrays during thermal drawing. Thus, consolidation strategies to avoid isothermal annealing were proposed. Finally, thermal drawing degrees of freedom were modelled and their importance to reflow and crystallization minimization was explained. The concepts and preliminary tests introduced in this chapter provide the groundwork for the architectures achieved in the following chapters.

2. Harnessing capillary instabilities

The previous chapter described challenges related to thermally drawing semiconducting thin films, and alternative strategies considered for reaching micron or sub-micron dimensions where photodetection sensitivity is maximized [21]. Preventing thin film dewetting during consolidation and thermal drawing was a major hurdle. However, the following chapter demonstrates that this fundamental limitation can be harnessed rather than prevented as a novel microfabrication process for nanowire (NW) self-assembly. Parts of the presented work are also published elsewhere [56].

Motivation

Owing to their large aspect ratio and intrinsic electronic and optical properties, one-dimensional architectures such as NWs are at the heart of innovative components in sensing, energy harvesting and photonics. Made with the right materials from III-V alloys to oxides or chalcogenide (ChG) glasses, NW arrays can be used as low power phase-change memory devices [3], [4], low-loss waveguides [59] for high confinement, highly-localized near-field optical sensing [60], or form efficient optoelectronic systems [18], [61]. Optical properties can also be engineered to enhance light absorption or scattering as desired [62] [63], and when well-engineered, high index ordered filament arrays can enable the integration of functionalities such as lensing over distances orders of magnitude smaller than traditional methods [64].

NWs are usually obtained by cleanroom methods, such as lithographic top-down and bottom-up approaches [65]–[69]. Despite intrinsic advantages such as high accuracy and repeatability, dimensions are limited to that of the wafer, with NWs of a few millimeters in length at most. Obtaining ultra-long (a few tens-of-meters) NWs organized as an array in a flexible support remains however a significant challenge. Beyond gas phase deposition approaches, fluid dynamics-based strategies have been proposed to generate longer NWs within different types of substrates and three-dimensional arrangements, such as fluid-spinning [70], [71] or sonochemical growth [18]. However, none of these methods allow regular positioning and alignment of the NWs. To produce arrays, pressure-assisted melt filling [72] or chemical vapor deposition [73] inside microstructured glass optical fibers has been demonstrated within channels down to several hundred nanometers over lengths up to a few centimeters. However, the deposition time in this process scales as the square of its length, thereby limiting upscaling [74].

To overcome this limitation, thermal drawing has attracted considerable attention as an alternative for fabricating directly NW arrays with extreme aspect ratios [18], [36], [47], [75]–[77]. One method to manufacture ordered nanoarrays through thermal drawing relies on the stack-and-draw technique [78], whereby a single-core fiber is drawn, cut into equal sections, assembled into a bundle, and re-drawn. Obtaining regularity in fiber spacing and filament diameter depends on the precise stacking and uniformity of the previous steps. Reaching the nanoscale typically requires three successive draws [79], which often lead to intermediate preform shrinkage and rupture because of residual stress [12]. Direct thermal drawing of micron-thick films has been shown to lead to dewetting transversal to the fiber axis, giving rise to arrays of filaments. Flow in the axial direction has the effect of scaling down surface perturbations, hence preventing capillary break-up and preserving filament continuity over the entire fiber length [27], [46]. Semiconducting filaments at the nanoscale could be produced, opening exciting opportunities in scalable manufacturing of NW arrays[47]. Nevertheless, irregular transversal dewetting limits control over geometrical parameters. This is particularly detrimental to many practical applications in photonics which require a high

degree of order. The possibility to reduce inter-filament spacing is also desirable, allowing for collective interaction and interference effects. Indeed, the physics of capillary break-up (i.e., the wavelength of the fastest growth mode [49]) determine large filament spacing and inherently hinder control over the wire diameter-to-period ratio, key to advanced photonic applications.

Template dewetting is another fluid-based process leading to better control over geometrical parameters of the resulting nanoarrays. It consists of the reflow of a thin viscous layer on a textured substrate that imposes dewetting at specific locations [80]–[82]. This approach has been recently exploited to generate ChG NWs on a rigid wafer-like substrate [83]. While the results were promising, the conditions to engineer reflow-induced dewetting faster than capillary break-up are very challenging, limiting diameter uniformity and achievable feature sizes. Moreover, the NW length is limited by the nano-imprinted area, typically of a wafer-scale. To date, the challenges associated with understanding and controlling fluid dynamics-based processes to realize ordered NW arrays with extremely large aspect ratios, with well controlled size and periodicity, remain unresolved.

Herein, we propose dynamic template dewetting as a novel viscous flow process to achieve unprecedented control over diameter and periodicity of ordered NW arrays, potentially kilometers in length. We propose to tune the modes of dewetting in a textured thin film of a material obtained from angle deposition on a nanoimprinted polymer substrate. This assembly is then thermally drawn, continuously triggering instabilities at prescribed positions in the fiber cross-section while preventing instabilities in the drawing direction. We demonstrate meter-long *periodic* arrays of ChG NWs in a single drawing step, encapsulated within a flexible polymer, and with diameters down to 50 nm. We also successfully master the ability to independently tune NW diameter and spacing, providing unprecedented control over transverse geometrical parameters. Further combining several films into a single preform, 3D stackings of 2D arrays are fabricated, enabling the integration of multiple photonic functionalities over reduced distances. Using multi-scale fluid dynamics simulations, we develop a model to account for the rearrangement process down to nanometric dimensions. The model further establishes universal conditions under which such filamentation occurs, applicable to other materials such as metallic glasses [76], [84] or conductive composites [85]–[87]. Finally, since the versatility of the drawing process allows engineering of the NW array to fit optical requirements, we propose an architecture for applications that benefit from the high refractive index of ChG. In particular, we achieve controlled diffraction effects and the scalable fabrication of flexible 1D optical all-dielectric metamaterial, demonstrating the impact of our nanofabrication approach for flat optics and nano-photonics.



Figure 2.1 - High throughput NW array fabrication process and observation. a) 1. A microscopic square pattern with period P is imprinted on a thermoplastic polymer with a PDMS stamp. 2. The polymer film is then reflowed to smooth out the pattern. 3. A ChG As2Se3 (or Se) is thermally evaporated onto the polymer substrate at an angle resulting in a thickness fluctuation. 4. The films are encapsulated into a "preform" by hot-embossing another polymer film on top. 5. The preform is thermally drawn to microscopic dimensions by adjusting furnace temperature, drawing, and feeding speeds. The film breaks up periodically into long ordered NWs. b) During thermal drawing, the continuous film in the preform (top) is heated and stretched, subjected to fluid instability and subsequently producing well-ordered filament arrays(bottom). c) SEM cross section of a fiber thermally drawn, demonstrating the transversal breakup. d) Close-up picture of a ChG NW array encapsulated inside a polymer fiber. e) Meters of flexible fibers can be manufactured in a single drawing step. Scale bars are respectively: b: 10 μ m (top), 5 μ m (bottom), c: 1.4 μ m, d: 10 mm.

Description of the process

The proposed process is shown in Figure 2.1a and starts with soft lithography [88] where a primary silicon master mold with line arrays of fixed periodicity P obtained by photolithography (see Experimental section) is used for drop-casting and curing of Polydimethylsiloxane (PDMS) negative texture replicas. Such soft stamps allow for hot embossing the initial positive texture onto thermoplastic substrates. Polyetherimide (PEI) was chosen as a cladding material for its high glass transition temperature $T_g \sim 217$ °C [89], suitable for co-drawing with ChGs such as As_2Se_3 [27], [90] ($T_g \sim 174$ °C) [91]. Polysulfone (PSU, $T_g \sim 143$ °C) [17] has also been employed in combination with Se ($Tg \sim 47$ °C) [36], at a lower processing temperature and higher cladding-to-film material viscosity ratio during thermal drawing.

The next step involves thermal reflow of the texture, which smoothes out the square surface profile into a sinusoidal interface [53]. We will later develop two models for predicting the evolution of a viscous film's thickness fluctuations under anisotropic stretching, and we demonstrated the validity of this theory for predicting capillary break-up dynamics for sinusoidal perturbations, but other templated dewetting geometries could be investigated [83]. We envision that sharper substrate features at precise locations could provide an even stronger localized drive to dewetting (higher $P_L = \gamma \kappa$). However, deposition onto a square template without an intermediate substrate reflow step resulted in a peculiar film geometry. The film was 9 times thicker at the top of the squares than on the groove walls, and 6 times thicker at the bottom of the grooves, as can be seen on Figure 2.2. Such a geometry doesn't lend itself to regular periodicity but could result in having sub-periodicity with one small and one big NW given by the top and bottom horizontal surfaces, as shown in Figure 2.14f.





In a third step, the ChG is thermally evaporated at an angle (Figure 2.3) to ensure a variation in film thickness following the substrate pattern. The deposition is performed on a rotating platform. This provides uniformity between different samples placed at the same radius. However, the source is place off-rotating axis so that an *effective* deposition angle must be calculated. Additionally, to tilt the sample further to the desired angle, pyramidal scaffolds (3D printed) are inserted between the rotating sample platform and the polymer films. The deposition angle, sum of the scaffold angle and evaporation angle, can therefore be calculated as being between -34° and 83°, or 24° on average. The two extreme positions of a sample placed in such a way are represented in Figure 2.3. The deposition thickness was calibrated by placing a Silicon fragment on the scaffold, beside the polymer film, and measuring the depth of a scratch with an optical profilometer.



Figure 2.3 - Thermal evaporation geometry and setup. Average deposition angles were measured experimentally and adjusted using tilted scaffolds.

In the process described in Figure 2.1a, the final and most critical step of preform preparation is encapsulation of the deposited ChG film into another layer of the polymeric substrate material, done either by (i) consolidation (annealing under light pressure to ensure intimate conformity between film layer and cladding), or (ii) by solvent casting of the encapsulating material. A key feature of our

process is its ability to suppress the instabilities along the fiber axis and ensure a homogeneous filamentation solely during *anisotropic stretching* [47] (c.f. Figure 2.1b). In both cases, it is therefore important to limit dewetting before the assembly is downscaled, when the film might be prone to dewetting both along and perpendicularly to the fiber axis [83]. Limiting nucleation and growth of holes prior to stretching incentivizes the use of films with minimal initial thickness beyond a critical threshold (~300 nm), which can also pose a limit to the maximal evaporating angle one can resort to. While consolidation implies a longer nucleation and growth of hole stage, dip-coating of thick encapsulating layers often leaves significant residual stress within the encapsulating material, which may lead to delamination. In the rest of this paper, we resort solely to the use of the consolidation technique, which is the most practical.

Furthermore, when annealing the sample for consolidation, before the top layer softens and encapsulates the ChG film, open-air reflow can be beneficial to increasing templated film thickness fluctuations.

Increasing the varicose mode initial amplitude by open-air reflow

As detailed later in the model, capillary break-up of the deposited film occurs because of the disjoining pressure resulting from thickness variations (varicose mode). To induce a templated amplitude large enough to overcome the spontaneous "Rayleigh-type" instability, one needs to impart an initial thickness fluctuation at the desired wavelength. When depositing the ChG orthogonally to the templated substrate, the film thickness is even. Such a sinuous mode for a glass film in a polymer matrix only reflows and flattens out under Laplace pressure. An alternative to depositing at an angle which was explored experimentally could be to induce some open-air reflow by isothermal annealing of the ChG film right after deposition, as opposed to inside the fiber cladding during drawing. The two interfaces would then not be symmetrical. The top one would be between air and the ChG (air-fluid), the bottom one between the ChG and the polymer substrate (fluid-fluid). We expect the bottom interface to have a stronger interfacial tension, therefore reflowing and flattening faster than the top one. To verify this assumption, different annealing times were used for similar samples. Cross-sections were then prepared for optical characterization of the film geometry. Figure 2.4 shows a film after deposition, before and after open-air annealing (15 mn at 220°C) on a hot plate. Although this annealing step could have been used in our process, we preferred to rely solely on PVD at an angle, for three reasons. First, isothermal annealing introduces an additional step. Second, thermal processes are challenging to reproduce consistently. External temperature, air convection, or polymer film contact with the heating device may vary slightly from sample to sample, a few degrees difference resulting in a large viscosity discrepancy, challenging to assess. Finally, and most importantly, isothermal annealing may lead to the appearance of holes in the film wherever imperfection, dust, or any irregularities were present. In the absence of stretching (i.e. drawing), instabilities along the lines (axial) are not dampened enough compared to those across the lines (transverse) to ensure that capillary break-up only happens in the desired direction.



Figure 2.4 - Extended depth-of-field cross-section micrographs of As_2Se_3 films on a PEI substrate. The top (resp. bottom) image is taken before (resp. after) open-air reflow at 220°C for 15 mns. The top interface flattens faster than the bottom one, leading to a strong thickness fluctuation. Scale bar: 20 μ m.

Finally, the preform is lowered into a furnace and thermally drawn into a fiber. During annealing and stretching (see Experimental section), the ChG film breaks up into an array of NWs (Figure 2.1b and c) encapsulated in meters-long flexible fibers (Figure 2.1d and e).

Experimental in-situ observation of the dewetting process

By interrupting fiber drawing abruptly, surrounding air cools down the ChG film and its cladding fast (~ 20 °C/s), effectively quenching it for observation in situ. Starting from the continuous film, as deposited after PVD and preform consolidation, we were able to identify three stages in the threedimensional capillary break-up process, complementing the cross-section description. A more detailed overview of the break-up process based on optical micrography is shown in Figure 2.5. First, holes nucleate in the film wherever nanoscopic imperfections or roughness lead to a slightly higher thickness fluctuation. Secondly, assisted by anisotropic stretching, these holes grow along the lines, following areas of smaller thickness. Third, in between holes, the film reflows laterally into long, regularly spaced cylindrical filaments. As apparent in the topmost micrographs, filamentation does not occur regularly over the entire film. Conversely, very regular filaments can be observed once the fiber is scaled down. This observation can be directly linked to the presence/absence of anisotropy in the dewetting process. Prior to stretching, the film is mobile, and dewetting is initiated without anisotropy along the fiber axis. During downscaling (bottom micrographs in Figure 2.5), growth of longitudinal instabilities is inhibited while that of transversal instabilities is enhanced, which leads to the filamentation dewetting pattern observed. The steady-state and capillary breakup pathway remain the same for any cross-section considered, which confers stability and reproducibility to our process. The top view, however, does not capture precise thickness fluctuation, as it only discriminates between the continuous ChG film and holes. For a dynamic visualization of thickness fluctuations, one needs to look at a cross-section as it travels through the furnace, as captured by the model below.



Figure 2.5 - In situ top-view transmission micrographs of the capillary break-up process unfolding during thermal drawing in the neck-down region. Scale bars: first zoom-in level (left column): 200 μ m, second zoom-in level (right column): 50 μ m.

Filamentation model

During thermal drawing, the evolution of the textured film is determined by two competing phenomena [48], [49]. On one hand, interfacial surface energy is minimized by texture flattening, driven by surface tension and interface curvature. On the other hand, Van der Waals (VdW) interactions are intrinsically destabilizing [92]. Any deformation of either film interface (top/bottom) from an initial situation of constant thickness H is referred to as a "perturbation", which can be decomposed as a sum of modes [47]. When both interfaces exhibit symmetry along the mid-film plane, thickness remains constant along the cross-section ("sinuose" mode). Conversely, anti-symmetric perturbations correspond to thickness fluctuations ("varicose" mode) [47].

This fundamental understanding of thin film dewetting dynamics led us to propose substrate nanoimprinting and glancing angle deposition (or thermal reflow, see above) to engineer the initial film thickness at the preform level to control the dewetting path during drawing, resulting in a combination of sinuous and varicose modes termed "template instability/perturbation" (Figure 2.7a). We anticipate that as the fiber is scaled down (Draw Ratio DR(t)) between insertion into the drawing furnace at time t = 0 and exiting it at t = t_f, sinuose modes decay while varicose modes grow,
leading to film thinning and rupture at prescribed locations (Figure 2.7b). However, for flat films, given the randomness of the initial amplitude distribution, filaments with a broad distribution in both size and spacing are obtained with very limited control. Our strategy is instead to select the dominant dewetting instability of the textured film by imposing initial perturbations at the preform level via imprinting and angle deposition to realize the preferred wavelength.

Initial amplitude ratio estimation

As in the linearized model for anisotropic instability of a stretching viscous sheet (AISVS) [47], we consider the perturbation corresponding to the maximal total growth rate Ω_{max} [32], [47]. We now compare it to the templated total growth rate Ω_T (for $\lambda_{\perp} = P$) and therefore its amplitude a_T to that of the fastest-growing instability a_{max} (explicit definitions for Ω and a in Chapter 1). We need the templated perturbation to (i) grow, and (ii) dominate over the perturbation of maximal growth for a flat film, despite the latter growing faster ($\Omega_T \leq \Omega_{max}$), by definition. Adapted from Xu et al.'s work [47], the linearized model used here was implemented in Matlab by Bingrui Xu, predicting templated and fastest-growing instability growth. The simulation parameters can be found in Table 1.

Top layer	Bottom layer	γ Interfacial	Hamaker	Drawing	V_{feed}	Draw
pressure (Pa.s)	pressure (Pa.s)	tension (N.m ⁻¹)	constant (J)	length L (m)	(m.s ⁻¹)	Ratio
10 ⁵	10 ⁵	0.03	10 ⁻¹⁷	0.2	1.6 10 ⁻⁵	30

Table 1 - Parameters used in the linearized model numerical calculation

Based on this simulation, dashed lines in Figure 2.7c give, for different initial film thicknesses H_0 , minimum thicknesses required for (i), i.e. $\Omega_T > 0$, once Van der Waals forces play a pronounced role over the surface tension. Moreover, (ii) requires the templated instability amplitude $a_T(t)$ to remain larger than the fastest-growing mode amplitude $a_{max}(t)$ throughout the draw, i.e. their ratio should remain larger than 1. This translates to: $\frac{a_T(t)}{a_{max}(t)} = \frac{a_T(t=0)}{a_{max}(t=0)}R_{growth}(t) > 1$, where $R_{growth}(t) = \exp([\Omega_T - \Omega_{max}]t)$ is the relative amplitude growth during the draw.

We measure from image analysis on SEM cross sections initial varicose amplitudes ~600 nm for deposited templated films. We consider $a_{max}(t = 0)$ to be at most given by the roughness of a film as deposited. This is a conservative assumption, as the film reflows during preform annealing. An AFM measurement can be found in Figure 2.6 showing peak-to-trough roughness of at most 6 nm, i.e. $a_{max,initial} \leq 6$ nm.



Figure 2.6 - AFM roughness measurement of an As_2Se_3 film after deposition (and before annealing for preform consolidation) to estimate an upper limit for the initial amplitude of the Rayleigh-type instability.

Based on these experimental observations, we estimate for a typical textured film: $\frac{a_T(t=0)}{a_{max}(t=0)}$ ~ 100, and therefore a sufficient condition is that : $R_{growth}(t_f) > \frac{1}{100}$. In Figure 2.7d, dashed lines delimit maximum thicknesses for which (ii) is fulfilled in this conservative case.

Quantitative predictions should be considered with care, as they stem from a linear analysis for small perturbations [93]. Nevertheless, they offer physical insight into the underlying dynamics at play. Fully modeling the non-linearized case can also be achieved by numerically solving (Navier-Stokes) fluid dynamics equations, which we now turn to.



Figure 2.7 - Filamentation models: linear theory, numerical simulation and experimental validation. a, Cross section schematic showing how a thickness fluctuation is obtained by glancing angle deposition on a templated substrate. b, Lagrangian description of in-fiber templated instabilities. Cross section schematics and SEM cross sections show sinuose/varicose modes evolution and dominant competing pressures in the capillary breakup process. c, Linearized model of the total instability growth rates during thermal drawing at three experimental template periodicities (termed "initial period") and for the fastest-growing perturbation, for varying deposition thicknesses. Vertical dashed lines show the maximum thickness for which growth rates

remain positive (horizontal dashed line). d, Relative amplitude growth R_{growth} , for varying film thicknesses. The horizontal dashed line shows the limit above which the template instability remains 100 times larger than the fastest growing one. Using vertical dashed lines from (c), a range of thicknesses for regular filament formation is estimated for each of the three cases (sections in bold). e, Time-discretized Lagrangian CFD simulation: (top) For $R_{height,0}$ varying from 0.6 to 0.8, evolution of R_{height} in time evaluated using the complete expression of the VdW potential. $H_0 = 0.5 \ \mu\text{m}$; (bottom) Associated DR as a function of time. Note that it is held constant at 30 during the late stages of the draw to model the fiber's exit from the oven.

While surface tension obviously tends to flatten a thin film by smoothing the interface to reduce the total interfacial energy, implementing the disjoining pressure in the general case of large amplitudes is comparably more challenging. Based on previous works [94], a complete non-retarded VdW force can be expressed for both the cladding and the film (Appendix 1), relying essentially on the Hamaker procedure combined with the Lifschitz approach [94], [95]. Multiphase computational fluid dynamics (CFD) modeling can now be used to solve (non-linear) Navier-Stokes equations implementing this body force.

Multi-scale physics at play during fiber thermal drawing are simulated using an interactive script, downscaling a cross-section at each step. We adapt a Lagrangian specification for the flow field, following an elementary fiber unit slice during the draw. The velocity field along the fiber axis is in first approximation assimilated to a plug flow [85]. We discretize in time the simulation, which works in two main steps, as described in the schematic in Figure 2.8: (i) Direct solving of Navier-Stokes equations determines the evolution of the two film interfaces at constant cross-sectional dimensions between times t and t+dt; (ii) The cross-sectional profile at t+dt is scaled down to account for the drawing process. The simulation then loops between steps (i) and (ii) until the final cross-sectional dimensions are reached or forces diverge. Re-meshing at every time step ensures solver accuracy spanning over a large set of length scales.



Figure 2.8 - Schematic illustrating the functioning principle of the time-discretized Lagrangian CFD simulation.

To study the evolution of the film, we introduce a dimensionless height ratio $R_{height} = \frac{H_{max} - H_{min}}{H_{max} + H_{min}}$ where H_{max} (resp. H_{min}) is the maximal (resp. minimal) thickness over a unit period. R_{height} characterizes the reflow associated with the varicose mode: $R_{height} = 0$ indicates complete reflow, while $R_{height} = 1$ indicates film break-up. Evolution of this parameter in time is plotted in Figure 2.7e, for different initial values. Sensitivity to simulation parameters can be found in Appendix 2.

When reaching smaller dimensions towards the end of the draw (high DR), the disjoining pressure becomes sufficiently strong to induce local thinning. R_{height} grows rapidly and the divergence of the destabilizing forces beyond this point becomes challenging to capture. In these cases, the curves are extrapolated in dashed lines. Conversely, when the initial varicose mode amplitude was lower ($R_{height,0} \leq 0.6$), the film remains continuous.

The initial Height Ratio $R_{height,0} = \frac{H_{max} - H_{min}}{H_{max} + H_{min}}$ for the film can be measured from SEM image analysis, as shown in Figure 2.9.



Figure 2.9 - $H_{min,0}$ and $H_{max,0}$ measured on an SEM image cross section of the initial film before drawing to calculate $R_{height,0}$. Scale bar: 4 μ m

To validate experimentally for which value of $R_{height,0}$ filamentation occurs, a glancing angle *gradient* was used for PVD. As shown in Figure 2.10a, the nanoimprinted templated film was placed on a curved 3D-printed scaffold. Its slope was designed to make an angle θ linearly increasing with x, the distance along the film's width (longitudinal), with respect to the vertical axis (Figure 2.10b). Clips were also 3D-printed to bend and maintain the film against the curved surface. The whole structure was then placed inside the evaporator chamber for ChG PVD. The film was then placed in a preform and drawn into a fiber, as described earlier. Microtomy was used to produce SEM image crosssections of (i) the fiber and (ii) the initial film in different locations (Figure 2.10c). For H₀ = 550 nm, the initial $R_{height,0}$ was measured from image analysis in nine locations on the film (Figure 2.10d). A linear regression gives $R_{height,0}$ as function of x. The exact location $\frac{x_{lim}}{DR}$ at which filamentation starts in the fiber (middle SEM images) was measured and correlated to the corresponding critical $R_{height,0}(x_{lim}) \approx 0.7$.



Figure 2.10 - Experimental validation of the critical R_{height,0}. a, A ChG film is evaporated onto a templated polymer substrate held with clips against a curved 3D-printed scaffold. b, The scaffold is designed for the angle θ with respect to the vertical axis to increase linearily with x, the film's longitudinal distance. c, (top) SEM images of the initial film's geometry in the <u>preform</u> at some of the locations where R_{height,0} was measured, and (bottom) the film after drawing in the <u>fiber</u>. d, Linear regression of R_{height,0} as a function of the ChG deposition angle θ , allowing experimentally to determine that for $H_0 \sim 500 nm$ and R_{height,0} > 0.6, NW formation occurs. Scale bars: preform: 2 µm, fiber: 2.4 µm.

It is interesting to note that our filamentation threshold obtained through numerical modelling rested on the hypothesis of a non-retarded VdW potential, which overestimates the strength of destabilizing Van der Waals interactions typically beyond 10 nm [96]. Turning to the characteristic minimal film thicknesses H_{min} , it appears that the onset of filamentation typically occurs when H_{min} is of the order of 10 nm, i.e. at distance where the retardation effects are not yet pronounced. The reduced discrepancy between retarded and non-retarded VdW potential at such reduced distances could help explain why our experimental and theoretical predictions are well in line.

Finally, in order to compare linearized and general models, we run simulations for each disjoining pressure method, for different thicknesses (e.g. 0.4 and 0.5 µm). The effective surface tension option stems from the linearized model. We monitor its Height Ratio R_{height}^L and compare it to that of the general non-linearized body force approach R_{height}^{NL} . The absolute difference is plotted in Figure 2.11. Although we are fairly in the linearization approximation (varicose amplitude $a_0 \approx 500 \text{ nm} \ll \lambda_0, \text{with } \lambda_0 = 10, 20 \text{ or } 40 \text{ µm}$), significant deviation between both approaches appears in the late stages of the draw when the film thickness becomes small. This shows that the classical disjoining pressure expression fails to capture well the dynamics once destabilizing interactions become preponderant.



Figure 2.11 - Height ratio discrepancy evolution for $H_0 = 0.4$ or 0.5 μ m and DR_f = 30 using two distinct methods to incorporate the disjoining pressure: (i) through an effective surface tension and (ii) through a body force

approach. Evolution of DR is shown below against normalized drawing time $\frac{t-t_f}{t_0-t_f}$ to show when downscaling is highest, and film thickness lowest.

This difference between disjoining pressure and body force approach can also be found in the critical thickness yielding filamentation. Our simulation results show that as the fiber is scaled down, both linear and general potentials predict an onset to filamentation (e.g. inversion of the Height Ratio curve, not shown here) in the final stage of the process, for sufficiently reduced initial thicknesses. However, while the linearized disjoining pressure shows a filamentation threshold between 400 nm to 500 nm, the non-linear potential shows a transition from presence to absence of filamentation between 500 nm and 600 nm. This highlights the difference between the two disjoining pressure approaches.

Moreover, two important features should be pointed out. First, the system dynamics are highly sensitive to interfacial energy (see Appendix 2). If the actual interaction coefficient was lower than the one calculated, reflow would be highly disfavored and break-up enhanced. Secondly, additional shearing effects occur perpendicularly to the cross-sectional profile studied here [97], which are neglected in our case. Nonetheless, our Lagrangian framework monitoring the evolution of in-plane instabilities during the draw still unravels the rationale behind the process presented in this work, driven by the interplay between disjoining and Laplace pressures.

Achieved geometries

For NWs to be used as building blocks for optics and electronics, a high degree of control over their diameter and spacing is required. Based on our process and fundamental understanding, we now demonstrate our ability to effectively control dewetting periodicity and access additional degrees of freedom in NW array architectures, compared to previous studies. After drawing, a fiber section was prepared to characterize the final geometry of the dewetted film. Figure 2.14a shows the well-ordered filamentation occurring along the entire cross-section of the drawn film. Indeed, compared to the flat film case described by Xu et al. [47], it provides better control over diameter or spacing regularity. From an SEM cross-section of a fiber, we measured the NWs' diameter distribution using image analysis in ImageJ. The distribution is plotted in Figure 2.12, showing a standard deviation $\sigma = 9$ nm for NW mean diameter m = 252 nm. This process relies on a single fiber draw, the diameter/spacing regularity being on par with NW arrays obtained by redrawing [25].



Figure 2.12 - NW diameter distribution. a, SEM cross section of a NW array inside a fiber used for image analysis. Scale bar: 3.5 μ m. b, Diameter distribution from image analysis, grouping in 10 nm bins and fitting for a Gaussian distribution (σ = 9 nm, m = 252 nm).

Although our study did not focus on achieving NWs as thin as possible, for P = 10 μ m and DR = 60, we achieved meters-long 50 nm-diameter NWs in a single draw, an extreme aspect ratio. An SEM cross-section of a NW array achieved for 50 nm diameters is shown in Figure 2.13.



Figure 2.13 - SEM image cross section of a 50 nm-diameter NW array. Scale bar: 100 nm.

The only limit to the number of ChG filaments is given by the size of the drawing tower furnace that limits the preform diameter. For example, for a 30 mm-wide preform and P = 10 μ m, one can expect an array of 3000 filaments. Smaller diameters and periods could be attempted at higher DR (10² to 10³ is typical for optical fiber drawing), by successive redrawing [25], or using templates with smaller periods. As explained previously, thermal drawing confers a strong dampening force to longitudinal instabilities [98], allowing in principle for ChG NW diameters in a PEI matrix to reach sub-10 nm dimensions [25].

In nanophotonics, wavelength dimensions are beneficial to tight optical confinement, reaching single-mode guiding regimes, and increasing the proportion of evanescent power of the guided mode for near-field optical sensing [60]. We further demonstrate that by selecting the right deposited ChG film thickness and template period (Figure 2.14b), one can tune NWs to the desired diameter *and* spacing (Figure 2.14c). The different fibers tested thus far span period/diameter ratios between 2 and 6 (Figure 2.14d). For equal film thicknesses, various periods can be achieved. By contrast, for a given thickness, a flat film would break up around some mean period, given by the fastest-growing instability wavelength described above in the model, if it breaks up at all. By volume conservation, this would impart the wire diameter. Therefore, for flat films, the period/diameter ratio would be solely a function of initial film thickness, estimated numerically in Figure 2.14d (solid line) with our linearized model [47]. This extra degree of freedom accessed by templating transversal instabilities opens applications in far-field coherent scattering applications, as will be discussed in the applications.



Figure 2.14 - Versatility in geometries and structures. a, SEM picture of long-range ordered filaments in a fiber cross-section. b, optical micrographs of cross-sections of the ChG films after deposition onto polymer substrate with different template periods. c, SEM pictures of the corresponding NW array geometry. d, Period/diameter ratio for some fibers tested, compared to the flat film case (solid line), plotted against deposited film thickness. In the latter case, only one period/diameter ratio is accessible for a given film thickness. e, Filaments can be accessed individually when dissolving the cladding. f, Small satellite NWs can be seen for each larger NW, demonstrating the possibility to achieve sub-period dewetting. g, Layers can be stacked to make three-dimensional architectures. Scale bars are respectively: a: 10 μ m, b: 20 μ m, c: 200 μ m (top), 100 μ m (middle), 50 μ m (bottom), e: 1 μ m, f: 2 μ m, g: 1.5 μ m.

The cladding can also be dissolved for the wires to be used separately (Figure 2.14e) or in a bundle (Appendix 3). By exposing them, they can be contacted and become electrochemically sensitive to their surrounding environment, as has been done for functionalized NW FET devices [99], [100, p.], [101], leveraging the high surface sensitivity of their extreme aspect ratio. They can also be manipulated into optical assemblies using optical trapping and optoelectronic tweezers [59]. To increase the density of NWs for optics applications relying on 3D arrangements such as photonic crystals [102] and metamaterials [64], we also show that our process is not limited to a 2D space. By using other template shapes, PVD anisotropy can be used to deposit thicker layers at prescribed locations to achieve sub-period dewetting [83]. We here demonstrate that by evaporating directly a layer onto a template made of rectangular grooves [103] (Figure 2.2), several NWs can be obtained for each period (Figure 2.14f): a second array of NWs can be seen in a different plane from the main

one, enabling "quasi-3D" architectures. Finally, to achieve matrices of filaments truly spanning all dimensions of space, we prepared a preform consisting of several stacked films. In a single step, they were drawn together, breaking up into multiple arrays of filaments simultaneously. The SEM cross-section in Figure 2.14g shows three such layers, paving the way towards 3D NW arrangements.

Optical applications

Diffraction

The additional degrees of freedom in fiber dewetting enabled by our process call for new applications. In optics, the long-range order of the filament array leads to far-field diffraction, which makes these arrays ultralong flexible gratings, both in transmission (Figure 2.16a inset) and reflection. The fiber can be cut into pieces for making numerous individual gratings, at very high throughput and low manufacturing costs: a preform can be drawn within hours into a fiber whose length scales quadratically with DR. A 50 cm-long preform, for instance, for DR_f = 100, yields a 5 kmlong fiber, corresponding to 50'000 10 cm-long flexible gratings. Moreover, as aforementioned, by adjusting the template period and deposited thickness, one can not only adjust the grating period but also the wire diameter to best achieve the desired diffraction efficiency at a given wavelength, as will be shown in this section. These parameters are analogous to groove density and groove shape in conventional gratings. To demonstrate this ability, we drew two fibers of similar periods p (1405 nm \pm 60 nm), but of different NW diameters d (236 nm and 329 nm). Using a rotating stage (see Experimental section), we compared the spectra of the first-order diffraction efficiency to the specular one for both fibers. In Figure 2.16a, we ploted the intensity ratio $R_{01} = \frac{\eta_{m=1}}{\eta_{m=0}} = \frac{I_{m=1}}{I_{m=0}}$ where η_m is the diffraction efficiency of the transmitted order m, and I_m its intensity. Although they diffract at the same angles, the two fibers exhibit different efficiency spectra between orders. The fiber with thinner NWs shows a dip in R_{01} in the red when the one with thicker NWs peaks.

To simulate diffraction behavior for arrays of filaments at various periods, diameters and wavelengths, we used rigorous coupled-wave analysis (RCWA), a semi-analytical method in computational electromagnetics. It is usually employed to predict scattering from periodic dielectric structures. It builds upon a Fourier-space method so that geometries and fields are represented by a sum of spatial harmonics. This method is implemented in a MATLAB environment, based on an open-source package called RETICOLO [104], [105]. It is an efficient and accurate toolbox for simulating and describing the electromagnetic field through the grating. We defined a 1D periodic geometry whose unit cell is an As₂Se₃ cylindrical (circular cross sections) filament of diameter d, in a PEI cladding. The geometry must be discretized in slices, as visible in the inset in Figure 2.15. The top and bottom PEI cladding layers are not considered for simplicity. Refractive indexes for As₂Se₃ were measured with a spectroscopic ellipsometer Sopra GES 5E [83]. Refractive indexes for PEI were taken from literature [106], [107]. The simulation calculated absolute efficiencies for the different reflected and transmitted orders for a given geometry, wavelength and number of terms used in the Fourier series expansion of the approximated solution. By looping over wavelengths from 400 to 1000 nm, one can plot efficiencies for all orders, as shown in the example in Figure 2.15, for instance for d = 328 nm, p = 1.43 μ m. For most simulations, we used slices 5 nm thick to reduce computation time. We verified the sensitivity of the results to this parameter by running our script in a simple case for 0.5 nm slices. We estimate this thickness to be much smaller than both wavelength and wire diameter (50 nm at minimum) and thus a reference to compare with. Results for 5 nm slices deviated at most by 1%, when the simulation time was reduced by about a factor 10. We also verified sensitivity to the number of Fourier series terms. This time, the reference taken was 50

terms. Again, we didn't see more than 1% deviation when using only 15 terms, when the simulation time was reduced by a factor 2.



Figure 2.15 - Simulated absolute efficiencies for the transmitted and reflected orders for d = 328 nm, p = 1.43 µm using RCWA simulations. The inset shows how the unit period geometry was described spatially.

We further explored R₀₁ by simulation for a wide range of diameters and incident wavelengths λ_i . Figure 2.16b shows an example of the obtained spectra for *d* varying from 200 to 400 nm, at constant period $p = 1.4 \mu m$. Dotted lines situate the two fibers assessed experimentally. For a chosen operating wavelength our process enables tuning period and diameter independently so that, for instance, R₀₁ can be optimized. To predict how efficient the grating can be at diffracting in the first order, for a given $\frac{p}{d}$ ratio, diameters and periods were swept within ranges obtained experimentally ($d \in [50 \text{ nm}, 400 \text{ nm}]$ and $p \in [2d, 6d]$) to find maximal values for R₀₁. Maxima were combined in a heatmap in Figure 2.16c. It is noteworthy that high diffraction is rather achieved for wavelengths larger than 650 nm and filaments as close to each other as possible with respect to the period. This effect can be explained by describing inter and intra-filament modes in a multiple scattering framework [108] which we envision to develop in future work.



Figure 2.16 - Optical characterization and applications. a, Experimental measurements of R01 against incident beam wavelength for two fibers of similar NW array period $p \approx 1.4 \mu m$, with different NW diameters. b, From RCWA, R01 spectra for various NW diameters d ($p = 1.4 \mu m$). The two fibers assessed experimentally are represented with dotted lines. c, For given values of incident beam wavelength λi and period/diameter p/d, we vary p and d (respectively in [50 nm, 400 nm] and [2d, 6d]) to find maximal R01. A heatmap of R01 is plotted showing high diffraction for $\lambda i > 650$ nm and high grating fill factors (filaments closer to each other). d, Simulated scattering cross-section spectra of a single ChG NW of varying diameter under a normally incident plane wave in air. Three Mie resonant modes are identified with dashed lines and maps of their normalized field intensity around the wire are plotted as inserts, for a wire diameter of 240nm. e, Simulated phase shift spectra in transmission for a 300 nm-period NW array and varying diameters. f, Normalized transmission amplitude and full phase shift coverage (dashed line in (e)) through As2Se3 NW arrays of varying diameter, with period p = 300 nm, under normally-incident illumination at 800 nm. In figures a to f, for clarity, only results for an incident beam polarized parallel to the NWs are shown. g, Long-range metaperiodicity following the template. The distance between filaments can be tailored individually, paving the way towards one-dimensional metasurfaces.

1D Metasurface

High index contrast $(\frac{n_{As_2Se_3}}{n_{PEI}} > 2$ for $\lambda_i > 650$ nm) and relatively low-loss [109] ($k_{As_2Se_3} < 0.4$ for $\lambda_i > 650$ nm) [83] dielectric inclusions such as ChG NWs can exhibit subwavelength localization of light. Such Mie resonances benefit from lower losses than their plasmonic counterpart [83]. These nanostructures thus offer a new way to manipulate light efficiently below the diffraction limit based on their well-defined shapes and dimensions. To illustrate this assertion, we numerically investigated

the scattering response of a single ChG NW to a normally incident plane wave using a finitedifference time-domain (FDTD) software. Figure 2.16d shows the multipolar scattering response in air for varying wavelengths and NW diameters in the range we achieved experimentally. The first three main Mie resonances [109] are represented with dashed lines. The cross-section normalized field intensity of these modes is represented in inserts. Such high-index inclusions are subwavelength building blocks which can be assembled into metasurfaces for wavefront manipulation. As an example, we showed in Figure 2.16e the resulting transmitted phase (for transmitted amplitude and details, see Appendix 4) of NWs arranged in a periodic array, using FDTD simulations. We investigated various diameters, under visible/near-IR illumination. Figure 2.16f is a cut through the map at an 800 nm illumination. At this wavelength, a full 0-2 π phase coverage can be achieved while maintaining high transmission (>75% of incident amplitude), enabling wavefront control [110]. Based on this principle, flat focusing gratings have been proposed [111]. We further showed the possibility to tune independently every single spacing (and diameter) between two consecutive NWs. As an example, a substrate was templated with supercells consisting of linearly increasing periods P = 20 μ m to 40 μ m, in 4 μ m increments. This supercell was repeated over the entire imprint to template the ChG film. The resulting filamentation still followed well the template aperiodicity, leading to a "meta-arrangement" of NWs. An SEM cross-section of the filaments in the fiber cladding is shown in Figure 2.16g. Such geometrical arrangements in transmitting arrays are exploited as subwavelength-thick beam deflector devices [112]. Thus, we believe the proposed filamentation process demonstrated here opens a new pathway with minimal steps for the manufacturing at large scale of in-fiber 1D photonic metasurfaces and flat optics devices.

Conclusion

Based on a model for anisotropic instabilities in a viscous sheet under stretching, we proposed a process to obtain large-scale extremely long nanowires with controllable spacing in a single fiber drawing. This was achieved by templating the fiber preform, followed by a well-chosen glazing incident deposition, to induce strong film thickness fluctuations. After drawing, the resulting ultralong NWs exhibit a high degree of order. Film dewetting dynamics were described as two competing forces, namely surface tension to maintain stability and Van der Waals forces to drive the instability. We used a linearized model approximation to describe under which conditions the selected thickness perturbation wavelength of templated thickness dominates film break-up. We further developed a script to predict the evolution of any film geometry throughout thermal drawing by running iteratively scaled CFD simulations. As opposed to flat films, we then demonstrated that our process enables tuning independently NW diameter and spacing, based on the initial template period and deposited thickness. Several arrays can be stacked to make three-dimensional structures. Chalcogenide arrays were characterized for optical diffraction. The ability to tune independently NW diameter and spacing allows tuning of diffraction efficiencies. Finally, since the template for deposition can be designed to an arbitrary periodicity, we hinted at the possibility to obtain metasurfaces in multimaterial fibers by self-assembly during fiber drawing. This novel yet simple high throughput process opens a pathway to manufacture cost-efficient ultralong tunable NW arrays for nano-photonics and optoelectronic applications requiring long-range order over several meters.

Experimental section

PDMS micro-imprinting

The PDMS mold is replicated from a silicon one obtained by dry reactive etching and photolithography at EPFL's Center for Microtechnology clean room. To obtain the Silicon master template, a standard silicon wafer is coated with 1 μ m AZ ECI 3007 photoresist, then exposed in a Heidelberg VPG 200 laser pattern generator, and dry etched in an Alcatel AMS 200 SE with fluorine chemistry. The PDMS mold is finally used in a NanoImprint EHN-3250 thermal nanoimprinter to hotemboss a thermoplastic (PEI or PSU) film. Imprints are checked with optical profilometry. In this work, the mold's period P was chosen to be P = 10, 20 or 40 μ m.

Chalcogenide deposition

ChGs (As₂Se₃ or Se) are deposited in a custom-built thermal evaporator comprising an Oerlikon UNIVEX 250 chamber. Current heats up glass chunks in a boat under high vacuum. The imprinted/embossed films are taped onto a stage rotating for deposition homogeneity. The setup and average deposition angle are detailed in Figure 2.3. This angle is controlled by placing the sample on custom-made pyramidal structures. The deposited thickness is measured by a quartz crystal microbalance, calibrated by measuring the depth of a scratch in the ChG film on a Si fragment by optical profilometry.

Preform consolidation and thermal drawing

To encapsulate the ChG film after deposition into the fiber preform, it was placed between a thermoplastic (PEI or PSU) plate and a flat 100 μ m-thick film. The stack was placed in a Meyer hot press at 250°C for 10 minutes. This preform "consolidation" time is kept to a minimum to limit isotropic annealing to the minimum required for encapsulation of the ChG. The fiber was then drawn in a custom-built drawing tower. The preform was fed into a furnace, typically at 1 mm/mn. The final draw ratio was usually 30 (drawing at 0.9 m/mn), except for achieving 50 nm-wide filaments, for which a draw ratio as high as 60 was reached. The furnace temperatures were set to 210, 360 and 130°C for the top, center and bottom parts respectively. The actual air temperature inside the oven is thought to be about 50°C lower. Drawing faster (feed speed = 2 mm/mn for the same draw ratio) was also successfully attempted using ~10°C higher furnace temperatures.

Fiber cross-sections characterization

When the NW array gets small, optical microscopy is hindered by the diffraction limit. In transmission, only interference patterns can be seen, although this gives a first idea of the regularity of the filamentation. A clean cross-section of the fiber is therefore required to precisely understand the final ChG film geometry at the nanoscale within the polymer cladding. The best results were obtained using a Gatan ILION II ion polisher. Reasonably good surfaces could also be prepared faster using a Leica UC 7 ultramicrotome. The cross-sections were then carbon coated (10 nm) for observation in a Zeiss GeminiSEM field emission SEM equipped with a GEMINI II column operating at 3.0 kV with a 30μ m aperture. For small NWs at high magnification, a lower acceleration voltage (<1kV) had to be used to avoid sample degradation. One could also dissolve the fiber cladding to analyze the wires, but doing so destroys their periodic spacing and encapsulation. Diameter and spacing distributions were computed from image analysis of the SEM pictures in ImageJ.

Diffraction setup

Diffraction efficiency was measured using a PM100D Thorlabs Digital Power Meter with the S120C Photodiode Power Sensor on a rotating stage to follow the first transmitted order at different angles. The incident beam was prepared from a SuperK EXTREME supercontinuum laser from NKT photonics through a 100 μ m-wide slit restricting the beam to the NW array area in the fibers tested. The laser was used at 10% of its maximum power with a 10 nm bandwidth. See Appendix 5 for the experimental setup. Although laser power depends on the wavelength, by measuring the first order diffraction relatively to the specular, such power variations are cancelled out. The power meter photodiode's distance to the fiber was adjusted to encompass whole transmitted orders despite some angular dispersion due to the NW diameter dispersion (see distribution characterization in Figure 2.12), but far enough not to measure several orders at the same time.

Appendix 1: Body force from a reconstructed Van der Waals potential for a corrugated free film

Using the Hamaker procedure to obtain the body force potential has two advantages: (i) in contrast to the disjoining pressure approach it can easily be formulated for any interfacial corrugated state of the film's interfaces and is therefore applicable to both short and long wavelength disturbance regimes; (ii) it is computationally easier to formulate the Hamaker potential for an unsymmetrical film system than it is to calculate the disjoining pressure of such a system. Details on how to implement the body force for Van Der Waals (VdW) interactions based on the general case of a corrugated interface are provided below. Electromagnetic retardation effects, which may reduce the strength of VdW interactions with increased interatomic distance, are here neglected at this stage for the sake of simplicity. The body force is simply the opposite of the gradient of this potential. This derivation stems from (ref. [94], [95], [113]). The result for the VdW potential depends on the region of study. The change in potential energy is derived by first computing the potential energy of interaction (due to the VdW force) of molecules in an infinitesimal volume of continuum with respect to (i) the rest of the molecules in the film system and (ii) the rest of the molecules in the infinite system. The subtraction between these two energies is termed the excess VdW potential; the negative gradient of this potential is the body force which is introduced into the equation of motion.



Figure 2.17 - 2D schematic of the film system. The origin of the system is taken as the midplane of the unperturbed film. Let h be the mean thickness of film II. ζ and η are interface corrugations. Adapted from (ref. [94]).

The VdW potential $w_{i,j}$ between two molecules i and j can be written in the far field approximation as:

$$w_{i,j}(r) \sim \frac{C_{i,j}}{r^6}$$
 (2.1)

$$A_{i,j} = \pi^2 \rho^i \rho^j C_{i,j} \tag{2.2}$$

 $F_{i,j}(s)$ represents the potential energy (per unit volume) at a point r in phase i due to an infinite plane of phase j that is located at a perpendicular distance s from r (valid in 3D):

$$F_{i,j}(s) = \rho^i \rho^j \int_{s}^{\infty} 2\pi r w_{i,j}(r) dr = \frac{\rho^i \rho^j C_{i,j} 2\pi}{4 s^4} = \frac{1}{2\pi} \frac{A_{i,j}}{s^4}$$
(2.3)

Where $A_{i,j} = \pi^2 \rho^i \rho^j C_{i,j}$. The function $H^1_{i,j}(x, y, z, t)$ (resp. $H^2_{i,j}(x, y, z, t)$) is the perturbation in the potential energy (per unit volume) at a point in phase i, with coordinates (x,y) and located at a distance |z| from the unperturbed upper (resp. lower) interface, caused by the displacement of phase j with the corrugation of the interface.

$$H^{1}_{i,j}(x,z,t) = \rho^{i} \rho^{j} \int_{\beta=-\infty}^{\infty} \int_{\alpha=-\infty}^{\infty} \int_{\gamma=0}^{\xi(\alpha,t)} w_{i,j} (((z-\gamma)^{2} + (x-\alpha)^{2} + (y-\beta)^{2})^{1/2}) d\beta d\alpha d\gamma$$
(2.4)

$$H^{2}_{i,j}(x,z,t) = \rho^{i} \rho^{j} \int_{\alpha=-\infty}^{\infty} \int_{\beta=-\infty}^{\infty} \int_{\gamma=0}^{\eta(\alpha,t)} w_{i,j} (((z-\gamma)^{2} + (x-\alpha)^{2} + (y-\beta)^{2})^{1/2}) d\beta d\alpha d\gamma$$
(2.5)

Developing these terms using the potential yields (in 2D):

$$H^{1}_{i,j}(x,z,t) = \rho^{i} \rho^{j} \int_{\beta=-\infty}^{\infty} \int_{\alpha=-\infty}^{\infty} \int_{\gamma=0}^{\infty} \frac{\xi(\alpha,t)}{((z-\gamma)^{2} + (x-\alpha)^{2} + (y-\beta)^{2})^{3}} d\alpha d\beta d\gamma$$
(2.6)

$$H^{2}_{i,j}(x,z,t) = \rho^{i} \rho^{j} \int_{\beta=-\infty}^{\infty} \int_{\alpha=-\infty}^{\infty} \int_{\gamma=0}^{\eta(\alpha,t)} \frac{C_{i,j}}{((z-\gamma)^{2} + (x-\alpha)^{2} + (y-\beta)^{2})^{3}} d\alpha d\beta d\gamma$$
(2.7)

Development of the flat film contribution

For any point in Film I (top layer):

$$\rho^{I}W^{I}{}_{NP}(x,z,t) = \int_{z-h/2}^{\frac{h}{2}+z} F_{I,II}(u) \, du + \int_{\frac{h}{2}+z}^{\infty} F_{I,I}(u) \, du + \int_{0}^{\infty} F_{I,I}(u) \, du + \int_{z-\frac{h}{2}}^{0} F_{I,I}(u) \, du - \int_{z-\frac{h}{2}}^{0} F_{I,I}(u) \, du + \int_{0}^{0} F_{I,I}(u) \, du + \int_{z-\frac{h}{2}}^{0} F_{I,I}(u) \, du - \int_{z+\frac{h}{2}}^{0} F_{I,I}(u) \, du + \int_{z+\frac{h}{2}$$

where NP stands for not perturbed, i.e. the flat film situation. After simplification:

$$\rho^{I}W^{I}{}_{NP}(x,z,t) = \frac{1}{2\pi} \left(A_{I,I} + A_{II,II} - 2A_{I,II} \right) \frac{1}{3\left(\frac{h}{2} + z\right)^{3}}$$
(2.9)

For any point in Film II :

$$\rho^{\parallel}W^{II}{}_{NP}(x,z,t) = \left(\int_{\frac{h}{2}-z}^{\infty} F_{II,I}(u) \, du + \int_{-\infty}^{z+\frac{h}{2}} F_{II,I}(u) \, du + \int_{0}^{0} F_{II,II}(u) \, du + \int_{z+\frac{h}{2}}^{0} F_{II,II}(u) \, du\right)$$

$$- \left(\int_{-\infty}^{\frac{h}{2}+z} F_{II,I}(u) \, du + \int_{\frac{h}{2}+z}^{0} F_{II,II}(u) \, du + \int_{0}^{\infty} F_{II,II}(u) \, du\right)$$

$$- \left(\int_{0}^{\frac{h}{2}-z} F_{II,II}(u) \, du + \int_{-\infty}^{0} F_{II,II}(u) \, du + \int_{\frac{h}{2}-z}^{\infty} F_{II,I}(u) \, du\right)$$

$$\rho^{\parallel}W^{II}{}_{NP}(x,z,t) = -\int_{-\infty}^{\infty} (F_{II,II}(u)) \, du$$

$$(2.11)$$

For any point in Film III (bottom layer):

$$\rho^{III}W^{III}{}_{NP}(x,z,t) = \int_{0}^{\infty} F_{I,I}(u) \, du + \int_{0}^{-\frac{h}{2}-z} F_{I,I}(u) \, du + \int_{-\frac{h}{2}-z}^{\frac{h}{2}-z} F_{I,II}(u) \, du + \int_{\frac{h}{2}-z}^{\infty} F_{I,I}(u) \, du + \int_{0}^{\infty} F_{I,I}(u) \, du + \int_{0}^{-\frac{h}{2}-z} F_{I,I}(u) \, du + \int_{-\frac{h}{2}-z}^{\infty} F_{III,III}(u) \, du + \int_{0}^{-\frac{h}{2}-z} F_{I,II}(u) \, du + \int_{\frac{h}{2}-z}^{\infty} F_{I,III}(u) \, du + \int_{0}^{\infty} F_{II,II}(u) \, du + \int_{\frac{h}{2}-z}^{\infty} F_{I,II}(u) \, du + \int_{0}^{\infty} F_{I,II}(u) \, du + \int_{\frac{h}{2}-z}^{\infty} F_{I,II}(u) \, du + \int_{\frac{h}{2}-z}^{\infty} F_{I,II}(u) \, du + \int_{0}^{\infty} F_{I,II}(u) \, du + \int_{\frac{h}{2}-z}^{\infty} F_{I,II}(u) \, du + \int_{0}^{\infty} F_{I,II}(u) \, du + \int_{\frac{h}{2}-z}^{\infty} F_{I,II}(u) \, du + \int_{\frac{h}{2}-z}$$

To obtain the body force, we can derivate along relevant directions:

- Derivative along x

$$-\frac{\partial \rho^{l} W^{l}{}_{NP}(x,z,t)}{\partial x} = 0$$
(2.14)

$$\frac{\partial \rho^{II} W^{II}{}_{NP}(x,z,t)}{\partial x} = 0$$
(2.15)

$$-\frac{\partial \rho^{III} W^{III}{}_{NP}(x,z,t)}{\partial x} = 0$$
(2.16)

- Derivative along z

$$-\frac{\partial \rho^{I} W^{I}{}_{NP}(x,z,t)}{\partial z} = \frac{1}{2\pi} \left(A_{I,I} + A_{II,II} - 2A_{I,II} \right) \frac{1}{\left(\frac{h}{2} + z\right)^{4}}$$
(2.17)

$$\frac{\partial \rho^{II} W^{II}{}_{NP}(x,z,t)}{\partial z} = 0$$
(2.18)

$$-\frac{\partial \rho^{III} W^{III}{}_{NP}(x,z,t)}{\partial z} = -\frac{1}{2\pi} \left(A_{I,I} + A_{II,II} - 2A_{I,II} \right) \frac{1}{\left(\frac{h}{2} - z\right)^4}$$
(2.19)

Development of the corrugation contribution

Let us calculate the film I excess VdW potential considering that the reference system is the corrugated interface (I, II) with the interface (II, III) at infinity. The function $H^{1}_{i,j}(x, y, v, t)$ (resp. $H^{2}_{i,j}(x, y, v, t)$) is the perturbation in the potential energy (per unit volume) at a point in phase i, with coordinates (x, y) and located at a distance |v| from the unperturbed upper (lower) interface, caused by the displacement of phase j with the corrugation of the interface

$$\rho^{J}W^{I}{}_{P}(x,z,t) = H^{1}{}_{I,II}\left(x,-z+\frac{h}{2},t\right) - H^{1}{}_{I,I}\left(x,-z+\frac{h}{2},t\right) + H^{2}{}_{I,I}\left(x,z+\frac{h}{2},t\right) - H^{2}{}_{I,II}\left(x,z+\frac{h}{2},t\right) - H^{2}{}_{I,II}\left(x,z+\frac{h}{2},t\right) - \left(H^{1}{}_{I,II}\left(x,-z+\frac{h}{2},t\right) - H^{1}{}_{I,II}\left(x,-z+\frac{h}{2},t\right) - \left(H^{2}{}_{II,I}\left(x,z+\frac{h}{2},t\right) - H^{2}{}_{II,II}\left(x,z+\frac{h}{2},t\right) - H^{2}{}_{II,II}\left(x,z+\frac{h}$$

where P stands for the perturbed case with respect to the flat film case, i.e. the additional corrugation. This further simplifies:

$$\rho^{I}W^{I}{}_{P}(x,z,t) = H^{2}{}_{I,I}\left(x,-z+\frac{h}{2},t\right) + H^{2}{}_{II,II}\left(x,-z+\frac{h}{2},t\right) - 2H^{2}{}_{I,II}\left(x,-z+\frac{h}{2},t\right)$$
(2.21)

$$\rho^{II}W^{II}{}_{P}(x,z,t) = -H^{1}{}_{I,II}\left(x,-z+\frac{h}{2},t\right) + H^{1}{}_{II,II}\left(x,-z+\frac{h}{2},t\right) - H^{2}{}_{II,II}\left(x,z+\frac{h}{2},t\right) + H^{2}{}_{I,II}\left(x,z+\frac{h}{2},t\right)$$

$$-\left(-H^{1}{}_{I,II}\left(x,-z+\frac{h}{2},t\right) + H^{1}{}_{II,II}\left(x,-z+\frac{h}{2},t\right)\right) - \left(-H^{2}{}_{II,II}\left(x,z+\frac{h}{2},t\right) + H^{2}{}_{I,II}\left(x,z+\frac{h}{2},t\right)\right)$$

$$\rho^{II}W^{II}{}_{P}(x,z,t) = 0$$

$$(2.23)$$

$$\rho^{J}W^{III}{}_{P}(x,z,t) = H^{1}{}_{I,II}\left(x,-z+\frac{h}{2},t\right) - H^{1}{}_{I,I}\left(x,-z+\frac{h}{2},t\right) + H^{2}{}_{I,I}(x,z+h/2,t) - H^{2}{}_{I,II}(x,z+h/2,t)$$

$$-\left(H^{1}{}_{II,II}\left(x,-z+\frac{h}{2},t\right) - H^{1}{}_{II,I}\left(x,-z+\frac{h}{2},t\right)\right) - \left(H^{2}{}_{I,I}\left(x,z+\frac{h}{2},t\right) - H^{2}{}_{I,II}\left(x,z+\frac{h}{2},t\right)\right)$$

$$\rho^{J}W^{III}{}_{P}(x,z,t) = 2H^{1}{}_{I,II}\left(x,-z+\frac{h}{2},t\right) - H^{1}{}_{I,I}\left(x,-z+\frac{h}{2},t\right) - H^{1}{}_{I,II}\left(x,-z+\frac{h}{2},t\right)$$

$$(2.24)$$

$$(2.24)$$

Let us develop the integral terms:

$$H^{1}_{i,j}(x,y,\nu,t) = \rho^{j} \rho^{j} \int_{\alpha=-\infty}^{\infty} \int_{\beta=-\infty}^{\infty} \int_{\gamma=0}^{\zeta(x,t)} \frac{C_{i,j}}{((\nu-\gamma)^{2} + (x-\alpha)^{2} + (y-\beta)^{2})^{3}} dX dY d\gamma$$
(2.26)

We substitute: $X = \alpha - x$ and $dX = d\alpha$. Similarly: $Y = y - \beta$ and $dY = d\beta$; $Z = \gamma - z$ and $dZ = d\gamma$:

$$H^{1}_{i,j}(x,y,\nu,t) = \rho^{i} \rho^{j} \int_{Y=-\infty}^{\infty} \int_{Z=+\nu}^{\zeta(x,t)+\nu} \frac{C_{i,j}}{((Z)^{2} + (X)^{2} + (Y)^{2})^{3}} dX dY dZ$$
(2.27)

Let us integrate along Y first, given that $\zeta(x, t)$ is not dependent on Y :

$$H^{1}_{i,j}(x,\nu,t) = \rho^{i}\rho^{j} \int_{X=-\infty}^{\infty} \int_{Z=+\nu}^{\zeta(x,t)+\nu} \int_{Y=-\infty}^{\infty} \frac{C_{i,j}}{((Z)^{2} + (X)^{2} + (Y)^{2})^{3}} dX dY dZ$$
(2.28)

For that, we consider $C = \sqrt{X^2 + Z^2}$ and do a variable change considering Y = C.tan(u) and $dY = \frac{c}{cos^2(u)} du$:

$$H^{1}_{i,j}(x,\nu,t) = \rho^{i} \rho^{j} C_{i,j} \int_{X=-\infty}^{\infty} \int_{Z=+\nu}^{\zeta(x,t)+\nu} \int_{u=-\pi/2}^{\pi/2} \frac{1}{(C)^{6} (1 + tan^{2}(u))^{3}} \frac{C}{\cos^{2}(u)} dX du dZ$$
(2.29)

$$H^{1}_{i,j}(x,\nu,t) = \frac{3}{8\pi} A_{i,j} \int_{\alpha=-\infty}^{\infty} \int_{\beta=0}^{\zeta(x,t)} \frac{1}{((\nu-\beta)^{2}+(x-\alpha)^{2})^{5/2}} \, d\alpha d\beta$$
(2.30)

To obtain the body force, we can derivate along relevant directions:

- Derivative along x

$$-\frac{\partial H^{1}_{i,j}}{\partial x} = \frac{3}{8\pi} A_{i,j} \left[-\frac{\partial \zeta}{\partial x} \int_{\alpha=-\infty}^{\infty} \frac{1}{((\nu-\zeta(x,t))^{2} + (x-\alpha)^{2})^{5/2}} d\alpha d\beta + 5 \int_{\alpha=-\infty}^{\infty} \int_{\beta=0}^{\zeta(x,t)} \frac{(x-\alpha)}{((\nu-\beta)^{2} + (x-\alpha)^{2})^{7/2}} d\alpha d\beta \right]$$
(2.31)

- Derivative along z

$$-\frac{\partial H^{1}_{i,j}}{\partial z} = \frac{15}{8\pi} A_{i,j} \left[\int_{\alpha=-\infty}^{\infty} \int_{\beta=0}^{\zeta(x,t)} \frac{\partial \nu}{\partial z} \frac{(\nu-\beta)}{((\nu-\beta)^{2}+(x-\alpha)^{2})^{7/2}} \, d\alpha d\beta \right]$$
(2.32)

Considering that $\nu = -z + \frac{h}{2}$ for film III:

$$\rho^{I}W^{III}{}_{P}(x,z,t) = 2H^{1}{}_{I,II}\left(x,-z+\frac{h}{2},t\right) - H^{1}{}_{I,I}\left(x,-z+\frac{h}{2},t\right) - H^{1}{}_{II,II}\left(x,-z+\frac{h}{2},t\right)$$
(2.33)

- Along the z-axis:

$$-\frac{\partial \rho^{III} W^{III}{}_{P}(x,z,t)}{\partial z} = -\frac{3}{8\pi} (A_{I,I} + A_{II,II}) - 2A_{I,II} \int_{\alpha=-\infty}^{\infty} \left[\frac{1}{\left(\left(-z + \frac{h}{2} - \zeta \left(\alpha, t \right) \right)^{2} + (x - \alpha)^{2} \right)^{5/2}} - \frac{1}{\left(\left(-z + \frac{h}{2} \right)^{2} + (x - \alpha)^{2} \right)^{5/2}} \right]$$
(2.34)

- Along the x-axis:

$$-\frac{\partial \rho^{III} W^{III}{}_{P}(x,z,t)}{\partial x} = \frac{3}{8\pi} \left(A_{I,I} + A_{II,II} - 2A_{I,II} \right) \left[\frac{\partial \zeta}{\partial x} \int_{\alpha=-\infty}^{\infty} \frac{1}{\left(\left(-z + \frac{h}{2} - \zeta(\alpha,t) \right)^{2} + (x-\alpha)^{2} \right)^{5/2}} d\alpha d\beta - 5 \int_{\alpha=-\infty}^{\infty} \int_{\beta=0}^{\zeta(x,t)} \frac{(x-\alpha)}{\left(\left(-z + \frac{h}{2} - \beta \right)^{2} + (x-\alpha)^{2} \right)^{7/2}} d\alpha d\beta \right]$$
(2.35)

Considering that $\nu = z + \frac{h}{2}$ for I:

$$\rho^{I}W^{I}{}_{P}(x,z,t) = H^{2}{}_{I,I}\left(x,z+\frac{h}{2},t\right) + H^{2}{}_{II,II}\left(x,z+\frac{h}{2},t\right) - 2H^{2}{}_{I,II}\left(x,z+\frac{h}{2},t\right)$$
(2.36)

- Along the z-axis:

$$-\frac{\partial \rho^{I} W^{I}_{P}(x,z,t)}{\partial z} = -\frac{3}{8\pi} (A_{I,I} + A_{II,II}) - 2A_{I,II} \left[\int_{\alpha=-\infty}^{\infty} \left(\frac{1}{\left(\left(z + \frac{h}{2} - \eta (x,t) \right)^{2} + (x-\alpha)^{2} \right)^{5/2}} - \frac{1}{\left(\left(z + \frac{h}{2} \right)^{2} + (x-\alpha)^{2} \right)^{5/2}} \right) d\alpha \right]$$
(2.37)

- Along x-axis:

$$-\frac{\partial \rho^{I} W^{I}{}_{P}(x,z,t)}{\partial x} = -\frac{3}{8\pi} \left(A_{I,I} + A_{II,II} - 2A_{I,II} \right) \left[\frac{\partial \eta}{\partial x} \int_{\alpha=-\infty}^{\infty} \frac{1}{\left(\left(z + \frac{h}{2} - \eta(x,t) \right)^{2} + (x-\alpha)^{2} \right)^{5/2}} d\alpha - 5 \int_{\alpha=-\infty}^{\infty} \int_{\beta=0}^{\eta} \frac{(x,t)}{\left(\left(z + \frac{h}{2} - \beta \right)^{2} + (x-\alpha)^{2} \right)^{7/2}} d\alpha d\beta \right]$$
(2.38)

Total contributions

For any point in film I (top layer):

$$\rho^{l}W^{l}_{total}(x,z,t) = \rho^{l}W^{l}{}_{NP}(x,z,t) + \rho^{l}W^{l}{}_{P}(x,z,t)$$
(2.39)

For any point in Film II:

$$\rho^{''}W^{II}_{total}(x,z,t) = \rho^{''}W^{II}{}_{NP}(x,z,t) + \rho^{''}W^{II}{}_{P}(x,z,t)$$
(2.40)

For any point in Film III (bottom layer):

$$\rho^{I}W^{III}{}_{total}(x,z,t) = \rho^{I}W^{III}{}_{NP}(x,z,t) + \rho^{I}W^{III}{}_{P}(x,z,t)$$
(2.41)

Appendix 2: CFD model sensitivity analysis

Mesh and time discretization

To validate the accuracy of the numerical model, we first considered the influence of spatial and time discretization on film dynamics (Figure 2.18). To assess mesh accuracy, we monitored the film's Height Ratio using the simulation framework for increasing meshing density (decreasing numbers indicate increasing solver accuracy). The limited deviation apparent in the graph highlights that a meshing density of 5 is sufficient for accurate calculations. The system seems significantly more dependent on time discretization. Simulation time is also sensitive to the time discretization step. We set for the rest of this work a time discretization in 20 steps as a compromise between simulation time and convergence of results.



Figure 2.18 - Final R_{height} obtained for a film of initial thickness $H_0 = 1 \mu m$ and initial height ratio R_{height,0} = 0.5 as a function of (left) the number of time discretization steps (COMSOL-MATLAB scaling-remeshing steps) and (right) COMSOL mesh density. As a compromise between accuracy and computational requirements, we choose a mesh density of 5 and a time step of 20.

Draw ratio

A study of height ratio dynamics for an identical film thickness and varying final draw ratio DR_f reveals a limited influence of the draw ratio on reflow (Figure 2.19). Indeed, similar reflow dynamics reflect the similarity of the initial systems, whose final reflow factor essentially depends on the final length scale involved.





Interfacial energy

Interfacial tension between the polymer matrix and the substrate is a fundamental parameter which largely determines the texture reflow dynamics. In Figure 2.20, the height ratio is plotted for interfacial tensions increasing from γ_{12} = 3.85 mN/m to γ_{12} = 385 mN/m with DR = 50 and H₀ = 1.5 µm. The reflow is significantly increased for higher surface tension, which leads to completely flat films for interfacial tension of the order of 385 mN/m. The overall system sensitivity to this parameter is an important element of this study, and hence calls for particularly accurate values. In the present case, the interfacial tension coefficient γ_{12} can be estimated based on geometric means [97]:

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2\left[\left(\gamma_1^d \gamma_2^d\right)^{1/2} + \left(\gamma_1^p \gamma_2^p\right)^{1/2}\right]$$
 Eq. 2.42

with γ_i the surface tension associated to component i = 1 (As₂Se₃) or 2 (PEI), γ_i^d the dispersive component and γ_i^p the polar component of the surface tension associated to component i. In this equation, the interfacial tension of a polymer with similar values for γ_i^d and γ_i^p would be much smaller than the surface tension of each component. In our case, considering the similarity of As and Se atomic electronegativity, we consider that there is no polar component in As₂Se₃. Electronegativity of As and Se atoms are χ_{As} =2.18 and χ_{Se} =2.55 on the Pauling electronegativity scale. Typically, a maximum difference of 0.2 - 0.5 indicates nonpolar covalent, which makes the covalent bonding As-Se a non-polar covalent bond, hence justifying our assumption above. We thus consider $\gamma_1^p \sim 0$ and $\gamma_1^d \sim \gamma_1$. Based on (ref. [114]), we have $\gamma_1 = 0.1 N.m^{-1}$; $\gamma_2 = 41.0 mN.m^{-1}$; $\gamma_2^d =$ $26.32 mN.m^{-1}$. The interfacial tension γ_{12} thus amounts to $\gamma_{12} = 38.5 mN/m$. This value is significantly lower than the free surface tension of the ChG γ_{11} =100 mN/m, which would be the relevant surface tension parameter in the case of open-air reflow (e.g. exposed film on a substrate). Therefore, the use of a polymer cladding plays a key role in limiting reflow and reducing the varicose mode decay. This is in line with previous observations in purely polymeric systems [53].



Figure 2.20 - Evolution of height ratio versus time for increasing interfacial tension.

Film thickness

We further proceeded to compare the evolution in time of R_{height} depending on the initial film thickness H₀. Results of the simulation for this parameter swept from 0.4 µm to 0.8 µm are shown in Figure 2.21.



Figure 2.21 - Evolution of R_{height} in time for R_{height,0} = 0.5, DR = 30, and different initial mean film thicknesses H₀.

Appendix 3: Filament bundle



Figure 2.22 - SEM picture of filament bundle after dissolving the cladding. Scale bar: 2 µm.

Appendix 4: Scattering response of NWs

The scattering cross-sections of individual As₂Se₃ NWs of varying diameters, both in air and in PEI, are presented below. We used the Finite Difference Time Domain (FDTD) software Lumerical [115]. The refractive index of As₂Se₃ is taken from our own measurements (see RCWA) and the refractive index of PEI was taken from literature [106], [107]. For a given cylinder radius, scattering cross-sections values were obtained using Lumerical TFSF source (Total-Field Scattered-Field). This broadband plane wave and unit amplitude source is in the form of a 2D square frame surrounding the scattering object - here, an As₂Se₃ disc, representing a cross-section of an infinitely long cylinder. One side of the frame is the injection plane. We chose an injection direction normal to the cylinder axis and a TE-polarization. Regions outside the frame record only the scattered field, by subtracting the incident field contribution to the total field. The scattered power is recorded with monitors surrounding the TFSF source. Normalizing this power with the source intensity yields cross-section values. In PEI, the refractive index contrast is lower than in air, resulting in a broadening of the resonances [116].



Figure 2.23 - Scattering cross-section spectra of individual As_2Se_3 NWs of varying diameters, both in air and in PEI, for a polarization parallel to the wires.

We then simulated scattering of *periodically arranged* NWs under normally-incident plane wave illumination. Periodic boundaries were applied in the direction transverse to illumination. Complex transmission coefficients were extracted using an S-parameter analysis [117]. The data shown Figure 2.16 at λ_i = 800 nm is highlighted by a dashed line in Figure 2.24. We chose to arrange the NWs with period p = 300 nm, to ensure working in the non-diffraction regime for all wavelengths of interest (500 nm to 1 µm). Both TM and TE polarizations were simulated to verify that although scattering responses differ, phase coverage and high transmission are still present.



Figure 2.24 - Scattering response (normalized amplitude and phase) in transmission for a 300 nm-period NW array, for polarizations orthogonal and parallel to the wires.

Appendix 5: diffraction setup

To measure diffracted beams from the ChG NW array in the fiber, the optical setup depicted on Figure 2.25 was used. For one measurement, the collimated laser beam is operated at a fixed wavelength λ , with a 1 nm bandwidth. A polarizer is used to control the incident beam's polarization with respect to the fiber. A slit is used to limit the beam to the area where the NWs are, since in the fibers tested, the NW area was approximately 300 µm wide, when the laser beam was around 1 mm in diameter. The slit has an opening of about 100 µm, aligned with the fiber by gluing them together under a microscope in transmission. Finally, transmitted orders are measured at different angles θ using either a spectrometer or a power meter on a rotating stage. The fiber and its slit are mounted together on a multi-axis stage and positioned so that the grating is at the center of the rotating stage. They are also mounted on a goniometer for precise alignment. Indeed, this is required for good horizontality of the diffracted beams, so that the detector's height does not need to be adjusted when measuring at different angles. This is a particularly sensitive requirement for good coupling into a spectrometer device, since it requires focusing into an optical fiber connected to the spectrometer. A lens was used for this purpose, whose focal point was centered on the optical fiber's opening. However, because of some inevitable dispersion in the fiber spacings, some angular dispersion also affects the diffracted beams. This results in some off-optical axis focusing and imperfect coupling into the spectrometer. Thus, we preferred using a power meter without any focusing optics, its 9.5 mm-opening large enough to encompass the whole diffracted order. The distance to the fiber was adjusted to measure only one order at a time.



Figure 2.25 - Diffraction characterization setup, able to measure intensities for beams diffracted at different angles $\theta(\lambda)$

3. Preform microfabrication for nanophotonics

Chapter 2 demonstrated for the first time templated dynamic dewetting as a scalable approach to NW array fabrication. For an even higher degree of control over geometrical arrangements and to pave the way towards their insertion between electrical contacts for light sensing and harvesting, we now turn to advanced preform microfabrication. By coupling standard cleanroom processes to fiber thermal drawing, we demonstrate the possibility to scale down photolithographic geometries by orders of magnitude and to scale up fabrication by generating nanostructures beyond wafer dimensions. This chapter focuses on the NW array geometry, its optical properties, and potential applications. It also lays the groundwork for an integration between viscous nanocomposite electrodes in Chapter 4. A manuscript is under preparation based on the presented results.

Motivation

Conventional optics rely on refractive index variations to accumulate phase, such as in centimetrethick glass lenses in air. From the Greek "meta" meaning "beyond", metasurfaces promise to change this paradigm. In 2019, the World Economic Forum described them as one of the top 10 "worldchanging" emerging technologies [118], with its main applications in the fields of AR/VR, automotive sensing and mobile devices [119]. This novel class of materials emerges from periodic assemblies of elementary scattering elements such as jutting pillars or drilled holes called "meta-atoms", whose optical behaviour can be predicted and engineered by tuning shape and lattice constants. Typically thinner than a micron, metasurfaces can be apprehended as an interface of discontinuity where abrupt changes in amplitude and phase occur to match any desired optical behaviour such as near unity reflection, beam steering, focusing... Such arbitrary wavefront manipulation at the subwavelength scale promises both extreme compacity for integrated optics, and access to a new range of tunable optical properties.

Most metasurface structures are made on rigid substrates such as silicon wafers or silica glass. However, many applications require their functionality to be distributed over curved or deformable structures. Fabrication of flexible metasurfaces may not only solve this conformability challenge, but also provide an extra degree of tunability: as the surface is bent or stretched, the meta-atom lattice period changes; the metasurface can be tuned doing so, or some period-dependant optical behaviour can be harnessed for highly sensitive sensing.

Conventional fabrication of sub-wavelength structures in the visible regime requires advanced clean room techniques, such as costly e-beam lithography or focused ion beam (FIB) machining. By contrast, photolithography is the most common technique used for fabricating electronic and optical integrated circuits. By exposing a photosensitive resist through an optical mask, standard UV lithography enables microscale patterning on flat substrates with a high degree of geometrical control and reproducibility. Optoelectronic structures are typically obtained on a 30 cm-wide silicon wafer by subsequent etching, deposition, implantation, and development steps. However, reaching sub-micron dimensions requires more advanced, and thus costly, resist exposure. Some key DRAM industrial player are moving to sophisticated lower wavelength light sources such as extreme UV light sources at 13.5 nm [120], [121].

Thermal drawing as a scaling technique for advanced optoelectronic nanostructures in fibers

In this chapter, we propose a scaling technique to fabricate nanoscale optoelectronic structures beyond the wafer scale with standard photolithography. Based on dielectric chalcogenide glass, we demonstrate fabrication of a one-dimensional metalens working in transmission, embedded into a flexible substrate. This novel yet simple process opens a pathway for the high-throughput production of one-dimensional flat optics. Our process relies on the combination of microscale photolithography combined with fiber thermal drawing to reach dimensions one or two orders of magnitude smaller. As the latter process relies on glass transition materials, standard clean room microfabrication steps are performed on a thermoplastic substrate, later embedded in a fiber preform for thermal drawing. The process is described in Figure 3.1.



Figure 3.1 – Process flow from photolithography to thermal drawing.

Arsenic selenide (As₂Se₃) was identified as a dielectric high refractive index material ($n_{As_2Se_3} \sim 2.7$ at $\lambda = 650$ nm) with excellent shaping ability: as a glass, it has a "long" glass transition [122] (i.e. $\frac{d\eta}{dT}$ low during glass transition) with slow crystallization kinetics (crystallization entropy $\Delta H_{crystallization} \sim 92 J. g^{-1}$ [123]), leading to a rheology compatible with the requirements of thermal drawing: a sweet spot in viscoelestaticity can found by adjusting the pulling strain and temperature in the drawing furnace. Additionally, its properties provide stability during moderate annealing (T < 250 °C) when making the preform by thermal treatments such as hot pressing

(thermal diffusive consolidation, described in Chapter 1). As₂Se₃ is therefore compatible with thermal drawing as a bulk material [124] or inside a high T_g polymer cladding such as PEI ($T_{g,As_2Se_3} = 180$ °C, $T_{g,PEI} = 215$ °C), as demonstrated in Chapter 2. To provide encapsulation, we indeed employed PEI as a substrate and scaffold for optoelectronic fiber structures.

The index contrast between As₂Se₃ and PEI is relatively high ($n_{As_2Se_3} > 2$ at $\lambda_i > 650$ nm) [56]. Dielectric inclusions such as ChG NWs can therefore exhibit subwavelength enhanced field confinement. Moreover, optical losses (or absorption) in As₂Se₃ are moderate in the visible regime ($k_{As_2Se_3} < 0.4$ at 650 nm) and low in the infrared ($k_{As_2Se_3} < 0.05$ at 1550 nm) [125].

Chapter 3 introduced a dynamic dewetting process for fabricating NW arrays. It was shown that by tuning the soft lithography pattern and the thickness of deposited material, the NW array period p and NW diameter d could be decoupled. However, as the deposited thickness remains the same for the entire design, multiple p and d within a single array could not be decoupled simultaneously. Multiple points in the (p, d) space could not be freely accessed within a single array.

To overcome this limitation, we propose herein to structure chalcogenide glass by microfabrication techniques. Multiple line spacings and widths can be selected for a single design at the preform stage, and thus multiple (p, d) couples in a NW array at the fiber stage. This comes at the cost of using clean room processes for the preform, but thermal drawing still offers a change of paradigm by generating surface beyond wafer dimensions and reducing lateral dimensions by stretching.

We leveraged this full freedom in NW array design to attempt fabrication of 1D metasurfaces encapsulated in polymer claddings. A 1D metalens was designed and fabricated. We first simulated and optimised the design for focusing efficiency, and then optimised the microfabrication process for design fidelity.

Nanowire sub-wavelength Mie resonance

During thermal drawing, viscoelastic materials such as glass and thermoplastic polymer are stretched to extreme dimensions. The geometry is governed simultaneously by macroscopic strain (drawing) and microscopic intermolecular forces governing spontaneous reflow. At the interface between two materials, interfacial tension γ leads to Laplace pressure P_L , a drive to minimizing interfacial energy:

$$P_L = \gamma \kappa$$
 Eq. 3.1

where κ is the interface curvature. At the sub-micron scale, small features lead to high κ , thus high P_L , and a high drive to flattening curvature reduction. To minimizing the total interfacial energy, cross-sectional geometries tend to become rounder, especially for the smallest features. Figure 3.2 shows the reflow of chalcogenide glass rectangular bars (Figure 3.2a) into circular nanowires after thermal drawing (Figure 3.2b). In contrast, polymers can be chosen to minimize γ at their common interface, achieving nanoscale shape stability through thermal drawing, as demonstrated in Figure 3.2d [52], [53].



Figure 3.2 – Reflow through thermal drawing. a) Chalcogenide glass rectangular bars on a PEI substrate. SEM picture at a 30° tilt, artificially colored. b) Cylindrical NWs in the drawn fiber. SEM picture of a cross section prepared by microtomy, artificially colored. c) Oval NWs in the drawn fiber, for a reflow timescale longer than that of drawing. SEM picture of a cross section prepared by microtomy, artificially colored. d) Reflow engineering by reducing interfacial tension. Preform grooves (top image) can still be seen at the nanoscale after fiber drawing thrice (bottom), despite high curvatures. Adapted from ref. [52]. Scale bars are respectively: a: 6 um, b: 400 nm, c: 2 um.

It is possible to decrease the drawing temperature to increase the materials' viscosities, at the cost of a higher drawing stress σ_{zz} (see Chapter 1), as long as it remains below breaking stress, and that the drawing system can accommodate for the larger pulling force required. As viscosity is essentially resistance to flow, at high σ_{zz} , geometry reflow takes longer and might happen over a timescale higher than drawing. Figure 3.2c shows chalcogenide bars not entirely reflown into cylinders, their cross section still oval after drawing. However, slight differences in temperature lead to high differences in viscosity, which in turn lead to uncertainty in the partial reflow of a cross-sectional shape, left somewhere between the preform shape and a circle. Drawing at sufficient temperature to have full reflow was therefore preferred; we base the present study on perfect cylinders.

Mie solutions for a cylinder and simulation tools comparison

Based on the assumption of perfect and infinitely-long cylinders, we computed their optical response using Mie theory. This theory was established by Gustav Mie more than a century ago to model the scattering of a particle under monochromatic excitation. Analytical solutions of the scattered field are derived for simple geometries such as sphere or cylinder. The scattered field is expressed in terms of Mie coefficients, of either electric or magnetic type. They correspond to the

nature of induced currents in the particle. For a single dielectric cylinder, the scattering crossefficiency is simply expressed as [126]:

$$Q_{scatt} = \frac{2}{x} |a_0|^2 + \frac{4}{x} \sum_{n=1}^{\infty} |a_n|^2$$
 Eq. 3.2

for electric excitation transverse to the cylinder axis (TM-polarization),

and:

$$Q_{scatt} = \frac{2}{x} |b_0|^2 + \frac{4}{x} \sum_{n=1}^{\infty} |b_n|^2$$
 Eq. 3.3

for electric excitation along the cylinder axis (TE-polarization),

where $x = \frac{2\pi r}{\lambda}$, r being the cylinder radius and λ the incident wavelength, and a_n , b_n are the Mie coefficients. Expressions of the Mie coefficients can be found in [127].

If we now consider the final geometry in the fiber, we need to take into account the nanocylinder array, as they form a periodical arrangement. The scattering response of a dielectric nanocylinder array was evaluated with 3 different tools:

- 1°) analytical solutions, established from Mie theory
- 2°) numerical solutions, using a rigorous couple-wave analysis (RCWA) solver (Reticolo [105])
- 3°) numerical solutions, using the FDTD finite-difference time-domain solver (Lumerical Inc.)

The system considered is an array of infinitely long dielectric nanowires (NWs), made of As₂Se₃ and with a given diameter *d*. The nanowires are aligned periodically, with a period *p*, along a direction transverse to their axes. We considered the 2-dimensionnal problem where light is impinging the array perpendicularly to the NWs's axis. Furthermore, we considered only normally incident light, i.e light with a wave vector $k = \frac{2\pi}{\lambda}$ perpendicular to both NWs' and array's axis.

Tool n°1 is a direct analytical formulation for the scattering of an array of dielectric cylinders. The formulation was adapted from [108] and implemented in Mathematica. Two main assumptions are made: 1°) the cylinders are lossless dielectric (no absorption), and 2°) the cylinders are modelled through their two lowest electric and magnetic dipoles (i.e we consider only the first two terms of the Mie coefficients: a_0, a_1 and b_0, b_1). This last assumption is true only when the ratio $\frac{d}{\lambda}$ is small enough [128].

Tool n°2 (Reticolo) is based on a semi-analytical method. The system is discretized into successive grating structure layers, where Maxwell's equations are solved analytically. The fields are expressed in a Fourier basis, with a finite number of harmonics. More harmonics simulate more accurately the system, but at the cost of simulation time.

Tool n°3 (FDTD) is another numerical method to get the optical response. The system is spatially discretized into nodes (spatial grid, or *mesh*), where Maxwell's equations are solved iteratively. The field is expressed in a temporal basis. A finer mesh simulates more accurately the system, but at the cost of memory and simulation time.

A quick benchmark test was performed to compare all three tools. In the test, we set $p = 1.2 \ \mu m$, $\lambda = 2 \ \mu m$ and we take a range of diameters ($d \in [150nm - 500nm]$). The polarization was transverse electric (i.e incident electric field along the NWs' axis). We also considered polyetherimide (PEI) as the background medium. The results are shown in Figure 3.3.



Figure 3.3 – Benchmark of the three tools available for computing a NW's transmitted response to a transverse electric plane wave. Courtesy of Pierre-Luc Piveteau.

On this figure, the left graph gives the amplitude of the transmitted wave, and the right graph the phase of the transmitted wave. Regarding the amplitudes, all three tools give similar results. In particular, the strong resonance for NWs with diameter $d \sim 210 nm$ is well predicted by all three tools. At large diameters, the analytical solution (Mathematica) deviates from the two others, due to the lack of high-order multipoles in the analytical model. This deviation at large diameters is also visible for the phase graph, on the right. On this graph, the phase reference for the analytical and numerical methods is also different, leading to an overall shift of the analytical curve (yellow curve).

We finally retain Reticolo for our simulation tool, as it offers both quick simulation time compared to FDTD, and no geometric assumptions compared to the analytical model.

Fabrication constraints

The next challenge is to estimate the NWs which can be fabricated in a single array. In a metasurface, the phase response of a periodic array is given by the dimensions of the subwavelength objects constituting it. To tune this response to any given phase and engineer the wavefront to the desired optical behaviour, there should be a variety of periodicities corresponding to multiple, and ideally all, phase shifts. In our case, we can vary NW diameters d and array period p, hoping for a full phase coverage in transmission or reflexion. However, achieving a wide range of d and p may be hampered by fabrication constraints, a challenge which we now turn to.

We propose the model in Figure 3.4 for estimating the achievable (d, p) space: after deposition and lift-off, chalcogenide rectangular bars are aligned on the substrate. We call t the deposited thickness, W_n the width of the nth bar, X_n the position of its center, and S_n the spacing between bars n and n+1. The bar's cross-section is considered constant in the drawing direction. Its length only impacts how long the multimaterial fiber might be. For an 8 cm-long bar, using DR = 30, we get a total length $L = 0.08 * 30^2 = 72 m$ of fiber. The initial deposited bar length should only be ~ 1 cm to have a few meters of fiber to characterize. After encapsulation and drawing, as its viscosity decreases, one can imagine a virtual transitory step, whereby each bar n first reflows into a cylinder with diameter D_n and a spacing S'_n between bar n and n+1. Then the reflowed array of microwires is

stretched down into nanowires with a scaling ratio DR, with diameters d_n at position x_n and spacings s_n between wire n and n+1.

By conservation of volume, in the cross section, as rectangles reflow into circles, we get:

$$W_n t = \frac{\pi D_n^2}{4}$$
 Eq. 3.4

As the centers of mass remain at X_n during reflow, the new spacing S'_n can be calculated using :

$$X_{n+1} - X_n = \frac{W_n + W_{n+1}}{2} + S_n = \frac{D_n + D_{n+1}}{2} + S'_n$$
 Eq. 3.5

Then, after drawing :

$$d_n = \frac{D_n}{DR}$$

$$s_n = \frac{S'_n}{DR}$$

Eq. 3.6

It follows that d_n and s_n can be obtained from the geometry of elements n and n+1 at the lithography level:

$$\begin{cases} d_n + s_n = \frac{1}{DR} \left(\frac{W_n + W_{n+1}}{2} + S_n \right) & \text{Eq. 3.7} \\ d_n = \frac{2}{DR} \sqrt{\frac{W_n t}{\pi}} \end{cases}$$

Note that for a periodic arrangement, $d_n + s_n$ would be p_n .



Figure 3.4 – Model and main cross sectional geometrical parameters for the virtual reflow and scaling (by DR) steps of the deposited structures after lift-off into perfect cylinders.

Therefore, theoretically, given bar n (W_n), we could pick the position and width of the following bar (S_n, W_{n+1}) to obtain in fiber the desired d_{n+1} and spacing s_{n+1} . Iterrating over n, we can construct the array of bars leading to any aperiodic array of NWs after drawing (i.e. reflow and scaling). However, predicting the optical response of any large-scale aperiodic NW array is an optimization problem of itself, referred to in the metasurface design community as "inverse design"[129].

By contrast, in the locally periodic approximation (LPA), the optical response to a plane wave, the transmitted phase and amplitude, can be easily calculated or simulated for an ideal infinite periodic array of "meta-atoms", here NWs. Locally periodic arrays associated to a given (complex) transmission coefficient, can then be picked and assembled into a metasurface to engineer the wavefront of the transmitted or emitted wave (e.g. for lensing, reflection, beam steering, etc.). It is a computationally inexpensive design leading to regular geometries, straightforward to fabricate. Phase and amplitude for a periodic array can be rapidly simulated using rigorous coupled wave analysis (RCWA) [105], a semi-analytical method in computational electromagnetics. It is employed to predict scattering from periodic dielectric structures, building upon a Fourier-space method so that geometries and fields are represented by a sum of spatial harmonics. Under the conditions mentioned above for Mie scattering, emitted phase and amplitude can even be formulated analytically. However, we will remain in the general case covered by RCWA to avoid deviation from the latter ideal hypothesis.

Under the LPA, the previous geometrical conditions yield for a periodic array with period *p*:

$$\begin{cases} p = d + s = \frac{W + S}{DR} \\ d = \frac{2}{DR} \sqrt{\frac{Wt}{\pi}} \end{cases}$$
 Eq. 3.8

Thus, fabricating NW with small d should be easy. One only needs to deposit very little material (small t) at high DR. For $W = 1 \mu m$, DR = 50 and t = 100 nm, d would reach 7 nm. However, having a large variation in d, corresponding to large variations in the optical resonance, is required for full phase coverage. It is therefore important to assess what limits the accessible d range $[d_{min}, d_{max}]$. Based on preliminary lift-off experiments, several fabrications limitations emerged, illustrated in Figure 3.5a:

i. For a given photoresist thickness t_{resist} , the smallest feature width (also called critical dimension CD) is in first approximation proportional to t_{resist} . In other words, the aspect ratio of the resist features after exposure and development is limited:

$$AR_{resist} < \frac{CD_{resist}}{t_{resist}}$$
 Eq. 3.9

Note that there is also a hard limit to this resolution CD_{resist} given by the exposure tool optics or diffraction through the exposure mask, which we neglect for now. Since lift-off is only possible for a deposited film thickness t lower than t_{resist} (see Microfabrication challenges and optimizations below), this limitation applies to W and S, and thus p and d. Given a negative photoresist undercut (see Exposure and below), CD_{resist} is even lower as the base becomes too thin. For $t_{resist} = 6.5 \ \mu$ m, we could obtain at best $CD_{resist} = 1.2 \ \mu$ m, or $AR_{resist} < 5.4$. This limits S_{min} , and in turn, s_{min} (or p_{min}), since we derive from Eq. 3.8 and Eq. 3.9

$$s > s_{min} = tAR_{resist} + \frac{\pi}{8t}(d_1^2 + d_2^2) - \frac{d_1 + d_2}{2}$$

or for a periodic array :

$$s_{min}(d) = tAR_{resist} + \frac{\pi d^2}{4t} - d$$
 Eq. 3.10

$$or p_{min}(d) > tAR_{resist} + \frac{\pi d^2}{4t}$$
 Eq. 3.11

After drawing, we demonstrated for $t = 7.16 \ \mu\text{m}$: $p_{min} \sim 1.3$ (Figure 3.2c). In the general case, we can plot $p_{min}(d)$ for various t (Figure 3.5b at DR = 10 and c at DR = 50), or rather $\frac{p}{d}$ as a function of d (Figure 3.5d). It is noteworthy that as p_{min} is not proportional to t, a quadratic minimum $\min_{d \in [d_{min}, d_{max}]} (\frac{p_{min}}{d})$ can be found, where NW are as close as possible. The limitations in d are described hereafter.

ii. For the layer deposited on the resist to be lifted-off well, a good separation from the bottom layer on the substrate is required: $t_{resist} = B_1 t$, where B_1 is a constant higher than 1. Depending on the anisoptropy of the deposition, this separation can be decreased. In our case, we estimated C ~ 1.3. At lift-off, we therefore get the following limitation:

$$\frac{CD_{resist}}{B_1 t} < AR_{lift-off} < AR_{resist}$$
Eq. 3.12

Figure 3.2a shows successful lift-off for CD_{resist} = 1.2 µm and t = 3 µm, i.e. $B_1 \simeq 2.2$ and

 $AR_{lift-off} \sim 2.5$. We estimate B_1 to be at best approximately 1.4. This limits W_{min} and in turn, d_{min} .

iii. When W is high, reflow of a long rectangle into a cylinder requires more flow. Surface energy may rather find a local minimum by the rectangle breaking-up into two NW during drawing.

$$AR_{capillary} > B_2 t$$
 Eq. 3.13

We estimate B_2 to be at most 5. This limits the maximum W_{max} , and in turn, d_{max} .

For a periodic array, the maximum d range is therefore given by ii and iii, such as:

$$\frac{d_{max}}{d_{min}} = \sqrt{\frac{AR_{lift-off}}{AR_{capillary}}}$$
Eq. 3.14

Given d, condition i yields $p_{min}(d)$, whereas there is in principle no limit to p_{max} . However, collective effects (constructive interference) between NW in an array are rather obtained for $p \sim d$. Moreover, we remain in the sub-diffraction regime for $p < \frac{\lambda_i}{n_{PEI}}$, where λ_i is the incident wave wavelength.



Figure 3.5 – Fabrication constraints. a) Limiting aspect ratios summarized; Accessible (p, d) space for various film thicknesses considering limiting ARs proportional to thickness t, at a) DR=10 and b) DR=50. c) Accessible p/d ratios for DR=10. For a given thickness t, the accessible space is above the corresponding colored curve.

Also note that the above maximal AR have been considered proportional to t in first approximation, when in reality, an optimum AR may be found by varying t. This could then be compensated by scaling the whole geometry and using a different DR in [1,50]. Such an optimization was beyond the scope of the present study.
Optical response to a polarized plane wave

Given limitations in fabrication expressed by the resist, lift-off, and capillary break-up aspect ratios, we can now simulate optical behaviour for all (d, p) in $\Sigma = [d_{min}, d_{max}] \times [p_{min}, \frac{\lambda_i}{n_{PEI}}]$ using RCWA. As the propagation length through an array of NWs varies with d, a PEI spacer was used to compare phases through a constant distance, regardless of d. The simulation geometry is illustrated in Figure 3.6.



Figure 3.6 – Simulation geometry: cross section of the one-dimensional geometry. The phase ψ through each locally periodic NW array is computed for a constant slab thickness equal to d_{max} , up to a constant phase ϕ_{ref} .

We first run preliminary tests showing that full phase coverage can be obtained for $n_{As_2Se_3} > 3.1$. Indeed, a higher refractive index contrast to that of PEI enhances resonant effects such as the transmitted phase shift. From literature and ellipsometry measurements, we match this condition for $\lambda_i > 650$ nm. We choose to design a device specifically for $\lambda_i = 650$ nm, as absorption increases sharply at lower wavelengths: $k_{As_2Se_3}(650 \text{ nm}) < 0.1$. We discretize Σ in $\approx 20 \times 20$ nodes and run RCWA simulations for each. Software, simulation parameters and algorithm convergence are discussed in the Experimental section. Simulations were run for both transverse electric (TE) and transverse magnetic (TM) polarizations. Figure 3.7a and b show respectively the phase and amplitude maps obtained for all nodes in Σ , for TE polarization. One can also visualize all images in phase-amplitude polar coordinates (Figure 3.7c) or view phase coverage by normalizing over the amplitude (Figure 3.7d).



Figure 3.7 – Transmission maps for (p, d) in the accessible space Σ given fabrication constraints. a) Phase map $\psi(p, d)$. b) amplitude map T(p, d). c) Polar map of all simulated nodes, where the radial and angular coordinates are ψ and T, respectively, d) or ψ and 1 to view conveniently phase coverage.

To build the desired metasurface, one now needs to select locally periodic arrays with given p and d so that all phase shifts are available (up to a small discretization error), at as high amplitude as possible. We select for example 20 points, shown in bold orange in Figure 3.7c and d. This constitutes our "library" of transmission coefficients.

Application to a 1D metalens

We now turn to tuning the phase response to that of a (cylindrical) lens. The ideal phase profile along x, as shown in Figure 3.8, for a one-dimensional lens of width D, converging in the focal plane at z = f is [130]:

$$\phi(x) = \frac{2\pi n_{PEI}}{\lambda_i} \left(\sqrt{x^2 + f^2} - f \right) + \phi_0 \left[2\pi \right], \qquad x \in \left[-\frac{D}{2}, \frac{D}{2} \right]$$
Eq. 3.15

This expression is valid for a focal spot in the considered PEI medium. To get a focusing effect in air, one should take into account the additional refraction of the focused light rays emerging from the lens, at the PEI/air interface.

We reproduce this profile using "meta-atoms" of a constructed library. Each meta-atom consists of a NW with a defined diameter d and period p. The period is the one considered for a periodic array of identical NWs. In other words, each meta-atom can be considered as a (p, d) couple, with an associated complex phase response, noted $t_{p,d}$, with $\psi = \angle(t_{p,d})$ the transmission phase shift and $T = |t_{p,d}|$ the transmission amplitude.

We construct the lens profile in an iterative way:

- For the central position (x = 0), we pick the meta-atom with the closest phase to the ideal one ($\phi(x = 0)$).
- Once meta-atom number n-1 is placed, we look for the next meta-atom n in all those available in our library. Let p_n and d_n be its associated period and diameter, its position would be $x_n = x_{n-1} + \frac{p_{n-1}+p_n}{2}$. Given a meta-atom i in our library with (p_i, d_i) , we call the desired phase for this meta-atom placed at x_n : $\phi_n = \phi(x_n)$. We retain the meta-atom (p_n, d_n) that verifies:

$$\min_{i \in library} |\phi_i - \psi(p_i, d_i)|$$
 Eq. 3.16

We can further account for the transmitted amplitude by retaining instead:

$$\min_{i \in library} \frac{|\phi_i - \psi(p_i, d_i)|}{T(p_i, d_i)}$$
Eq. 3.17

We proceed this way iteratively until the edges of the metasurface are reached.

In our algorithm we picked (p, d) among 20 elements in our discrete phase map evenly spread over $[0,2\pi]$ with highest amplitude. We could have run the loop above searching for a minimum for all $(p, d) \in \Sigma$, instead of restricting our library, at a higher computational cost. Another possible construction algorithm uses a continuous path in the $\phi(p, d)$ space covering the full $[0,2\pi]$ range (in an area of high amplitude T) to minimize discontinuities and remain as much as possible in the LPA [131]. This comes at the cost of sub-optimal T.

The result of our construction algorithm is visible in Figure 3.8:



Figure 3.8 - Lens phase distribution. The black line corresponds to ideal phase profile $\phi(x)$; each green step segment corresponds to a single type of meta-atom, periodically arranged.

The phase distribution is modulo 2π , so as in a Fresnel lens, the whole phase coverage is used several times. A constant reference phase ϕ_{ref} needs to be chosen, often the phase at the centre (optical axis). ϕ_{ref} can be chosen wisely so that it corresponds to a meta-atom $(p_{ref}, d_{ref}) \in \Sigma$, where:

$$\begin{cases} \phi_{ref} = \psi(p_{ref}, d_{ref}) & \text{Eq. 3.18} \\ T(p_{ref}, d_{ref}) = \max_{p, d \in \Sigma} T(p, d) & \end{cases}$$

If ψ corresponds to ϕ_{ref} , an array without any glass – pure PEI – can even be used to reach maximal transmission and be part of the library. However, such an array only emits in the specular direction. High emission angles actually depend on the meta-atom radiation pattern, a general issue in metasurface design, which is often overlooked; accounting for large NA and high deflection angles through the metasurface requires alternative design techniques [129], [132].

It is noteworthy that at high phase variation $\frac{d\phi}{dx}$, $|x_i - x_{i-1}|$ decreases, each step segment is shorter and $[0,2\pi]$ is covered several times. Each locally periodic array is shorter and there are more discontinuities: we deviate from the LPA and the focalisation is less efficient [129], [132]. This effect worsens for high numerical apertures. As a first demonstration, we chose $D = 600 \mu m$, given by the preform width (24 mm) divided by DR = 40, and f = 5 mm, convenient for an optical characterisation of the focused beam spot. This corresponds to :

$$NA \sim \frac{n_{PEI}D}{2f} \sim 0.2$$
 Eq. 3.19

This low NA limits deviation from the LPA, as explained above. Making a beam deflector was also considered, but was not allowed by the resolution of our process:

Should we desire for instance
$$\theta = 45^{\circ}$$
 at $\lambda = 650$ nm, as $\phi(x) = \frac{2\pi n_{PEI}}{\lambda} \sin(\theta) x$:

$$\Delta \phi = 2\pi \leftrightarrow \Delta x = \frac{\lambda}{n_{PEI} \sin(\theta)} \sim 300 nm$$
Eq. 3.20

This would imply discretizing 300 nm into many locally periodic segments with increasing phase shifts covering $[0,2\pi]$. As one NW is typically 200 nm, this highly varying profile is not feasible. One might only consider small angles, such as $\frac{1}{\sin(\theta)} \sim 570$ for $\theta = 0.1^{\circ}$. One might also consider IR light, but at the cost of a reduced refractive index $(n_{As_2Se_3}(1.55 \ \mu m) \sim 2.6)$, a reduced phase shift resonant effect and reduced phase coverage. Part of the beam deflector array (\approx 30%) would be missing from the lack of suitable phase shifts, which could be considered as a lossy device.

Finally, we simulated the focusing efficiency of this 1D metalens by solving discretely Maxwell's equations around the NW array for a polarized plane wave. We employ the Finite-difference time-domain method (FDTD) software Lumerical, and map the electromagnetic field's amplitude around the intended focal plane (Figure 3.9). Simulation parameters are described in the Experimental section.



Figure 3.9 – Simulated light intensity map around the intended focal plane.

There is no standard definition for the focusing efficiency, as it depends whether light concentration or maximum intensity are most relevant for a given application. For light concentration, it also depends on the surface/volume considered. In our case, we use the same definition as Arbabi et al. [133] and define the focusing efficiency η_F in the focal plane as:

$$\eta_F = \frac{I_F}{I_T} = \frac{\int_{-3FWHM}^{3FWHM} |E(x, z = f)|^2 dx}{\int_{-\infty}^{+\infty} |E(x, z = f)|^2 dx}$$
Eq. 3.21

We also account for absorption and reflection through the metasurface with the transmission efficiency η_T , the fraction of incoming light intensity transmitted through the array. Therefore, if I_0 is the total incoming light intensity on the metalens:

$$I_F = \eta_F \eta_T I_0$$
 Eq. 3.22

The final figure of merit η_{lens} to be maximized is therefore:

$$\eta_{lens} = \frac{I_F}{I_0} = \eta_F \eta_T$$
 Eq. 3.23

Would the focal point spreading along the optical axis be relevant, we could also have defined η_F' over a surface, for example as:

$$\eta_{F}' = \frac{I_{F}'}{6FWHM_{x=0} I_{T}} \frac{\int_{z=-3FWHM_{x=0}}^{z=3FWHM_{x=0}} \int_{x=-3FWHM_{z=f}}^{x=3FWHM_{z=f}} |E(x,z)|^{2} dx dz}{\int_{z=-3FWHM_{x=0}}^{z=3FWHM_{x=0}} \int_{x=-\infty}^{x=+\infty} |E(x,z)|^{2} dx dz}$$
Eq. 3.24

Note that the FWHM is different dependent on the plane considered (x = 0 or z = f).

Accounting for fabrication constraints, both geometrical and design parameters can now be swept to maximize η_{lens} , as illustrated in Figure 3.10. However, finding a global maximum over multiple parameters requires either high computing capacities, or advanced mathematical optimisation such as gradient descent or Monte Carlo methods. Here, we only swept hyperplanes of the input parameter space to find a local maximum for the metalens design, allowing to focus on demonstrating the fabrication process.



Figure 3.10 – Metasurface design and optimization process. Input parameters which can be optimized over to maximize the lens performance are in bold. Other input parameters (f, D, polarization) are rather specific to the desired application.

Microfabrication challenges and optimizations

Substrate

Most clean room processes are designed to handle thin circular silicon wafers, on to which are deposited 10 to 100 nm-thick layers of conductors, semiconductors and insulators. An approximately 10 mm thick rectangular preform is not an option for most photolithographic devices. The surface of the substrate should be a thermoplastic, or transferrable onto a thermoplastic, and reasonably flat for good geometry control:

- i. Surface RMS roughness should be low for good geometry control, i.e. much smaller than the smallest feature width.
- ii. Total thickness variation (TTV) over the entire sample should be at most a few tens of microns to remain within the autofocus compensation range of the maskless lithography tool [134].

An off-the-shelf film from Goodfellow[®] was chosen for its smooth laminated surface (on one side) and glued onto a silicon wafer for photolithographic tools compatibility. (i) was verified by measuring RMS roughness $S_q < 100$ nm by optical profilometry. The film's thickness (160 µm) provided rigidity during manipulation. (ii) was improved by lamination: the PEI film was hot pressed onto the silicon wafer substrate to spread out the thermal glue and ensure planarity. Cmi's thermal nanoimprinter was used for its plates' parallelism, regularly calibrated. Hot pressing at Cmi also garanteed a dust-free environment, as opposed to the hot press used for preform consolidation. In order not to introduce scratches or dents when pressing, a second Silicon wafer was used between the sample and the top hot plate with its smooth surface facing towards the sample, spreading the thermal glue. This reduction in TTV greatly improved photoresist exposure by ensuring the surface of the sample was always in the exposure laser's focal plane. The thermal glue's stability was sufficient to keep the film in place up to 120°C, despite internal thermal expansion constrains in the film when annealing for the soft bake (after resist spin-coating, evaporation of the casting solvent) and post-exposure bake (PEB, thermally catalysing resist photochemical reactions and evaporating the remaining solvent).

Photoresist

Off-the-shelf photoresists were used from MicroChemicals and spin-coated onto the PEI film-silicon wafer substrate. Negative resists with undercuts are highly desirable for an optimal lift-off by maximising the separation of the top deposited layer (on the resist) from the bottom layer (on the substrate). AZ 15nXT (115CPS) [135] and AZ nLof 2020 [136] were chosen as standard negative resists with thickness ranges compatible with the desired ChG deposition thickness, respectively equal to 6-12 and 1.4-3 microns. The hot plate temperature was measured to be overestimated by about 10-20 degrees, which was accounted for, since PEB is critical to the undercut slope, as shown in Figure 3.11.





Exposure and development

Exposure dose is an important parameter to calibrate and select wisely. For a positive photoresist, there is a minimum exposure dose D_C for the resin to be cleared entirely upon development, in which case, the remaining thickness for the exposed areas is d' = 0. For a lower dose, some resist remains, with thickness $d' < d_0$, with d_0 the initial resist thickness. Below an exposure dose D_0 , no resist is removed by the developer. Figure 3.12a shows how plotting the drop of $\frac{d'}{d_0}$ as a function of the exposure dose D allows to measure the contrast of a resist $\gamma = \frac{1}{[\log_{10}(D_C/D_0)]}$. High contrast means exposure patterns are "binary" after development: either cleared or unaffected. Low contrast means "grey" areas with $0 < d' < d_0$ could be obtained after development. To avoid this issue detrimental to our process, we need to ensure $D > D_C$. However, overexposure leads to an increase of feature widths, distorting the intended design. We tested this for a 5 µm-wide line (Figure 3.12b): as D increases, the line width also increases, quadratically with the dose. D_C is dependent on a variety of parameters such as the resist type (AZ 15nXT, AZ nLOF ...), resist thickness, substrate reflection coefficient given by multiple reflection for transparent substrates such as PEI, etc.

In the negative resist case, this logic is just reversed: exposure leads to a carboxylic acid to be formed, cross-linking the resin during subsequent annealing (soft bake), making it insoluble by the developer, while unexposed areas remain soluble. However, for doses just above D_c , because of

light penetration effects, the top of the resist receives a higher dose and is better cross-linked. In other words, the bottom of the resist will be more developed, which leads to an undercut, as shown on Figure 3.12c. As a result, the base of a photoresist line will be thinner than the exposed width, an additional limitation to high AR features. Figure 3.12d shows a resist width gradient to estimate AR_{resist}. When the base is too thin, lines collapse. For a higher exposure dose, the bottom of the resist layer is more exposed, as shown in Figure 3.11 and the undercut slope is less pronounced. Smaller line widths are achievable, but lift-off may not be as effective, as described later in this chapter. To assess D_C for different line geometries, a calibration layout was prepared to vary the dose, line width (parameter S) and spacing (parameter W). Figure 3.12e shows a line width gradient, with S ranging from 0.5 to 2.5 μ m. To the sides of this gradient, similar gradients were exposed with doses D varying from 30 to 80% of the maximum exposure laser power (250mJ/cm^2). This whole row was duplicated in the orthogonal direction to vary resist line spacing from 1 to 3 μ m. The thickness chosen for the multi-gradient design was that of the optimized metalens design simulated above. Figure 3.12c and d show D just aboved D_C , as opposed to clear overexposure in Figure 3.12f. This dose calibration layout led to selecting $D_C < D = 140 m J/cm^2$ (55%). Considering the characterisation in Figure 3.12b, this corresponds to a 2% underestimation of the final resist features S, or 2% overestimation of the glass features W after-lift off, which can be accounted for in a corrected exposure design.



Figure 3.12 – Resist exposure. a) Resist contrast. Adapted from [137]. b) Line width as a function of laser intensity. c) Resist undercut. d) Resist line width gradient. e) A resist line width gradient (varying *S*) is duplicated: laterally varying the exposure dose *D*, vertically varying the resist line spacing *W*. f) Overexposure. Scale bars: c: 1 μ m, d: 10 μ m, e: 50 μ m, f: 2 μ m.

Development was also a critical step to the undercut obtained and the stability of thin lines. When a photoresist is exposed, its solubility increases (positive resist) or decreases (negative resist) drastically. Even when solubility is decreased, such as for the remaining lines in our experiment, marginal dissolution of edge features still takes place (Figure 3.13), albeit slowly. Exposure and development are therefore coupled parameters. For reproducibility and comparison, exposure of the final resist lines obtained should only be optimized for a constant development time.



Figure 3.13 – Development time study for various line widths.

Physical Vapour Deposition of the semiconductor glass

Once the resist line dimensions correspond to the intended negative design for glass, we place the sample in a PVD vacuum chamber for resistive heating (thermal) evaporation of the chalcogenide layer. Typically, samples are placed on a rotating platform for uniformity of the deposition thickness. However, this reduces the directionality of deposition. The resulting layer is also deposited on resist flanks, joining the glass layer on the resist (to be lifted-off) and the one on the PEI substrate (to be drawn). This makes it difficult to lift-off the top layer when stripping the resin [103]. To improve PVD anisotropy, rotation was stopped, the sample was placed precisely above the evaporation boat, as far as possible from it to reduce the deposition solid angle. For small samples, we neglect the thickness dependency on the deposition angle corresponding to off-center locations. For larger samples, this can be corrected by placing the sample on a spherical structure [103]. Finally, as scattering from air particles leads to isotropy, the vacuum was pumped until pressure was minimal. We also hypothesize that high evaporation rates by thermal evaporation could lead to excess heating and re-evaporation of material from parts close to the boat, at different angles. A low evaporation rate R = 0.1 nm/s was chosen, although 10 nm/s is also possible. An ideal anisotropic deposition cross-section is shown in Figure 3.14a and b. A thin connecting layer remains (Figure 3.14c), which can be broken by agitating the sample in an ultrasonication bath. As mentioned above, an important resist feature which enhanced lift-off is for resist lines to have inclined flanks, called an undercut, onto which deposition is less likely (see Figure 3.14b and d). The stronger the undercut, the thinner the connecting layer. A compromise needs to be found between high AR (grooves clogging, Figure 3.14e) and convenient lift-off.



Figure 3.14 - Resist profile and thermal evaporation. a) Anisotropic deposition: SEM cross section and b) view at an angle. c) Thin glass walls remain on resist flanks after development because of isotropic deposition. d) Schematic showing how an undercut profile facilitates lift-off as it prevents deposition on the flanks of the resist. e) At high evaporated thicknesses, grooves tend to clog, and the layer is not uniform. Both schematics adapted from [103]. Scale bars: a: $10 \mu m$, b: $1 \mu m$, c: 100 nm.

Lift-off

The resist supplier recommends a standard solvent for the exposed negative resist, called a remover. In theory, without this underlying support, the top glass layer should be conveniently lifted off where it was not desired. However, this standard remover also dissolves the PEI substrate. Acetone, a weaker solvent for the resist was preferred, despite low resist solubility. Heating of the solution and agitation was combined with ultrasonication to remove the resist more than dissolve it, as well as break the glass connecting layer. Figure 3.15a shows the resist starting to detach and the connecting layer breaking-off, and Figure 3.2a shows the final glass structure after lift-off. Figure 3.15b is a micrograph taken in transmission showing that high regularity is obtained.



Figure 3.15 – Lift-off and thermal drawing. a) The resist starts to detach during development. b) Micrograph in transmission. High regularity with small glass bar spacing is obtained. c) Top view of the NW array in the fiber with optical microscopy. Good regularity and few defects can be seen. d) SEM image: cross section of part of a locally periodic NW array in its PEI cladding. Scale bar: a: $3 \mu m$, b: $50 \mu m$, c: $10 \mu m$, d: $1 \mu m$.

Thermal drawing

After lift-off, the glass structure on the PEI film was dip-coated in PEI for encapsulation and placed on a PEI plate to provide cladding for thermal drawing. The drawn NW array shows high regularity, as shown in the optical micrograph in transmission in Figure 3.15c and cross section SEM image in Figure 3.15d, despite some sample preparation artifacts from microtomy (little voids aligned with the diamond blade cutting lines).

Characterization

The next step of this project would be to characterize whether the geometrical model of reflow and drawing for the NW is correct. There is for example considerable uncertainty at the deposition and lift-off steps. It is unclear whether the right amount of material for the rectangular bars is obtained between the resist lines, and how much remains exactly after lift-off. Figure 3.14e illustrates why less material may be deposited through a narrow gap. To correct for this effect, a resist line spacing (parameter W) gradient calibration design could be drawn, and the actual diameters d' could be measured by SEM image analysis as a function of W. We could then predict the correction required at the preform design level to obtain the desired geometries, compensating for fabrication biases. Without this correction, the preliminary metalens drawn did not show any focusing effect, as ϕ is highly dependent on d. The measurement setup is described in the Experimental section. A similar

experimental validation of $\psi(p, d)$ could be obtained for a few large periodic arrays of fixed (p, d) in an interferometric setup, comparing the phase shift obtained to a pure PEI fiber without any NW array.

Extraordinary reflection

For certain choices of p, d and λ , the array exhibits strong specular reflection, typical of a resonant behavior. In particular, we observed a phenomenon called "extraordinary reflection", which is already well-reported in the literature [138]. This phenomenon is a typical multiple scattering effect, where destructive interference occurs between direct transmitted light and forward scattered light. It has been observed experimentally on dielectric rod grating, close to the diffraction onset [139].

For a regular array with p = 649 nm, d = 227 nm (DR = 15), we performed analytical (see Mie solutions above) and numerical simulations (RETICOLO, see Chapter 2) of the transmittance for various infrared wavelengths. Results are plotted in Figure 3.16a. We then measured experimentally this spectrum for a section of a drawn fiber (Figure 3.16b) placed in an optical setup, and plotted it against the theoretical ones with good agreement. Despite the incident beam not being perfectly collimated and some reflection at the fiber cladding/air interface, we obtained a dip in transmittance corresponding to about 84% attenuation.



Figure 3.16 – Extraordinary reflection for index sensing. a) Simulated, analytic and experimental transmittance through a regular NW array. Courtesy of Pierre-Luc Piveteau. b) SEM images of a drawn fiber with high regularity, used to probe the the transmittance spectrum in the infrared for a normally incident illumination. c)

Normalized field intensity $M = \frac{|E_{inc}+E_{scatt}|^2}{|E_0|^2}$, at the resonant condition (p = 650nm, d = 230nm, normallyincident TM polarized field at 1078 nm). Light is propagating along x direction, and the array is along y direction. The rod is outlined in dark. Courtesy of Pierre-Luc Piveteau.

Microfluidic index sensing

Such strong resonances, provided by "extraordinary reflection" effects, can be exploited for sensing purposes, either to perform standard refractometric index sensing or to perform more advanced bio-analytes sensing. Indeed, any changes in the surrounding environment is expected to influence the observed resonance. For example, the resonant wavelength can shift with a change of the surrounding environment. Tracking of this shift can give information about the refractive index of the changing local environment. The better the overlap between the local enhanced electric field of the resonance and the local environment, the more sensitive the system [140].

To estimate the relevance of designing a sensing system, we simulate a resonant geometry and visualize the local electric field. Results are visible on Figure 3.16c. We can see strong field enhancement on the rod's surface and between the rods (maximum enhancement factor M = 207). Note that the field is closely confined around the rods. Thus, to design a sensitive system, the local probed environment needs to be in close proximity to the rod grating. This could be done by removing (through etching, milling, or polishing) the top cladding. Alternatively, if the NWs are deposited onto the PEI substrate and dip-coated with a thin PEI layer, e.g. 1 μ m, at DR = 20 this would translate into a 50 nm PEI layer over the NWs, lower than where strong field enhancement is predicted. By designing a microfluidic channel inside a PEI fiber (Figure 3.17a and b), microfluidic capillary sampling (Figure 3.17c) could be combined to highly sensitive index sensing.



Figure 3.17 – Proposed cross sectional fiber geometry. a) SEM image and b) schematic of fiber with a PEI cladding and a microfluidic channel at its core, a metasurface exhibiting extraordinary reflection allows sensitive refractive index sensing of the sampled fluid. c) Example of a fiber sampling a fluid by capillarity in its multiple microfluidic channels. Scale bar in a: $200 \,\mu$ m.

Conclusion

We proposed a new fabrication approach bridging the gap between the high degree of control and reproducibility offered by photolithography and the scalability enabled by thermal drawing. We first described resonant modes for NWs in the visible regime, and their potential as meta-atoms to be periodically arranged in a one-dimensional metasurface. Next, based on a geometrical model for reflow of deposited chalcogenide glass, we described and estimated fabrication constraints given by extremal aspect ratios. Then, phase and amplitude through the NW array were simulated over all the accessible period and diameter space. Based on this library of optical behaviours, we assembled

the meta-atoms into a metalens design and simulated its performance. Fabrication was demonstrated via lift-off and thermal drawing, although fabrication biases should be accounted for to obtain the intended wire diameters and metasurface properties. Finally, we pave the way for an application in microfluidic sampling and index sensing, harnessing extraordinary reflexion.

Experimental section

FDTD Lumerical simulation

A general description and details about Lumerical can be found in the Experimental section of Chapter 2. Here we used specifically a general mesh size of 25nm and an overmesh of 10nm around the NWs. The auto shut-off level for convergence was chosen at 10⁻⁵.

Rigorously Coupled Wave Analysis simulation

Description of the RETICOLO package was given in Chapter 2, as well as a simulation convergence study. Simulation parameters used here were even more conservative; 2 nm-thick slices and 15 Fourier orders were chosen for all simulations.

Experimental characterization of the metalens focusing efficiency

A supercontinuum superK laser was set to emit a collimated beam at 630 nm. A portable microscope was mounted on a micrometric translation platform with a 10 μ m resolution. A polarizer was interfaced between the laser and the metalens to be characterized, set for a transverse electric polarization with respect to the NWs. A pinhole reduced the incoming beam to a diameter smaller than the NW array. For each position of the (focale plane of) the microscope, a picture was taken, and the sum of RGB values was integrated as a proxy for the field's intensity. As the fiber's cross section if invariant by translation in the drawing direction, all intensity values could be averaged over the corresponding axis of the microscope's image. This 1D data was finally plotted over each of the microscope's positions, yielding a 2D intensity map of the field after the fiber.



Figure 3.18 – Metalens characterization setup.

4. Nanocomposite electrodes

Chapter 3 set the stage for additional control and degrees of freedom in NW array arrangements. It also paved the way for novel compatibility between photolithographic processes and thermal drawing. To harness electronic properties of semiconducting glasses such as photoconductivity at the nanoscale, we now consider requirements and potential solutions for compatible electrodes. In addition, this understanding of conducting nanocomposite processing opens applications for the electrodes themselves as elongated resistive and capacitive sensors for embedded functionalities in fiber reinforced polymer composites. Parts of the presented work are also published elsewhere [86].

Drawable electrodes

Motivation

A strong advantage to thermal drawing lies in the versatility and complexity of the cross-section geometry and the assembly of multiple materials. Conductors, insulators and semiconductors have been simultaneously drawn from a single preform, providing a platform for the continuous fabrication of potentially kilometer-long optoelectronic devices.

However, two challenges have limited the ultimate feature dimensions of such structures. Firstly, as materials viscosities decrease for the preform to be drawn into a fiber, the capillary forces described in Chapter 2 render semiconductor films instable, which leads to short-circuits between the electrodes. The problem is made worse by poor control over the viscosity of the electrodes themselves surrounding the semiconductor. Until now, the distance between electrodes has never been reported to reach dimensions smaller than 20 μ m [76], [141], [142]. To the contrary, light detection and harvesting over a large active surface requires a thin photoactive film planar geometry. All attempts at making light sensitive structures have either been for side illumination or NWs connected at fiber ends [25].

Secondly, a standard photocell geometry would involve one top transparent electrode, which has not yet been reported in literature. Preliminary work at FIMAP has shown the possibly for carbon nanotube nanocomposites to be drawn in a thermoplastic matrix, conducting after drawing and semi-transparent. However, the viscosity of these nanocomposites is currently too low in high Tg claddings (compatible with the glass' viscosity) to avoid the collapse of the photodetecting structure: when semiconducting glass thin films dewet, this results in short circuits (Figure 4.1a and b). In literature and our own preliminary experiments, the nanocomposites in Figure 4.1c and d also show poor shape retention.

In the first part of this chapter, we propose a process for the fabrication of potentially transparent highly viscous nanocomposite electrodes. Furthermore, we combine this material to a geometry where shirt-circuiting is unlikely, even at the nanoscale. This would allow drawability of a full photodetecting structure at an unprecedented scale.



Figure 4.1 – Electrode deformation with CB-PC. a) Opctial micrograph in transmission: a chalcogenide (here As₂Se₃) film was drawn in between a low melting temperature alloy (SnZn) and a CB-PC electrode. The SnZn electrode/busbar is seen reflowing from a rectangular shape. b) Optical micrograph in reflection: short circuits appear because of the reflow happening at the metal/CB-PC interface. The chalcogenide film cannot remain continuous under such loose geometry retention. c) Micrograph in reflection of a cross section of a drawn fiber with an amorphous Se core sandwiched in between two metallic glass (MG) ribbons, in contact with CB-PC nanocomposite domains. Again, despite the high viscosity MG, planarity is lost because of the low viscosities of Se and CB-PC during drawing. d) Micrograph in reflection: again, the CB-PC conducting layer should have remained flat, but a bulge is seen in the center. Adapted from [76]. Scale bars: a, 200 μ m; b, 50 μ m; c, 100 μ m, d, 50 μ m.

Process description

Selenium (Se) is a chalcogen semiconducting glass with photoconducting properties [143]. In a PSU cladding, Se should be processed during thermal drawing just above its melting temperature $T_{m,Se}$ = 221 °C, to make sure crystallization doesn't hamper drawing. On the other hand, to maintain good shape retention of the surrounding electrodes, their viscosity needs to remain as high as possible during drawing to slow down reflow of the preform geometry, at lower drawing temperature (all things equal). To demonstrate the effect of the drawing temperature on reflow, a fiber was drawn with a patterned CB-PC film at its core (Figure 4.2a). The fiber was first drawn at high stress (low temperature). The texture height remains around 6 μ m (Figure 4.2b). The rest of the fiber was drawn at low stress (high temperature), and the texture height decreased by 27% to 4.4 μ m (Figure 4.2c).

These two requirements, drawing at a temperature high enough for Se melting and low enough for low polymer viscosity, are incompatible. A solution is to use a higher T_g thermoplastic polymer such as PEI ($T_g = 215^{\circ}$ C [144]), whose minimum drawing peak temperature in the drawing furnace, around 250°C, is well above $T_{m,Se}$. However, at such temperatures, no conducting drawable electrodes have been reported in literature to have viscosities similar to the PEI cladding.

Here, we show successful processing of highly viscous nanocomposite conducting films, compatible with thermal drawing in a PEI cladding. Composed of a PEI matrix with carbon nanotube (CNT) fillers, as for the preliminary work undertaken with CNT-PC at FIMAP [145], they also hold promise for transparency at low thicknesses.

Processing of nanocomposite films, not to mention mastering their optoelectrical properties after drawing, is a scientific endeavour in itself [146]. We attempted to avoid fabricating our own by browsing for an off the shelf conducting PEI composite. Antistatic PEI 3D printing filament was the only corresponding material we could find. Such a material, made of a carbon black (CB) filler in a PEI matrix is used in the fabrication of electric circuit casing for electrostatic discharge. It was however necessary to test whether this material would be conducting enough after drawing in our geometry: would it conduct sufficient photocurrent laterally to the bus bars? Even when placing it alongside a CB-PC film (see Figure 4.2d) with relatively good conductivity, we could not measure any current flowing through the drawn structure. We believe the CB network in the PEI matrix was stretched below its percolating threshold. Developing our own PEI nanocomposite compatible with thermal drawing was necessary.



Figure 4.2 – Shortcomings of state-of-the-art and commercially available nanocomposites. a) A PSU cladding fiber was drawn with a CB-PC film in its core, embossed with a square texture. b) Drawn at low temperature, the features reflow much less than c) at high drawing temperature. d) Conductivity test after drawing CB-PEI. Scale bars: a: 200 μ m, b: 10 μ m, d: 5 μ m.

Two main processing routes have been considered: melt-mixing in double screw extruders [147], and solution-based mixing [146], [148]–[154].

Melt extrusion has the advantage of processing with shear, which allows a high degree of mixing of the CNT in the thermoplastic matrix (Figure 4.3a). Without solvent, there are fewer unknown

parameters to control for good reproducibility of the nanocomposite processing. Typically, a CNT-PEI masterbatch (pellets) with high CNT concentration would be mixed in the extruder with pure PEI to match the desired CNT weight percentage. However, no such blend is commercially available. The highest Tg thermoplastic matrix (with CNT fillers) we could find was PC. An attempt was made at extruding this blend with PEI, but at the temperature required for melt-mixing PEI, PC seemed to degrade (Figure 4.3c), as confirmed by Differential Scanning Calorimetry showing the onset of weight loss, i.e. degradation, as of 310°C (Figure 4.3b). Blending with PSU was successful, which increased the viscosity relatively to a PC matrix, although still sub-optimal for shape retention in a PEI cladding. The extrusion procedure is described in more details in the Experimental section. We determined the maximum drawable CNT weight percentage to be 5% of the total CNT-PC-PSU weight (Figure 4.3d). Beyond this content, the blend is not drawable anymore, as shown in Figure 4.3e.

The blend was also processed in solution by dissolving PEI and the CNT-PC masterbatch in chloroform. In this case, good dispersion of the CNT to avoid aggregates is the main challenge. CNT-polymer blends reported in literature propose ultrasonication, planetary mixing or addition of surfactants [146], [155]. Finding the process for optimal CNT dispersion is challenging as it changes at each processing step: the CNT may be well mixed in solution, but this dispersion is metastable. When drop-casting and evaporating the solvent, CNT may aggregate again. This was particularly the case when using NMP as a solvent, which showed strong phase separation upon drawing slowly. Again, the dispersion is affected by all subsequent thermal processing, such as hot pressing and thermal drawing, which provide energy to the nanoparticles to reorganize in the softened polymer matrix [145].

We focused on ultrasonication for simplicity and cast films on a teflon plate for drying. After removal of excess solvent in vacuum, films were hot pressed several times into 100 μ m films and placed in between two PEI plates for drawing. In a photodetecting structure configuration, bus bars can be drawn in the fiber to reduce the resistivity along the fiber. Photogenerated charges only need to travel laterally through the nanocomposite until they reach the bus bar. In the fiber, the nanocomposite resistivity should rather be measured laterally. Two channels were thus milled at either edge of the film for wire co-feeding, to be able to conveniently measure lateral conductivity of the nanocomposite film. A cross section of such a drawn fiber is shown on Figure 4.3f. Although drawing was successful, lateral resistivities were very high (of the order of 10^5 Ohm.m).



Figure 4.3 – Thermal drawing of polymer nanocomposites. a) Open micro-extruder chamber with mixing screws b) DSC of the CNT-PC, showing the onset of slow degradation at 310°C c) Granulated CNT-PC-PEI filament because of PC degradation d) Drawable semi-transparent CNT film. e) Not drawable CNT film; the percolated filler network does not flow with the polymer f) Fiber architecture using double wire co-feeding for measuring lateral conductivity.

Achieving nanocomposite processability, conduction and transparency simultaneously is a challenging balance between filler concentration (also called loading) and dispersion: it is our current assumption that the interconnected filler network, required for conductivity, also acts as a hard backbone preventing the flow necessary for drawing. High loadings yield high conductivity but hamper drawing. Similarly, the filler dispersion in the polymer has an important role to play; SEM analysis can help in understanding this dispersion at the nanoscale (Figure 4.4a). Figure 4.4b and Figure 4.4c show PSU fibers drawn with films with the same loading (7 wt% CNT in PC), but different

dispersions (different suppliers). The stress and shear present during drawing may not provide a sufficient force to break-up dense filler aggregates, which destabilize drawing as solid inclusions in the drawn fiber. When the dispersion of the fillers is more homogenous, they may flow with the polymer, as long as there is sufficient strain/shear. This latter condition sometimes results in a nanocomposite being drawable as a film encapsulated inside the fiber cladding, but not drawable itself. Indeed, the criterion for drawability described in ref [156], that the storage and loss moduli G' and G'' in shear rheology as function of temperature show a crossover, is absent above 5 wt% filler concentration. Figure 4.4d shows viscosities for a 5 wt% CNT concentration in PC-PSU with a crossover around 230°C. Figure 4.4e, for a 10 wt% CNT concentration, shows no crossover. The filler dispersion is also critical to transparency. When films are sufficiently thin, a percolating network may be both conducting and transparent, such as through a wire fence. Preliminary experiments predict that for CNT loadings around 5 wt%, processing by melt-extrusion and films thinner than 100 μ m, an optimum for transparency and conductivity can be found [145]. Whether the required dispersion can be obtained via the solution route remains an open question.



Figure 4.4 – Filler dispersion. a) SEM picture of the surface of a CNT-PC-PEI film, where CNTs can be seen. The right particles are from a conductive carbon paint used to avoid charging when imaging. b) The same preform had two films of the same filler loading on either side, but with different dispersion; the first one is not drawable, whereas c) is drawable and shows continuity. d) Shear rheology by ramping temperature by 3 °C/mn

under constant plate oscillation frequency 1 rad/s, for a CNT wt% in PC-PSU equal to 5%: a crossover of G' and G'' is seen around 230°C, and e) 10%: no crossover is seen.

Insulating spacer architecture

Equipped with new high Tg (semitransparent) conducting nanocomposites, better shape retention can be obtained through thermal drawing. In addition, we propose a design and a fabrication process with insulating spacers to reduce further the likelihood of short circuits between electrodes.

A 25 μ m insulating high Tg layer (PSU or PEI) is laminated onto a film made of the new nanocomposite. Openings are ablated through this insulating layer by laser machining to expose the underlying conducting layer (Figure 4.5a). Figure 4.5b is an SEM picture taken without any conductive coating for imaging. As a result, the sample charges from electron accumulation, but this only occurs at the top of the structure, where the conductive bottom electrode hasn't been exposed by laser ablation. Semiconducting chalcogenide glass is then deposited by thermal evaporation onto the structured films, and a top electrode made of the nanocomposite is hot pressed onto the stack (Figure 4.5c). Doing so, the glass flows into the machined openings (Figure 4.5d), and the top electrode adheres to the insulating layer by polymer chain interpenetration (diffusive adhesion). This avoids delamination through drawing. Figure 4.5e and f show respectively micrographs in reflection and transmission of a cross section of the hot-pressed stack. Top and bottom electrodes are well spaced, while grooves are filled with the chalcogenide glass.



Figure 4.5 – Laser openings through the insulating spacer structure for contacted chalcogenide wires. a) Schematic of a cross section of the geometry for laser ablation through the insulating layer, exposing the conducting substrate. b) SEM picture of 3 grooves etched with an excimer laser. Note some redeposition of the etched material on the sides of the lines. Scale bar: 30 μ m. c) Schematic: after PVD of the chalcogenide glass on the etched structure, a counter electrode is hot pressed at a temperature above the T_g of both the glass and the nanocomposite for d) thermal consolidation with the insulating layer, and for the chalcogenide glass to fill the grooves. e) Cross section micrograph in reflection of the structure after hot pressing. f) The same micrograph taken in transmission. The insulating layer is transparent.

Alternatively, to reduce the laser writing time of the grooves and increase resolution, dry etching was also demonstrated, illustrated in Figure 4.6a. The main upsides are twofold: (i) the ability to expose at once a photoresist through an exposure mask, to protect insulating spacers from dry etching. An entire wafer-size surface can therefore be prepared in one lithographic process, as opposed to laser machining groove after groove at \approx 5 s/mm (30 µm deep groove); (ii) improved resolution: photolithography typically allows micron resolution, which leads to smaller deposited chalcogenide bars, and smaller NWs in the fiber in fine, for compact optoelectronic structure

integration and increased photodetection sensitivity [21]. Lamination of the films onto a wafer (Figure 4.6c), compatible with spin-coating, exposure, development and dry etching is described in more detail in the Experimental Section. For this preliminary demonstration, a resist etch mask was used for simplicity, but its poor selectivity (measured to be 17:22 by interferometry, see the Experimental section) requires spin-coating a larger resist thickness than the insulating spacer film thickness. This results in reduced resolution, as the smallest pattern feature - or critical dimension CD - is proportional in first approximation to the photoresist thickness. An improvement to achieve micron resolution in photolithography (not attempted here) could be to spin-coat a thin negative photoresist and lift-off a metal etch mask, insensitive to an oxygen plasma dry etch. A layout, shown on Figure 4.6b, with three different periodicities was designed to explore achievable groove width and spacing for this 25 µm insulating spacer layer. Large pads were included on the edges of the design to be able to validate quickly that the bottom electrode had been exposed by contacting it with a metal tip. Figure 4.6c shows an SEM perspective of a resist line after exposure to an oxygen plasma: etching is anisotropic as the resist undercut protects well the insulating film under it. Details about the etch rate estimation are given in the Experimental section. After development, Figure 4.6d shows a spacer line as thin as 4 μ m was achieved after dry etching. How thin the insulating lines could get to maximize the chalcogenide cross-sectional surface while maintaining spacing between electrodes remains an open question. Verification that the conducting nanocomposite substrate had been reached was threefold: (i) the SEM picture in Figure 4.6e, taken without any conductive coating, shows charging on the top of the sample, where the insulating layer hasn't been etched, in contrast to the grooves; (ii) the SEM picture in Figure 4.6f shows a different topography and backscattered electron signal towards the bottom of the groove, where we believe is the interface between the nanocomposite and the insulating layer; (iii) When contacting the pads (Figure 4.6g), a resistance of a few tens of kOhm can be measured, as opposed to any other point outside the pad.

After chalcogenide glass deposition, the micrograph in Figure 4.6h shows the absence of dewetting in the grooves when hot pressing. For this characterization, a pure PEI film was hot pressed onto the polymer-glass stack instead of the top nanocomposite electrode. By contrast, the glass dewetts at edges where there is no groove to flow into. Note that lines don't appear entirely straight because some glass remains between the top PEI film and the insulating spacer film, but this doesn't increase spacing between electrodes by much, as can been see on the optical reflection micrograph cross-section in Figure 4.5e. Only a sub-micron thick glass layer remains at the interface, with little impact on the overall structure, and which might reflow during drawing. Hot pressing with more pressure may improve this.



Figure 4.6 – Dry etching through the insulating spacer structure for contacted chalcogenide wires. a) Process flow. b) Layout with lines or three different widths and periodicities, with large pads on the side for conduction tests. c) Resist line after dry etching. d) Minimum width spacer line achieved after stripping the resist. e) SEM picture of the insulator-nanocomposite interface in an etched groove. f) SEM picture of the top of the film

taken without coating, showing charging, in contrast to the etched grooves. g) Contacting on the 4 mm wide square pads to test the conducting layer has been reached. h) Micrograph in reflexion of the chalcogenide glass filling the grooves after hot pressing a transparent top layer for characterization. Scale bars are respectively: b, 2 mm; c, 2 μ m; d, 6 μ m; e, 10 μ m; f, 40 μ m.

Finally, another strategy for obtaining insulating spacers was considered. The concept is to prepare an alternated stack of nanocomposite and insulator layers, hot press them together and cut a very thin slice using a circular diamond saw (Figure 4.7a). The surface of the slice can then be wet etched in solvent. If the nanocomposite polymer matrix can be etched preferentially, the insulator layers protrude and would prevent contact with a top counter electrode. This concept is illustrated on Figure 4.7b. Note that a continuous conducting layer could be hot pressed against the bottom of the structure for connecting to an external circuit. Alternatively, if each conducting layer can be connected individually, each chalcogenide wire could be addressed individually. The relative depth of CB-PC compared to PEI during wet etching in acetone with agitation is plotted in Figure 4.7c. Measurement of the depth of the grooves using an optical profilometer is presented in Figure 4.7d. Good insulating spacing could be obtained.



Figure 4.7 – Wet etching as a scalable strategy to obtain conducting grooves through an insulating layer. a) A slice cut from a hot pressed stack of alternating nanocomposite and insulating films. b) Schematic presenting the wet etch concept. c) In acetone, CB-PC is etched preferentially with respect to PEI. The relative depth is measured against time, corresponding to a logarithmic increase. d) Snapshot of a Keyence profilometer software showing the regularity and depth measurement of the surface of the stack.

Two more strategies were considered unsuccessfully but are worth mentioning. Similarly to wet etching on to the surface of a slice cut through a nanocomposite/insulator stack, dry etching was attempted. Unfortunately, no difference in etch rates between the two materials could be measured. The SEM picture in Figure 4.8a is taken at one of the interfaces of the alternating layers of the stack. No height difference can be seen. Another hope was to be able to emboss through the insulating layer by soft lithography. Replication on thermoplastics using a PDMS stamp is a very cost-efficient way to pattern their surface without the need for costly lithography machine time.

However, it is unusual to emboss onto a dual-layer thermoplastic. A preliminary test was therefore performed to understand whether the insulating layer would flow into the grooves of a square PDMS stamp when hot pressing, and whether the conductive substrate could be exposed. Unfortunately, the top insulating film stretches and maintains full insulating coverage over the imprinted pattern, as seen on the cross section in Figure 4.8b. We hypothesize that this soft lithographic process could only achieve the desired structure if the conductive substrate would have a much higher viscosity during embossing. In such a case, the substrate could stay flat when the insulator flows into the stamp grooves, creating openings to the substrate electrode. However, such a viscosity mismatch would be detrimental to good fiber architecture geometry retention during drawing and may lead to short circuits. This strategy was therefore not favored over laser ablation or dry etching.



Figure 4.8 – Other strategies attempted to obtain a periodic insulating spacer structure. a) Dry etching of a slice of an alternated nanocomposite/insulator stack. The SEM picture shows the interface between two layers. The top material is a mask used to understand where the stack was etched. No depth difference is seen between the nanocomposite and the insulator. b) Transmission micrograph of a cross section of a 25 μ m PSU layer embossed onto CB-PC with a square PDMS mould. The insulator layer remains continuous. Scale bars: a: 10 μ m, b: 100 μ m.

Finally, based on the best strategy to contact the wires, we envision that light could be periodically concentrated into the chalcogenide wires by shaping the cladding surface. Shaping the cladding for air/polymer refractive lensing can easily be obtained by texturing the preform cladding surface by embossing it with a PDMS mould. Optical characterization would require shaving/etching the other side of the cladding to the desired depth and probing the light concentration profile. Simulations might help to predict the optimal shapes before drawing reflow, as it was done in [11]. Minimizing reflow during drawing can also be achieved with a sacrificial top CB/PE layer reducing interfacial tension when drawing, as it was done in [157].

Sensing electrodes - application to functionalizing composite parts

Motivation

We now turn to applications for the nanocomposites themselves, as piezoresistive and capacitive electrodes for embedded sensing. Fiber reinforced polymer composites (FRPCs) have become a central material platform for the aeronautics, automotive or sports industries, for the most part because they reconcile light weight with high specific strength and stiffness. One of the most prominent processing routes for producing FRPCs is Liquid Composite Molding (LCM) where a dry stack of fabric reinforcement (glass, carbon, natural fibers etc.) is impregnated by a thermoset resin flowing under an applied pressure gradient in a closed mold; the final product is demolded when the resin is partially or completely cured.[158] Prevalence of LCM processes is increasing in industry as high quality, net shaped parts can be realized at high volume of production with a significant potential for process automation.[159] At the current state of the technology, online monitoring and online control of these processes are becoming crucial for achieving reliable and fast production. Real-time monitoring and control of the process enable eliminating defects during impregnation, optimizing the curing stage, and coupling the collected data with a digital twin. Online monitoring is performed either by permanent sensors strategically placed in the mold or by sensors embedded in the part during fabric stacking. These sensors require access to a physical parameter related to the presence of resin, such as pressure, heat, or optical reflection/transmission for transparent molds.[160]-[162]

Embedded sensors are of particular interest, as they do not require adapted molds and can also be used for structural health monitoring during the service of the part. Various solutions are currently under development or were recently introduced to the market.[162]–[164] Notably, fiber-optic sensors offer cure monitoring as well as temperature and strain monitoring of the final part while minimally altering the microstructure.[161], [165]–[167] Other alternatives, rather at the development stage, consist in functionalizing either the matrix or the fibers with carbon materials (carbon nanotube, carbon black or graphene) for resistance measurement,[168]–[170] using metallic wires for time domain reflectometry[171]–[174] or dielectric[175]–[177] measurements with interdigital patches.[178]–[180] However, the existing solutions fail to provide a reliable measurement that is at the same time electrically insulated from carbon fibers, robust (glass fiber optic sensors are known to be very brittle[161], [181]) and small enough not to impact mechanical properties while offering scalability at low cost.

In this context, multi-material multi-functional fibers are emerging as a strong candidate for robust and precise embedded sensors within FRPC parts.[182], [183] Multi-material fibers are made using thermal drawing, as described in the thesis introduction: a macroscopic preform, in which different materials are assembled using simple methods such as milling or hot-embossing, is fed into a closed furnace, softens and is pulled into kilometer-long, thin and flexible fibers. Thanks to recent progress in the understanding of material viscous co-flow,[184]–[186] the preform's cross-section can be preserved in the fiber form, with its feature size being scaled down ten to a hundred times, reaching the sub-100nm scale.[187] A wide range of materials have been successfully integrated into the fiber's core, including metal, thermoplastic and biodegradable polymers, polymer composites and flexible co-polymers.[156], [185], [188]–[192] These advances allow for the fabrication of multimaterial multi-functional fibers that are used in various sensing application, such as photodetectors,[193] precise touch-sensing,[194], [195] microfluidic tracking[196], [197]. Such fibers have even shown recent promise for brain-recording devices[198] and monitoring multiple disease biomarkers in vivo.[199] Yet thus far, multi-material fibers have surprisingly not been exploited in the context of bringing advanced functionalities to FRPC. In this chapter, we demonstrate a novel design of advanced fiber-based sensors that can be integrated within FRPC parts and continuously and in-situ monitor the flow propagation during impregnation by a thermoset resin and the cure progression of the resin. We demonstrate that the embedded fibers can then be used as temperature and mechanical strain sensors during the service life of the final part, offering these capabilities at high scalability and low cost. The multi-material fiber sensors consist of different conducting polymer composite electrodes embedded in a polymer cladding that defines the cross-sectional geometry of the multifunctional fiber sensor. These fibers can be placed between the layers of the fabric while stacking and can be integrated inside the FRPC. We show that we can engineer the fiber geometry to minimize the disturbance to the flow caused by the resin channels around the sensing fiber, and that the flow front can be on par with typical flow rates associated with these types of processes, typically on the order of 1 mm/s. We then demonstrate that the fiber can monitor both the flow-front of the resin during impregnation, and its degree of curing, via the change of the fiber equivalent capacitance. Moreover, resistive measurements from multiple polymer composite electrodes integrated in FRPCs enable both sensing and decoupling of temperature and strain changes experienced by the cured part. Our approach constitutes a simple, scalable and potentially cost-effective platform for the low-profile integration of embedded sensors into composites parts for both their process monitoring and functionalization, leading to potential benefits in a large-scale cost-driven industry.

Proposed fabrication

Functional fibers were fabricated via the thermal drawing process (Figure 4.9a). The typical structure of such a fiber consists of high Tg thermoplastic cladding (polysulfone PSu), carbon-loaded conducting polymer composite strips and metal contacts. The conducting polymer composite strips form electrodes for capacitive and resistive sensing (Figure 4.9b), for which carbon black-filled polycarbonate (cPC) and carbon black-filled polyethylene (cPE) were employed, respectively. A low-melting point eutectic alloy (bismuth and tin Bi58Sn42, $T_m = 139^{\circ}$ C) bus bar was co-drawn in contact with cPC to enhance electrical conductivity along the fiber axis and improve the device's response time in capacitive measurements. Examples of fiber cross-sections are shown in Figure 4.9a and Figure 4.9b. Functional fibers are subsequently integrated into the FRPC during the mold preparation for Vacuum Assisted Resin Transfer Molding (VARTM, Figure 4.9c), placing it between two layers of fabric during the draping stage (Figure 4.9d). We monitored the capacitance change during the resin injection and curing steps following mold closure. For capacitance measurements we used a frequency of 150 kHz, which falls into the frequency range appropriate for such architectures.[197]



Figure 4.9 - Multimaterial functional fiber and fiber reinforced polymer composites (FRPC) production. a) Schematic of the thermal drawing technique and a fiber cross section. b) Cross-section of thermally drawn fibers. c) Schematic of Vacuum Assisted Resin Transfer Molding (VARTM) process. d) VARTM processing of an FRPC plate with an embedded multifunctional fiber.

Flow propagation and cure detection

We first verified that the capacitance measurement was independent from the resin impregnation speed by dipping the fiber sensor at controlled velocities between 2 mm/min and 60 mm/min. These tests were performed right after resin mixing to ensure that the change in capacitance response was solely due to the fiber length dipped in the resin (i.e., not affected from the resin curing). As seen in Figure 4.10a, the capacitance increases linearly with the dipped length, as the dielectric constant of the surrounding medium changes, for all studied velocities. The inset shows the slopes of the corresponding curves as a function of dipping speed following a linearly increasing trend (R2 = 0.999). Following this validation step, we assessed the precision and relevance of the capacitive measurement for impregnation monitoring and curing. We recorded the capacitance value during these two steps and plotted it against time in Figure 4.10b. The capacitance first rises as the resin penetrates and advances through the preform, then decreases with curing as the resin changes permittivity when reticulating. During injection, we also monitored the visual flow front location for comparison. The capacitance only started rising once the resin reached the fiber and its change matches very well with the impregnated length of the fiber. During curing, capacitance accounts well for the degree of cure (estimated through resin samples analyzed with the "residual heat of reaction" method[169], [200] based on Differential Scanning Calorimetry measurements using the same temperature profile as during the plate production) above a cure degree of 0.5. The slight difference below 0.5 is assumed to originate from the frequency dependency of these

measurements due to dipole rotation whereas the response in later stages of curing are frequency independent.[179], [180] Nonetheless, the latter stages of curing being the most relevant to an industrial process, this signal can be used to check the possibility to move on to the next step of production, demolding the part and preparing the mold for the next part (as depicted in Figure 4.9b). Also, the capacitance decrease has a reproducible shape which could be fitted/calibrated to get the exact cure degree at all times.



Figure 4.10 - Flow propagation and cure detection through capacitive sensing and temperature monitoring through resistive sensing. a) Response while dipping a fiber into a resin pool at various constant dipping speeds. The inset shows the slopes of curves as a function of dipping speed. b) Response during VARTM processing. Lower left inset shows the relationship with the visual flow front location and upper right inset shows the relationship with through DSC measurements. c) Influence of embedded fiber thickness on diversion from rectilinear flow. Inset graph shows the diversion as a function of fiber width, inset pictures show the flow front shape during impregnation and the micrographs show the microstructure modification due to the presence of fibers.

After analyzing the electrical response of the fiber to the resin flow and curing, it is important to investigate the influence of the fiber once placed between plies of fabric in the preform, to avoid the generation of void or alteration of the composite microstructure and mechanical properties. The effects of inclusions and resin-rich regions in composites has been studied extensively[201]–[204]. It was shown that sensors with a high aspect ratio could be embedded in the FRPCs without significant reduction in mechanical properties.[205] Empty regions formed around the inclusions are also known to alter the flow characteristics,[206] and can be exploited to reduce the processing time.[207] However, in the case of an embedded sensor, one should ensure that the flow

characteristics in the vicinity of the sensor are representative of the bulk behavior. Thus, we quantitatively assessed the effect of the embedded fiber dimensions on the flow by defining the "flow length" as the distance between a point on the flow front and the mold inlet. We also define the "length ratio" at a given time as the maximum flow length on a fiber divided by the minimum flow length at that moment. This ratio is larger than 1 if the flow is enhanced around the fiber and equal to one if the flow front is straight and parallel to the inlet, which is our objective. We made fibers with different aspect ratios and widths (thus fiber thickness), integrated them between fabric plies and tracked the length ratio during impregnation. Figure 4.10c shows that the fiber thickness defines the extent of resin-rich regions and, independent of the aspect ratio around unity) for the selected glass fiber fabric, which has a microstructure representative of industrially relevant textiles. Note that such fiber dimensions are easily achieved using multimaterial thermal drawing.

Functionalized composite parts

Once integrated in the final part, multi-material fibers can be further exploited during the life of the part to measure temperature or strain. Indeed, carbon black-loaded conductive polymer electrodes can also provide additional information if connected from both ends of the fiber, as the resistance of the composite strips changes with deformation and temperature. These additional functionalities come almost for free since additional electrodes for the longitudinal resistive measurement can be co-drawn in the same fiber cladding. The change in the resistance can be explained by the change in the geometry of the strips (strain or thermal expansion of the polymer matrix) and by the change in their conductivity (carbon percolation network) subjected to annealing.[208] Thus, resistance measurements enable temperature and strain tracking during both VARTM processing and operation of the produced parts. For temperature dependency of resistance characterization, we embedded a functional fiber with two cPE electrodes from different suppliers in an FRPC. We placed it in a temperature-controlled oven programmed to cycle through 8 preset temperatures: from 30 °C to 65°C with 5°C steps followed by 10-minute dwell times, as shown in the inset plot of Figure 4.11a, so that the FRPC and the fiber had time to stabilize. We acquired the resistance values at the end of each dwell plateau against temperature through 5 cycles.



Figure 4.11 - Temperature and strain dependency of resistance measurements and temperature-strain decoupling strategies. a) Normalized resistances of two different electrodes as a function of temperature. The inset shows the evolution of temperature and of normalized resistances throughout the test. b) Normalized slope of resistance-strain curves as a function of temperature. Insets show the resistance-strain curves at three different temperatures. c) Schematic of investigated fiber placement strategies. d) The architecture of the neural network trained and used for predicting the temperature and the strain.

As proposed by Chen et al. [196], an exponential fit in the form of:

$$\frac{R_i}{R_{i,0}} = a_{i,1}e^{b_{i,1}T} + c_{i,1}$$
 Eq. 4.1

matched the temperature dependence very well for both fibers as seen in Figure 4.11a. This matching was also maintained during the cycling of the temperature, which highlights the robustness of the sensor. In Equation 1, $R_{i,0}$ is the resistance at the reference temperature (21 °C throughout this work), $a_{i,1}$, $b_{i,1}$, and $c_{i,1}$ are fitting parameters for the ith electrode (for the two different cPEs).

We subsequently studied the strain (ε) dependency of resistance by performing cyclic uniaxial tensile tests at five different temperatures. Each test consisted of ten cycles where the coupon (with length of 180 mm, width of 35 mm, and nominal thickness of 2.4 mm) with embedded functional fiber was strained at a rate of 0.5 mm/min to $\varepsilon = 0.5\%$, to stay within the elastic regimes of FRPC and the functional fiber. The functional fiber was placed along the length of the coupon and it contained two cPE electrodes. We repeated the same test twice. The insets of Figure 4.11b show the R- ε curves of both electrodes at three different temperatures and show that the relationship is linear above $\varepsilon = 0.2\%$ at all temperatures for both electrodes. We approximated the R- ε relationship by using a linear regression for each loading and unloading step separately. Figure 4.11b shows the slopes of the fitted curves as a function of temperature, normalized with R_0 . The graph shows a larger scatter at higher temperatures due to the hysteresis between loading and unloading cases as seen in the insets of Figure 4.11b. The fitting parameter R² decreased from 0.99 to 0.83 as the

temperature increased, due to a combination of hysteresis and insensitivity at low strain. At higher temperature, this hysteresis results from a reorganization of the carbon black conduction network, due to a higher mobility and diffusion rate. However, this flocculation which reduces resistivity upon annealing, saturates after a few hours, as shown by Hilarius et al.[209] An exponential fit similar to Equation 1 captured the temperature dependence of the normalized slope $\frac{dR_i}{d\varepsilon} \frac{1}{R_{i,0}}$ as a function of temperature *T* for both electrodes:

$$\frac{dR_i}{d\varepsilon} \frac{1}{R_{i,0}} = a_{i,2} e^{b_{i,2}T} + c_{i,2}$$
 Eq. 4.2

where $a_{i,2}$, $b_{i,2}$ and $c_{i,2}$ are the fitting parameters.

Decoupling strain and temperatures sensing

We now address a potential shortcoming for resistive measurements. A typical FRPC undergoes both thermal and mechanical loads simultaneously during service, and the resistance of a conductive polymer embedded in FRPCs in such a case is affected by both in a coupled manner. Herein, we propose two strategies for decoupling the thermally and mechanically induced changes in resistance as depicted in Figure 4.11c. The first strategy relies on embedding in a single fiber two resistive electrodes with distinct monotonous dependencies to temperature and strain, such as the electrodes whose temperature and strain dependencies are reported in Figure 4.11a and Figure 4.11b. We propose training a neural network (NN) consisting of three hidden layers with a tanh activation function to predict the temperature and strain. Its architecture is similar to those reported in [210], [211] and is shown in Figure 4.11d. We excluded the cyclic tests at 43 °C (45 °C set temperature) from the neural network training process and evaluated the predictive capability of the neural network by comparing the measured temperature and strain with NN predictions for one of those excluded tests. We trained the neural network using the Levenberg-Marquardt method after mapping the resistance values between -1 and 1 and randomly reducing the number of resistance couples to $1/20^{\text{th}}$ of the original size. We divided the resulting dataset into three sets of training, validation and test with a split of 70:15:15.



Figure 4.12a and Figure 4.12b show the measured temperature and strain along with the predicted values. In general, NN successfully predicts the evolution of temperature and strain throughout the test.

Figure 4.12 - Decoupling temperature and strain induced changes in resistance measurements. a,b) Measured and predicted temperatures and strains throughout the test, respectively, in the case of two aligned electrodes. c) Normalized resistance evolutions of two orthogonally placed electrodes (orange lines belong to the orthogonal fiber) undergoing cyclic tensile tests at four different temperatures.

In Figure 4.12a, temperature predictions exhibit an undesired cyclic behavior but oscillate within a 0.2 °C range. The moving average follows a trend similar to the measured temperature. The measured temperature values fall within the predicted temperature band and the difference between the moving average and the measured temperature is less than 0.1 °C throughout the whole test. Figure 4.12b shows that the NN can predict the cyclic behavior of strain with the only limitation being the narrower range of strain in comparison to the measured strain.

NN results could be improved either by using more complex NN architectures such as long shortterm memory recurrent neural networks to account for the hysteresis [212] or by increasing the number of hidden layers or the number of hidden units in each layer, but these come at the risk of overfitting the training data and reduced accuracy at the prediction stage. Nonetheless, the use of NN for decoupling purposes is promising as it can be generalized to other cases easily. It also eliminates the need for curve fitting, which would require a priori knowledge about the dependency of the resistance on physical parameters (temperature and deformation in this case).
The second strategy for decoupling temperature and strain effects is to place two cPE electrodes orthogonally in FRPC as illustrated in Figure 4.11c. Figure 4.12c shows the resistance evolution with respect to the initial resistance of two such electrodes tested at four different temperatures. Resistances of the two electrodes throughout the ten-cycle experiments are in phase at the lower two temperatures, whereas they are out of phase at higher temperatures. This behavior can be attributed to the interplay between the dependency of fiber's and FRPC's Poisson ratios on temperature, the differences between the thermal expansion characteristics of constituents (conductive filler, polymer matrix etc.) and the fact that the orthogonal fiber is compressed along its length while being stretched along its width when the FRPC specimen experiences a tensile load. The orthogonal fiber acts as a binary switch with an out of phase signal above a threshold temperature (between 35 °C and 45 °C in this case). Above the threshold temperature, a comparative analysis of the two signals provides a straightforward route for detecting the presence of mechanically induced changes whereas below the threshold temperature a strategy similar to that which we proposed for aligned electrodes can be exploited to decouple temperature and strain effects. We note that in the case of local temperature variations (e.g. locally applied heat that increases the temperature in the vicinity of one of the fibers), this configuration would not be suitable to decouple the thermally and mechanically induced effects. We also note that the presented strategies, multiple electrodes in a single fiber or multiple electrodes placed orthogonally, can be combined and generalized by embedding several fibers with multiple electrodes oriented at different directions and spatially distributed if desired. Such an approach would enable assessing the load direction in addition to decoupling thermally and mechanically induced changes.

Strain-temperature analytical decoupling

An alternative to the use of neural networks to decouple temperature and strain effects is summarized below. Assuming that the relative resistance variation is the sum of the temperature and strain effects, we can combine Eq. 4.1 and Eq. 4.2 :

$$\frac{R_i}{R_{i,0}} = a_{i,1}e^{b_{i,1}T} + c_{i,1} + \varepsilon (a_{i,2}e^{b_{i,2}T} + c_{i,2})$$
 Eq. 4.3

yielding distinct resistance response surfaces for each electrode as shown in Figure 4.13a.

For each electrode, a given R/R_0 value corresponds to several (T, ε) couples, as shown in red lines in Figure 4.13a with their projections on the (T, ε) plane in blue and orange lines. Figure 4.13b shows a zoomed view of the (T, ε) combinations of the two electrodes (i.e. response lines). We assume that each electrode is subjected to the same temperature and strain, so the intersection of the two curves corresponds to the unique (T, ε) solution that yields the given resistances simultaneously.



Figure 4.13 - Decoupling temperature and strain induced changes in resistance measurements. a) Normalized resistance response surfaces of the two electrodes along with lines indicating the temperature-strain couples corresponding to an arbitrarily chosen normalized resistance for each electrode. b) An illustration of predicting the temperature and strain as the intersection of the response lines of two electrodes. c,d) Measured and predicted temperatures and strains throughout the test, respectively in case of two aligned electrodes.

To demonstrate the ability to solve this system (Eq. 4.3 given for i = 1, 2) for (T, ε) , we construct the response surfaces using the same set of results used in the neural network training. We assess the accuracy of the analytical decoupling method using the experiment we used for assessing the neural network's performance. Figure 4.13c and Figure 4.13d show the measured temperature and strain along with the predicted values. For both temperature and strain predictions, NN outperforms the analytical decoupling method. As seen in Figure 4.13c, the analytical model's temperature estimation exhibits a cyclic behavior, similar to the neural network predictions. However, the error is around 0.5 °C, much higher than that of neural network predictions. Figure 4.13d shows that the analytical decoupling has limitations in terms of strain predictions. Analytically decoupled strain cycles cover an even narrower range than NN predictions and there is a visible drift in the strain predictions that is more prominent in the last few strain cycles. A potential strategy for improving the analytical prediction would be the use of higher order polynomials or exponential relations for estimating the strain dependency of the resistance, in order to account for the insensitivity to low strains at high temperatures. In addition, separate curves can be fitted to loading and unloading cases to account for the hysteresis. This would however require an additional algorithm at the prediction stage to identify whether a data point belongs to a loading or unloading case and would further complicate the analysis.

We finally point to a strategy for further improving the decoupling of thermally and mechanically induced effects. Of course, the sensitivity to strain and temperature is crucial. This is equivalent to

maximizing each element in the $V_i = \begin{pmatrix} \frac{\partial R_i}{\partial T} \\ \frac{\partial R_i}{\partial \varepsilon} \end{pmatrix}$ vector (i=1,2 for each electrode material), or its norm in

the case of a trade-off between temperature and strain dependencies. However, had the same cPE been used twice, whatever its sensitivity to (T, ε) , decoupling would not be possible. By contrast, if the materials are slightly different, decoupling is possible, but with a high uncertainty. Ideally, one would indeed use a first electrode sensitive to strain only, and a second one to temperature only. As a result, in the $(\frac{\partial R}{\partial T}, \frac{\partial R}{\partial \varepsilon})$ space, V_1 and V_2 should be as orthogonal as possible, maximizing $\cos(V_1, V_2)$. If they are colinear, whatever the norms, unambiguous decoupling is impossible. The system given by Equation 3 would have redundant equations for i=1, 2. In practice, conductive polymers are always sensitive to temperature changes, be it by thermal expansion only. However, by tuning processing parameters, it is possible to change carbon dispersion (concentration, clustering and alignment) in the conductive polymer electrode, in order to produce a material with different dependencies.[152], [185], [208] Using the previous notations, we could pick V_i to maximize both norms $|V_1|$ and/or $|V_2|$. A combination of other materials routinely used in multimaterial fibers, whether polymer or metal-based, could be considered if they have "distinct" dependencies and/or higher sensitivities.

Potential for 3D printing functionalized parts

Not only can fiber sensors be embedded in VARTM composites, but they also show potential for Fused Deposition Modeling (FDM). 3D printed layers could be deposited around the fiber sensor for making a part with similar bulk/sensor materials. Alternatively, the multimaterial fiber could even be used directly as functionalized filament [213]. An early demonstration of the former strategy was attempted via a collaboration with the Laboratory for Processing of Advanced Composites (LPAC, EPFL). A sensing fiber's geometry and functionalities were preserved despite surrounding printing at 270°C. However, characterization of the functionalized part's voids surrounding the fiber highlighted the need for improving FDM to better embed the fiber.

A PEI fiber containing a CB-PC resistive electrode was placed and glued with cyanoacrylate (Loctite) onto a half polyamide matrix/carbon fiber 3D printed coupon, and printed over, for complete embedding (Figure 4.14). Fiber connections were made before placement within the composite, and remained accessible after it, protruding from the coupon. The composites coupons were made with the 3D printer Mark Two[™] from Markforged©. This printer possessed two nozzles: one for standard filament, in this case ONYX[™], polyamide with chopped carbon fiber inside it, and one for continuous fiber, in this case carbon. The first material, ONYX[™], mainly serves as encapsulation for the continuous carbon fibers. The latter provides the majority of the mechanical properties to the part and makes up its bulk.



Figure 4.14 - Preliminary test for fiber sensor embedding within FDM continuous carbon fiber composite parts. A resistive fiber sensor is glued onto a half coupon and printed over. Courtesy of Martin Maggi.

The functionalized 3D printed part was characterized by assessing the spatial distribution of voids using X-ray tomography. The μ -CT scan showed voids on one side of the fiber, where no cyanoacrylate was used (Figure 4.15a). Adhesion between the fiber and the surrounding composite could therefore be lost upon straining. By connecting the fiber during a strain test, one could indirectly probe fiber/composite adhesion, assessing whether the fiber is correspondingly strained by measuring the electrode's resistance variation. In a similar fashion, temperature dependency was assessed successfully by placing the whole coupon inside a temperature-controlled chamber. Temperature dependency was not affected by the FDM process, as fibers embedded in the 3D printed composite part gave similar resistive readings to reference fibers not embedded within the composite.



Figure 4.15 – Additive manufacturing using multifunctional multimaterial fibers. a) Rendering of a μ -CT scan, showing voids in blue at the interface between the fiber and the surrounding printed composite coupon (cross sections through the fiber and surrounding composite). Figure courtesy of Martin Maggi. b) Simplified representation of an AFP head used for tow/fiber placement. Adapted from ref. [214].

A strategy for removing voids during filament deposition is currently being considered. Automated Fiber Placement (AFP) [214], an FDM printer which continuously applies pressure with a compaction roller on the filament after or during melting, would serve this purpose. This process is illustrated in Figure 4.15b. It could potentially even be used directly for placement of the functionalized fiber sensors.

Conclusion

In summary, we first described the limitations of existing nanocomposites in achieving complex micro- and nanoscale architecture with good shape retention, compatible with the thermal drawing of electrically connected thin films or wires. We proposed processing routes based on melt mixing and solution to obtain semi-transparent conducting high T_g electrodes. We discussed the constraints and conditions under which a compromise between processability, conduction and transparency can be obtained. Filler concentration and dispersion are critical parameters, highly influenced by the processing strategy chosen and subsequent thermal history. We finally proposed several architectures based on insulating spacers to maintain a distance between electrodes, reducing the likelihood of short-circuits.

Then, turning to an application for the nanocomposite electrodes themselves, we demonstrated the suitability of thermally drawn fibers as a simple and scalable alternative for processing and structure monitoring of fiber reinforced polymer composites. We embedded different types of conductive polymer-based multi-material fiber sensors in FRPCs which allowed us to track the flow front position during Vacuum Assisted Resin Transfer Molding. We also showed that the same fiber could be used for isothermal cure monitoring which is a crucial step in processing to minimize the cycle times. In addition, we demonstrated that embedded fiber sensors could be used during the lifetime of the part, by monitoring the external temperature and applied strain. We explored embedding two different types of electrodes in a single fiber cladding as a sophisticated method to decouple the thermal and mechanical effects. This is possible by training a neural network using the electrodes' resistances to predict the temperature and strain. We also demonstrated that placing two fiber sensors orthogonally enables a qualitative approach to understand the presence of temperature and strain induced resistance changes. Even more strategies are suggested in the supplementary material, such as tuning the electrodes' compositions to improve the decoupling. Various carbonbased polymers as well as metal-based alloys have been shown to be compatible for co-drawing in the same fiber, [183] with different dependencies to strain and temperature. These novel multimaterial fibers pave the way towards a new generation of embedded and low-profile sensors within polymer composites for both process monitoring and life-time cycles engineering.

Experimental Section

Preform fabrication and fiber drawing: Polymers (PSu) and conducting composites (cPE, cPC) were purchased from Goodfellow Cambridge Ltd, UK; the eutectic alloy for the bus bar from Indium Corporation of America. The fabrication of multimaterial preforms was carried out using machine milling and hot embossing (Lauffer Hot-press[®]). The preforms were subsequently drawn using a custom designed draw tower built in the Institute of Materials, EPFL. The drawing furnace has 3 heating zones, and in a typical draw of PSu-cladding fibers, temperature of the 3 zones was set to 190 °C, 320 °C and 90 °C, respectively, and for PMMA-cladding fibers, to 150 °C, 200 °C and 90 °C, respectively. The typical feeding speed was 1 mm/min, and the drawing speed was varied as a function of the desired fiber size.

Capacitance and resistance measurements: Connections to the conducting polymer strips inside the fibers were made with copper wires and silver paint. For accessing cPC, the upper insulating layer of cladding was removed by sanding. cPE could be easily exposed by peeling off the PSu layer which does not adhere strongly to PSu. Capacitance was measured with an HF2LI Lock-in Amplifier, Zurich Instruments AG, Switzerland and resistance with a Keithley 6517B, with an in-house computer interface.

Vacuum Assisted Resin Transfer Molding (VARTM): 8 layers of a twill weave E-glass fabric (Suter Kunststoffe AG, 390 g/m² areal density) were placed on an aluminum flat plate and the

multifunctional fibers were placed between the 4th and 5th fabric layers. Consumables to form the resin inlet and vacuum outlet (Diatex Spiralnet), and to provide ease of demolding (Diatex PA80 peel ply) were placed. A vacuum bag (Suter Kunststoffe AG, 170 °C maximum processing temperature) was fixed to the aluminum mold using a sealant tape (Diatex LSM6000). The vacuum was applied (using AEG AMEB 71 vacuum pump with a vacuum pressure around 92 kPa) to the mold and was checked for any potential vacuum leakage. Subsequently, the resin (a mixture of Hexion Epikote RIMR 135 resin and Epikure RIMH 137 curing agent with 100:30 parts by weight) was fed into the mold through an inlet gate and impregnated the fabric with a rectilinear flow front. Flow propagation was recorded using a Canon EOS 700D camera and the capacitance was recorded as detailed above. Once curing at room temperature was completed, the plates were post-cured at 80 °C for 15 hours prior to further testing as recommended by the manufacturer.

Thermal and mechanical characterization: Temperature dependency of resistance was characterized in a Heraeus 6200 model oven equipped with a Eurotherm 818 controller. Temperature was varied between 30 °C and 65 °C with 5 °C steps and the dwell time was set to 10 minutes. The temperature cycle was repeated five times. Mechanical characterization was performed using an Universal Testing Machine (UTM, Walter+Bai AG Series LFL-125kN) equipped with a 10 kN load cell, an oven to perform tests at elevated temperatures and tensile testing grips. An HBM LY11-6/350 type strain gage was bonded to each specimen to measure the longitudinal strain. In both types of characterization, resistances of the electrodes were recorded as detailed above and temperature was recorded using a Texas Instruments HDC 1080 sensor controlled via Tinkerforge Humidity Bricklet.

Nanocomposite extrusion: In total, 15g of each of three compositions are prepared: 6.25%, 7.5% and 8.25 wt% CNT. Runs 1, 7 and 13 are not used: they only serve to dilute previous runs to the target composition. Hypotheses for calculation of the weights to be blended are the following: (i) the CNT-PC masterbatch has 15wt% CNT; (ii) the PSU (resp. CNT-PC) density is 1.25 g/mL (resp. 1.2); (iii) thermal expansion of the polymers at 300 °C corresponds to a 10% gain in volume; (iv) 1.5 mL remains in the return channel after extruding 3 mL (total 4.5 mL).



5 x 3g of each: CNT 8.75, 7.5, 6.25 wt%

Figure 4.16 – CNT-PC and PSU/PEI weights for the different runs required to obtain 15 g of each CNT weight percentage: 6.25%, 7.5% and 8.25%.

Dry etching of insulating spacers onto a nanocomposite film: A 200 µm high-T_g nanocomposite film was prepared from extruded pellets by hot pressing at 250 °C between metal plates at high pressure (5kN) or drop-casted from a chloroform solution onto a Teflon plate. A 25 µm insulating film was then hot pressed onto the nanocomposite film. This two-film stack was laminated onto a silicon wafer using QuickStick Temporary Mounting Wax (see Figure 4.17). This glue provides good thermal conduction with the wafer, when cooled from the back side with liquid helium during dry etching. The nanocomposite film shouldn't be any thicker than 200-300 µm or else the thermal gradient across its thickness leads to warping and delamination from the wafer. 30 µm AZ© 40XT photoresist was then spin-coated at 1000 rpm onto the stack and exposed with a 375 nm laser in an MLA 150 maskless lithography tool at 650 mJ/m² without defocus. At the polymer film stack edge, a bead effect results in a much thicker photoresist thickness [215]: we avoided using any parts of the sample 2 mm from the edge for consistency. Development in AZ© 726 MIF was done for 4 mn, before a rinsing step in water. The wafer with the polymer stack was then loaded into an STS Multiplex ICP for 35 mn oxygen plasma dry etching at $\approx 1 \,\mu$ m/mn.



Figure 4.17 –200 μ m nanocomposite + 25 μ m insulating (PSU or PEI) film stack laminated onto a 10 cm wafer with Quicktick glue for photolithography processing.

Oxygen plasma etch selectivity: Etch rates of the photoresist and PEI were estimated by interferometry. A laser beam was reflected from the sample, interfering with itself. The number of intensity fringes per unit of time provides the etch rate. Because of reflection, each period corresponds to half a laser wavelength. In our case, we measured for PSU and AZ 40XT respectively: $0.9 \,\mu$ m/mn, and $1.3 \,\mu$ m/mn, i.e. an approximately 1:1.5 selectivity.

5. Semiconductor junctions in fibers

The previous chapters have focused on processes for the design and placement of semiconductor micro- and nanostructures in fibers, and strategies for contacting them electrically with an order of magnitude shorter electrode distance. For an even more efficient charge extraction, whether for higher sensitivity or for energy harvesting, we now face the challenge of obtaining a continuous semiconductor junction along the fiber. A manuscript is under preparation based on the presented results.

Motivation

A junction is an interface between two different types of semiconductor materials, where one side has an excess of valence electrons, the "n" side, and one has a lack of electrons, the "p" side. This electron imbalance may result from the diffusion of electron acceptor and donor impurities (p-n junction), or from putting into contact semiconductors with different band structures (heterojunction). At this junction forms a region depleted of charge carriers, where conduction can be manipulated based on the voltage applied on each side of the junction. This conduction dependence, or diode behaviour, is the foundation for logic gates upon which electronic circuits are based. The built-in voltage which arises from the diffusion of charge carriers for power generation (forward bias), or for higher sensitivity and faster photodetection (reverse bias) than a bulk photoconducting material.

Several applications warrant the integration of semiconductor junctions in fibers. The integration of electronic functionalities in optical fibers would enable a platform for the simultaneous guidance, generation, modulation and detection of light[216]. When used as a photodiode for energy conversion, junctions in fiber would also permit self-powering at the microscale[217]. In a coaxial configuration, they can absorb light from all directions, as opposed to conventional planar structures[218]. Finally, drawing of multimaterial fibers could provide a means to the cost-efficient high throughput production of flexible photodiodes beyond wafer dimensions[141], [142].

Limitations to a planar geometry

Multiple methods have been reported for the fabrication of coaxial junctions in fibers, such as successive chemical vapour depositions (CVD)[66], [217], epitaxial growth[219], high-pressure chemical vapour deposition in microstructured optical fibers[216], [220] or successive dip-coating of the layers of organic solar cells on a metal wire[221]. However, none provide as few processing steps as the thermal drawing of the entire photodiode structure from preform to fiber. Although the span of literature about organic solar cell fibers is vast, organic semiconductors have so far not been drawn into multimaterial fibers. Research in multimaterial thermal drawing has focused exclusively on inorganic semiconductors. Several instances of doping silicon in silica preforms for thermal drawing have been reported[55], [222], [223], but none were planar, coaxial or continuous p-n junctions along the fiber length. This is due to Si being drawn in a molten state, contained in its silica cladding: if both n and p doped layers were in contact, they would intermix and the microstructures required for efficient photodiodes wouldn't be preserved. An alternative strategy is to synthesise one of the materials involved in a heterojunction during drawing. This concept was first reported by Orf et al.[141] in a thermoplastic cladding, by synthesizing ZnSe (otherwise not drawable in a thermoplastic cladding) at the interface between a viscous chalcogenide (Se₉₇S₃) and a low melting

temperature metal allow (Sn₈₅Zn₁₅). After crystalizing the drawn amorphous chalcogenide by postdrawing annealing, a heterojunction was hypothesized and characterized [142]. The corresponding band structure is shown in Figure 5.1a. No photovoltaic efficiency, nor photoresponse bandwidth were calculated. Note that drawing diffusion/synthesis[224], [225] was also reported recently in high temperature drawing. This strategy is a promising way to obtain a drawable heterojunction without intermixing of the two semiconducting materials.

However, two challenges need to be overcome to obtain performant photodiodes for light detection and harvesting. First, drawing heterojunction synthesis was not applied to a planar or annular geometry in fibers, as the low viscosity of the molten metal alloy precludes good geometry conservation, as opposed to glassy materials. This issue was encountered when drawing a fiber with a Se core between SnZn electrodes, shown in Figure 5.1b: intermixing results in poor control of the Se layer thickness, which may end up being too large for good performance and miniaturisation (high series resistance, bulk dark current and slow response time due to grain boundaries), or too low and result in short circuits. Secondly, a planar geometry requires light to be shun normally to the junction, as opposed to side illumination in ref [141]. This implies the development of a drawable transparent electrode with suitable rheology, absent from the literature, but proposed in Chapter 4 with thin CNT nanocomposites. We assume this building block can be added to the final heterojunction fiber architecture and focus for the rest of this work on the first issue, Zn being liquid during drawing. Solving it is required for ZnSe synthesis with controlled geometries.



Figure 5.1 – ZnSe/Se heterojunction. a) $Se_{97}S_3/ZnSe$ band structure, adapted from [142] b) A Se core is drawn in between SnZn electrodes, liquid during the draw.

ZnSe synthesis

We start by studying ZnSe synthesis. To this effect, a 50 nm-Zn layer was sputtered onto a 10 μ m Se layer on a glass slide and annealed at 230 °C (PSU drawing temperature) for different times corresponding to lower (25mns) and upper (70 mns) estimations of the dwell time in the drawing oven. X-ray diffraction (XRD) was performed on the different samples which showed the appearance of the ZnSe peak (111) and the decay of the pure Zn peaks (002) and (101) (reacted with Se to form ZnSe).





ZnSe formation was also attempted directly during thermal drawing, from a PSU preform made of Se powder and a SnZn metal ribbon. Although both liquids do not retain well their original shapes (Figure 5.3a), a chemical reaction takes place at their interface, where Zn migrates and reacts with Se (ZnSe). A fiber cross-section was cut by microtomy and TEM EDX was performed at the interface between SnZn and Se (Figure 5.3b). A line scan of atomic fractions across the interface is plotted on Figure 5.3c. It is surprising to see that no Zn is present in the Sn phase for at least 400 nm, as if it had all migrated to the interface for synthesis, consistent with the conclusions in ref [141].



Figure 5.3 – Characterisation of the SnZn/Se interface. a) Micrograph of a cross-section (microtomy) of a PSU fiber where b) a TEM EDX line scan is performed at the interface between ZnSn and Se. c) The atomic fractions of Zn, Se and Sn across the line scan are plotted, showing diffusion of Zn to the interface in equal proportion with Se, indicating ZnSe formation.

TEM Selected Area Electron Diffraction (SAED) at this very interface also demonstrates the formation of crystals of different lattice parameters. Four diffraction patterns were recorded with the aperture positioned respectively:

- Entirely in the SnZn region
- Partially in the SnZn region and partially at the interface
- Partially at the interface and in the Se region
- Entirely in the Se region

Those four positions and the corresponding diffraction patterns are shown in this order in Figure 5.4. This demonstrated that by sweeping across the interface through four different positions, we move from a Sn monocrystal (single spots) to the polycrystalline ZnSe (several spots arranged on smaller rings) to amorphous Se (smooth continuous rings).





Figure 5.4 – TEM SAED. From left to right: Sn single crystal, Sn single crystal with ZnSe polycrystalline rings, ZnSe polycrystalline rings with amorphous Se rings, amorphous Se rings.

Further SEM EDX analysis in Figure 5.5 showed that Zn aggregates instead of being dispered throughout the SnZn phase, which may make it difficult to have uniform ZnSe formation over a large heterojunction interface.



Figure 5.5 - SEM EDX line scan is performed at the interface between ZnSn and Se, showing Zn distribution (in cps) away from the interface (colours not consistent with previous figure).

Alloying with Sn

Although TEM SAED and EDX rather indicate alloying of Se with Zn, as Sn was also present in the previous geometry, we now investigate the alloying dynamics of Se with Sn, in the absence of Zn. It is both relevant to know which of Sn or Zn reacts preferentially with Se, but SnSe itself could be an interesting material to obtain at low drawing temperatures for its record thermoelectric properties [39]. Se crystalline NWs were grown chemically from a deposited seed layer (200 nm thick), following a recipe described elsewhere[18], onto which a 100 nm-thick Sn layer was deposited (Figure 5.6a). The sample was then heated for up to 10 hours at 200 °C and the resulting NWs (Figure 5.6b) were characterized using various methods. It is noteworthy that such NWs can also be grown in fibers[18].

Raman spectroscopy was first employed to identify a phase shift at 185 cm⁻¹ pertaining to the Sn-Se sample which is not visible on Se-NWs alone. Taub et al. have investigated the temperature-dependence of the Raman modes shifts of layered SnSe₂ nanosheets[226]. By using the equation and the parameters they provide and setting the temperature at 293 K, one finds a value of 185 cm⁻¹, which corresponds to what was measured here, plotted in Figure 5.6c.

High-Resolution TEM imaging (HRTEM) and selective area electron diffraction (SAED) were performed on a single SnSe nanowire, as shown respectively in Figure 5.6d and e, which showed polycrystallinity after the heat treatment, with the three first circles (a, b and c) at an approximative radius of respectively 1.6 nm⁻¹, 3.29 nm⁻¹ and 5.01 nm⁻¹. These radii correspond in the real space at interplanar distances of, respectively, 0.625 nm, 0.303 nm and 0.199 nm. Similar interplanar distances have been found in TEM analysis of SnSe₂ nanoplates where the interplanar distance of 0.61 nm has been identified for the (001) crystal plane in the hexagonal phase of SnSe₂[227]. The distances of 0.29 nm and 0.19 nm have been also identified for respectively the crystal planes (110) and (100) of the same phase. The interplanar distance of 0.29 nm has also been reported in HRTEM analysis of nanowire of trigonal selenium, where this distance has been assigned to the (001) and (100) planes of t-Se [228]. These two distances do not appear on the SAED pattern. This leads to the conclusion that the 0.29 nm distance found belongs indeed to SnSe₂ and no pure Se phase remains in the nanowire after 10 hours of annealing.

XRD analysis also showed the presence of SnSe₂, which can be seen on Figure 5.6f by the peaks appearing at around 12° and 32°[229]. It appears that there is no pure Se phase remaining in the sample after 10 hours annealing at 200 °C. Se has therefore either fully reacted with Sn or evaporated. However, it was not the case after only 5 hours annealing where Se peaks were still visible around 24° and 29°. This is an encouraging result, as it means alloying of Se with Sn appears to be slower than with Zn, and could be neglected during ZnSe synthesis from the reaction of SnZn with Se.



Figure 5.6 – SnSe synthesis characterization. SEM images of the sample for both a) before annealing and b) after annealing. Before annealing, Sn can be seen on the single crystal NW. After annealing, the wires do not appear to have two phases anymore. Sn may have reacted fully with Se. c) Raman spectroscopy on Se NWs grown from a 200 nm-thick deposition with 100 nm Sn deposited on top, before and after 10 h annealing at 200°C. d) High-resolution TEM image of a single nanowire. e) SAED pattern of the same single NW. Radii of the rings: (a) 1.6 nm⁻¹, (b) 3.29 nm⁻¹, (c) 5.1 nm⁻¹. f) X-Ray diffraction analysis of the same sample. SEM data: Tapajyoti Das Gupta. TEM and XRD data: Inès Richard.

Zn-wire feeding

For unambiguous ZnSe synthesis, we would however rather insert Zn only into the fiber. Two issues need to be overcome: (i) Zn's melting temperature $T_{m,Zn}$ = 420 °C would require drawing in a silica cladding. At such temperatures, polymer nanocomposite electrodes would degrade. No glassy conductor has been reported in silicon fibers to this date; (ii) if drawn in a liquid state, Zn's viscosity would be too low to prevent capillary break-up.

For good structure control during fiber drawing, we rather intend to feed a solid Zn wire into the polymer preform as it is drawn, compatible with the integration of Se-based chalcogenide semiconductors and nanocomposite (transparent) electrodes. A schematic explaining this configuration is shown in Figure 5.7a. The preform should be hollow for the wire to be inserted. As the preform is scaled down, the cladding comes in contact with the Zn wire, pulling it down as its core electrode, termed "co-feeding". In this configuration, a glass chalcogenide such as Se can flow against or around (if the viscosity is much lower) the Zn wire and fill the gap between Zn and the nanocomposite counter electrode. ZnSe is expected to form at the interface by thermally induced diffusion during or after drawing to achieve the desired heterojunction and photodiode architecture (Figure 5.7b). This structure was successfully achieved (Figure 5.7c), despite poor control of the distance between Zn and the counter electrode (here CB-PC, with a SnZn bus bar), leading to many fiber sections having short circuits.

Insulating spacer

An improved design was prepared with an additional insulating layer (the same polymer as the cladding) allowing for the Zn wire to come in direct contact with the nanocomposite side without short circuits. Similarly to Chapter 2, openings are cut out by milling from this layer through which Se can come in contact with Zn. Grooves could also potentially be obtained by laser ablation or dry etching to decrease each groove dimensions by one or two orders of magnitude. Figure 5.7d shows a top view of a preform with a spacer with milled openings as the Zn wire in inserted into it. At the cost of losing active area, this design permits control over the distance between Zn and the counter electrode, to achieve thicknesses down to a few microns. Figure 5.7e shows a cross section of part of the structure in fiber after drawing. Figure 5.7f is a zoom in on the insulating layer between two grooves. Note the white polymer dust in the grooves is an artifact from polishing the fiber cross section for the micrographs.



Figure 5.7 - Zn wire feeding and preform/fiber architectures. a) Schematic showing thermal drawing in the neck-down region. b) Cross-section schematic of the intended fiber with a zoom-in on the region where the expected ZnSe layer should be synthesized. c) Cross-section optical micrograph of the drawn fiber, showing a 100 μ m separation between the Zn wire and a CB-PC electrode. d) Preform for an improved design allowing to reduce the gap between electrodes using an insulating spacer. e) Cross section micrograph of the grooves milled through the insulating spacer after drawing. f) Close up micrograph of a spacer. The insulating layer can be seen at the top. The rest is CB-PC.

Next, we observed that the viscosity of the structure in contact with the Zn wire was too low. This was due to both the PSU cladding and the CB-PC counter electrode being drawn at too high temperatures, but as explained in Chapter 4, to avoid Se crystallization, it had to be drawn above its melting temperature $T_{m,Se}$ = 221°C. Figure 5.8a shows flattening of the part of the spacer/counter

electrode structure which came in contact with the Zn wire. We therefore sought to replace the PSU $(T_{g,PSU} = 190^{\circ}\text{C})$ cladding by PEI $(T_{g,PEI} = 215-220^{\circ}\text{C})$, and with the development of a PEI-based polymer nanocomposite in Chapter 4, we could replace CB-PC $(T_{g,PC} = 145^{\circ}\text{C})$ with our CNT-PEI. For simplicity, only one groove was milled in the new design. To avoid reflow during the consolidation of the preform, we opted for the multi-material consolidation described in Chapter 1, with a CB-PC intermediate layer. The improved architecture is presented in Figure 5.8b, and demonstrated for low T_g materials (PSU/CB-PC) in Figure 5.8c and high T_g materials (PEI/CNT-PEI) in Figure 5.8d, with better geometry retention. Note that for a higher control over the busbars, SnZn (liquid during the draw; poor geometry control as seen in Figure 5.8a) was replaced by a 125 µm Cu-coated stainless-steel wire, also co-fed during the draw.



Figure 5.8 – Zn wire feeding architecture for a contacted heterojunction. a) First design where flattening of the milled insulating spacer grooves is flattened by contact with the Zn wire. b) New design for improved positioning of the Zn wire against the Se channel. c) This architecture was achieved in a PSU cladding fiber, but with some strain resulting from the Zn wire fit. d) High degree of control of the geometry achieved in a PEI fiber.

These architectures were first drawn in the absence of Se for simplicity. Next, for precise positioning of Se in the spacer groove, a rectangular Se bar was fabricated by a first thermal drawing for it to be inserted in the groove between the Zn wire and the counter electrode (Figure 5.9a). Its height was chosen to be 50% more than the groove depth to ensure an oversupply of Se despite reflow, leakage and evaporation. However, two issues with consolidation occur, hampering reproducibility: (i) despite the lower temperature required by the CB-PC multimaterial consolidation, as $T_{g,Se} = 40^{\circ}$ C is very low, Se starts to reflow (Figure 5.9b), which might result in partial filling of its channel; (ii) As the preform is heated in the drawing furnace and CB-PC softens, thermal gradient-induced warpage may

lead to delamination, as visible on Figure 5.9c. These issues should be resolved by a diffusive solvent-assisted consolidation.



Figure 5.9 – Preform assembly. a) A 300 x 600 μ m rectangular Se bar is obtained via a first thermal drawing. The inset shows its cross section (micrograph) before being placed in a 400 x 400 μ m groove milled through the insulating spacer. b) after a multi-material consolidation, the preform is forced open to verify Se's presence and shape. Reflow into a droplet is seen, although most of the Se stayed in the milled channel. c) At the beginning of the draw, the two plates which make up the preform cladding delaminate with CB-PC softening and thermally induced internal stress.

Electrical characterisation



Figure 5.10 – Electrical characterization. a) The measured resistance decreases in time with crystallization upon annealing at 80°C. b) A rectifying behaviour is formed before 5h annealing at 150C, likely at the ZnSe/Se heterojunction. The inset shows a photodetecting effect: the resistance decreases upon illumination (in yellow).

An indirect way to show formation of a Se/ZnSe heterojunction is to measure a characteristic I-V curve. When the fiber busbars are connected to external wires with silver paint, no measurable current flows yet. However, upon annealing, Se crystallizes and its resistivity decreases by orders of magnitude (Figure 5.10a). After crystallization, Figure 5.10b shows the I-V characteristic of the fiber under illumination. The rectifying behaviour increases drastically upon heating for a few hours, hinting at the necessity of a post-drawing thermal treatment for further Zn diffusion and ZnSe formation. However, after 5 h heating, the rectifying behaviour starts to deteriorate, likely due to Se evaporation or reflow. The inset of the same figure shows a photodetecting effect: when the light is turned on (in yellow), the resistance decreases. However, experiments conducted so far were not successful in measuring an open-circuit voltage V_{OC} or a short-circuit current I_{SC} upon illumination, which could have led to calculating a photovoltaic efficiency. In the architecture obtained here, a transparent electrode was not yet integrated, so the light reaching the junction is likely very small; the dark current noise is much higher than the photogenerated current and V_{OC} cannot be resolved. Further work is needed for optoelectrical characterization in the full geometry (see below) to characterize responsivity, bandwidth, photovoltaic efficiency etc....

Future work

Full geometry

Ultimately, the high T_g electrode would have to be made thin enough for transparency, several smaller Se channels (through the insulating spacer) could come in contact with the Zn wire, and their total surface enlarged. This could be achieved either in a planar geometry against a flat Zn wire, or in a cylindrical geometry for omnidirectional light detection/harvesting. We couldn't find such an off-the-shelf rectangular Zn wire, but Zn electroplating of any conducting rectangular wire can be done easily. Indeed, Zinc and its alloys have been employed for decades as protective and aesthetic layers over numerous metals such as steel.



Figure 5.11 – Envisioned final geometry as an assembly of all elements developed within this thesis: Se wires, ZnSe/Se junction, wire feeding and a high T_g transparent nanocomposite electrode. a) planar geometry b) cylindrical geometry for omnidirectional light detection or energy harvesting

Schottky junction

Historically, the Schottky junction was the first semiconductor diode ever discovered, when in 1874 Karl Braun reported on electrical measurements across a metal-semiconductor contact. It is noteworthy that the semiconductor crystal was Galena, or PbS ore, a chalcogenide. When a metal and a semiconductor are put in contact, a potential energy barrier is formed, predicted in first approximation by the Schottky–Mott rule as proportional to the difference of the semiconductorelectron affinity and the metal work function. As the energy bands align, a built-in electric field is formed within the depletion area (Figure 5.12a). This enhances photogenerated charge carrier extraction and detection. An advantage of Schottky junctions with respect to regular p-n junctions is that semiconductors of various band gaps can be used, as long as their Fermi level is adequate, which can be tuned by doping. Many useful Schottky junctions can be formed without any doping at all, making these devices inexpensive to manufacture. One of the main applications is found in "solar blind" photodetectors, where photoexcitation of charges within wide band gap semiconductors is only possible at short wavelength, such as in the blue or UV range. In a p-n junction, as the penetration depth becomes lower, charges are generated in the p-type layer, where diffusion of charges is longer. In a Schottky junction, since there is only one semiconductor region against the metal, this issue is absent and charge extraction is faster, finding applications in high-speed applications (25-60 Ghz). Similarly, a Schottky junction could form in-fiber between a chalcogenide glass and a suitable drawable/feedable metal or metallic glass. A preliminary experiment showed indeed the formation of a rectifying junction between Se₈₀Te₂₀ and Cr/Au (or ITO) without any doping or heterostructure. The corresponding I-V characteristic is showed in Figure 5.12b. The literature confirms that Schottky barriers can be readily formed between Se and metals [230].



Figure 5.12 – Schottky junctions. a) schematic of a typical Schottky junction, adapted from ref [231]. b) I-V characteristic of $Se_{80}Te_{20}$ glass deposited on ITO, with a deposited Cr/Au top contact.

Conclusion

Semiconductor junctions are the basis for electronics and efficiency light-to-electricity conversion, whether for photodetection of photovoltaics. The challenges associated to a continuous in-fiber junction were discussed, namely interelectrode distance and planar illumination, which we solve with an architecture based on Zn wire co-feeding, electrode spacing and semi-transparent nanocomposites. A rectifying junction is demonstrated, although further work is needed for proper optoelectrical characterization of a final geometry.

Experimental section

The deposition of the Selenium was done in a *Univex 250* thermal evaporator at constant rate 0.1 Å/s under vacuum at 1.5 x 10^{-5} mbar. The deposition of Sn was done in an Alcatel EVA600 thermal evaporator at constant rate of 1 Å/s and under vacuum around 1.0 x 10^{-6} mbar. The photo-current measurements were performed by first creating a gold interdigitated electrode, sputtering 50 nm Au directly on the NWs. The SEM and HRTEM imaging were performed on respectively a *Zeiss Merlin* SEM column and on a *Tecnai Osiris* TEM. The size distribution of the nanowires' radii was performed with the software *ImageJ* and its plugin *DiameterJ*. The XRD measurements were performed using an *XRD Empyrean diffractometer*. The 380 µm-diameter Zn wire was purchased from Advent Research Materials Ltd.

Concluding remarks

Summary

First, processing challenges were addressed. Miniaturization of geometries and the benefit of scaling down semiconductor architectures were discussed, namely for higher photodetection sensitivity. Materials properties and their interplay with processing was addressed. The case of consolidation and thermal drawing was analysed. Semiconductor NW stability in thermal drawing with respect to thin films was explained as a motivation for designing compatible optoelectronic architectures. Next, scalable and cost-efficient manufacturing of high aspect ratio encapsulated flexible nanowire arrays with controlled size and periodicity was demonstrated and modelled, enabling nanophotonics applications requiring long-range order over several meters. This work was then expanded with a novel fabrication approach combing lithographic lift-off and thermal drawing. Fabrication constraints were modelled, and the process was demonstrated for optical applications in one-dimensional metasurface fabrication. Moving to in-fiber electrodes for these semiconductor structures, drawable conducting nanocomposites were optimized for high shape retention through drawing. A preform spacing geometry to avoid short-circuits was demonstrated. In addition, an application was shown for fiber nanocomposite electrodes for resin composite manufacture and functionalization. Finally, a geometry allowing short interelectrode distance and the chemical formation of a Se/ZnSe planar heterojunction in fiber was obtained.

General Conclusion

In this thesis, we addressed the processing challenges which hinder achieving fully drawable semiconductor architectures in multimaterial fibers. The fundamental limitations to the scaling down of optoelectronic structures from preform to fiber were addressed: in the viscous state, shape retention is an interplay between viscosity and interfacial tension. Disks – or wires in 3D – emerge as a stable shape during thermal drawing for semiconductor nanostructures (minimizing interfacial energy) with optical applications. They are compatible with (high viscosity) nanocomposite transparent electrical connections in structures microfabricated at the preform level. As the range of materials accessible by thermal drawing is ever expanding, adequate selection and combination of liquid-viscous-solid structures allows for the design of full photodiodes. In a nutshell, for the thermal drawing process, we discussed chalcogenide glass film stability, semiconductor NW architectures and their optical applications, nanocomposite electrodes and their electrical applications and full photodiode architectures. We sincerely hope this work brings the multimaterial fiber community one step closer to the scalable production of in-fiber photonic devices and elongated photodiodes.

Future directions

We envision many further developments for this thesis work. The following part is a summary of future directions suggested throughout the manuscript and an extension based on our latest findings. May this part provide the reader with ideas and leads for future research.

The semiconductor glass composition is often discussed in groups working on bulk chalcogenide thermal drawing for optical fibers in the infrared or on blends grown by epitaxy for phase-change memories and solar cells. However, we identified a knowledge gap in the understanding and predicting of the optimum between chalcogenide glass processability for thermal drawing and electronic performance. Previous literature has either focused on glass stability to avoid crystallization for maximal optical waveguiding transmission or on conductivity for bulk chalcogenide monocrystals. We believe the specific interplay between processing constraints and optoelectronic performance in the case of thermal drawing would deserve a systematic treatment.

In the case of 1D nanowire array metasurfaces, further calibration of the period and diameters obtained should allow the realization of a 1D metalens with a focusing efficiency of up to 29% according to our FDTD simulations (17% for the TM polarization and 41% for TE), despite accounting for period and diameter distributions (randomization based on measured standard deviations). To achieve this, a precise measurement of the lithographic fabrication bias could be accounted for, as discussed previously in Chapter 3. Direct laser machining of chalcogenide films was also demonstrated recently as a strategy to obtain bars with high aspect ratios (deep trenches), lifting some of the fabrication constrains. However, given the laser excimer resolution (~ 5 μ m), this would require using thick films in the preform and a high DR, with long machining times.

Post-drawing annealing schemes have been demonstrated by other groups for longitudinal nanowire dewetting. To move from 1D arrays to 2D metasurfaces, our continuous templated dewetting process could be combined with such treatments, if the nanosphere size distribution due to longitudinal non-templated dewetting was not detrimental to optical performance.

By combining microfluidic sampling and index sensing, thermal drawing emerges as a highthroughput and cost-effective production strategy for substrates which could be employed in pointof-care testing or disposable chemical test kits. The sensitivity of such devices depends on two factors. First and foremost, the geometry of the NW array dictates the wavelengths used for measuring a peak shift and its sensitivity to a refractive index change. Second, the wires would need to be somewhat exposed to the fluid sampled, as the field is locally enhanced around the NWs. If a cladding is absolutely necessary for the reproducible drawing of the NW array, it should be made as thin as possible. Our simulations with the geometries obtained in Chapter 2 show that good sensitivity (e.g. > 100 nm/RIU) requires a very thin cladding (e.g. sub-200 nm).

The performance of an optoelectronic structure hinges on the ability to draw a transparent electrode. Recent research has demonstrated the potential for CNT composites in PC and HDPE. The same strategy can be applied to polymers compatible (i.e. with high viscosity for shape retention) with chalcogenide thermal drawing. The preliminary tests presented in this work are encouraging but the dispersion of CNT should be further improved (breaking up CNT aggregates with sufficient metastability) to obtain higher conductivity. Extrusion seems to provide enough shear for CNT dispersion, but no CNT-PSU or CNT-PEI masterbatches could be found. It then requires hot pressing and the films obtained are not always thin enough or even. This additional thermal treatment further affects CNT dispersion. The solution route should also be considered, but the process flow for CNT dispersion should be developed. High sonication powers (such as using a sonication horn with cooling) in polar aprotic solvents (e.g. DMSO) or functionalizing CNTs for chemical dispersion hold great promise. The nanocomposite solution could then be dip or spin-coated to obtain even thin films.

Additionally, from an engineering point of view, this field would greatly benefit from a robust, systematic and convenient connectorization scheme (connection from the fiber electrodes to an external data acquisition circuit), such as using a customized clamping connector.

If we turn to applications for the nanocomposites themselves as resistive sensors, the decoupling of strain and temperature sensing could be optimized by selecting resistive materials with orthogonal dependencies in the $\left(\frac{\partial R}{\partial T}, \frac{\partial R}{\partial \varepsilon}\right)$ space (e.g. one material dependant to strain only, the other to

temperature only). The proof-of-concept described above was patented and deserves to make its way into the industry as an embedded sensor for composite parts.

Finally, the reaction kinetics of Se with pure Zn deserve to be further understood. By finding ideal annealing and crystallization schemes (varying time, temperature, localized, etc.), the junction could be optimized for optoelectronic performance. Using a transparent top electrode, an open-circuit voltage should be measured. This might require reducing the number of defects due to dust, Zn wire surface roughness, Se polycrystallinity and drawing in an inert atmosphere. All previous building blocks (semiconductor nanostructure, electrodes, insulating spacers) could then be assembled into a full photodiode fiber.

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EDUCATION

EPFL

Lausanne, CH / 2018 - 2023

PhD in materials science

- Polymer nanocomposites
- Semiconducting glasses
- Cleanroom microfabrication
- Nanoscale characterization

PSL UNIVERSITY

Paris, France / 2015 - 2016

Pre-doctoral higher diploma for

research and innovation

- Quantum Engineering
- HealthTech
- Innovative materials

MINES PARISTECH

Paris, France / 2011 - 2014

Master of science and executive engineering

- Applied mathematics
- Solid-state physics
- Energy production and efficiency

SKILLS

- Public speaking (Toastmaster)
- EPFL PhD representative at doctoral school committees
- Innosuisse Start-up Training: "Business Concept"
- French and English: native German and Spanish: B2

HOBBIES

- Effective Altruism Geneva board member
- Real estate professional & stock market investor

WILLIAM ESPOSITO

PROFILE

I am an enthusiastic, self-motivated and hard-working individual, passionate about energy transition and fundamental science. From microfabrication to advanced characterization, I design, manufacture and optimize multimaterial soft optoelectronic devices. I am always reflecting on how science can translate to impactful innovation, leveraged by highly committed and collaborative teams.

EXPERIENCE

EPFL SPIN-OFF FOUNDER

Corto Bioelectronics / Geneva, Switzerland / 2023

Early-stage venture developing tomorrow's brain-computer interfaces and cardiovascular devices for interventional cardiology. We leverage our microfabrication expertise for the scalable production of implants.

EPFL RESEARCH ASSISTANT

FIMAP lab, School of Engineering / Lausanne, Switzerland / 2018 - 2023

Doctoral programme in materials science and engineering

Thesis: "Semiconducting multimaterial fiber architectures" Interdisciplinary design, fabrication and characterization of elongated sensors and devices by thermal drawing, a high throughput microfluidic novel process

- Cleanroom microfabrication: photolithography, thin film deposition, SEM
- Applications in nanotechnology, functional composites and light sensing
- 3 publications (nature.com/articles/s41467-022-33853-1) and a patent

EPFL SPIN-OFF CO-FOUNDER

FiberLab / Lausanne, Switzerland / 2021 - 2022

FiberLab is an EPFL healthTech early-stage spin-off producing the first generation of lab-in-fiber devices, a miniaturized, cost-effective and versatile microfluidic platform for multianalyte point-of-care testing. This novel sampling device holds the promise to revolutionize rapid fluid testing for SMEs and professionals in the field.

- R&D to bring the science to market
- Product/market fit
- Fundraising and marketing strategy

CERN PROJECT ENGINEER

CMS experiment, LHC / Geneva, Switzerland / 2016 - 2018

Technical developments for the CMS experiment, delivering upgrades for safety systems and project management tools

- Design and implementation of an asset management strategy
- Enhancement of emergency preparedness using data visualization
- Support to technical coordination for underground experiment access

UNIVERSITY OF GENEVA RESEARCH INTERN

Applied Physics Group, Quantum technologies / Geneva, Switzerland / 2016

Quantum optics and entanglement: set up and implemented a Quantum Random Number Generator

TOOLS AND SOFTWARE

- Electron microscopy, ultramicrotomy, photolithography, dry & wet etching, PVD
- Matlab, COMSOL, Python, Catia, Adobe Suite, Advanced Excel