INSTITUTE OF PHYSICS PUBLISHING MEASUREMENT SCIENCE AND TECHNOLOGY

Meas. Sci. Technol. **16** (2005) 111–118 doi:10.1088/0957-0233/16/1/015

MEMS tools for combinatorial materials processing and high-throughput characterization

A Ludwig[1,2], J Cao[1], J Brugger[3] and I Takeuchi[4]

[1] Combinatorial Materials Science Group, Center of Advanced European Studies and Research (CAESAR), Ludwig-Erhard-Allee 2, 53175 Bonn, Germany

[2] Faculty of Mechanical Engineering, Institute of Materials, Ruhr-Universität, 44780 Bochum, Germany

[3] Microsystems Laboratory, Institute of Microelectronics and Microsystems, Ecole Polytechnique Fédérale de Lausanne (EPFL), 1015 Lausanne, Switzerland

[4] Department of Materials Science and Engineering and Center for Superconductivity Research, University of Maryland, College Park, MD 20742, USA

E-mail: ludwig@caesar.de

Received 17 May 2004
Published 16 December 2004
Online at stacks.iop.org/MST/16/111

Abstract

Using the combinatorial material synthesis approach, materials libraries can be produced in one experiment that contain up to several thousand samples on a single substrate. In order to identify optimized materials in an efficient way using screening methods, adequate automated material characterization tools have to be designed and applied. Microsystems (micro-electro-mechanical systems: MEMS) offer powerful tools for the fabrication and processing of materials libraries as well as for accelerated material characterization on planar substrates such as Si wafers. MEMS can be used for parallel materials processing, either as passive devices such as shadow mask structures, or as active devices such as micro-hotplates. Microstructured wafers, which incorporate sensor or actuator structures such as electrode or cantilever arrays, can be used to identify materials properties in an efficient way.

Keywords: combinatorial materials science, MEMS, shadow masks, nanostencil, micro-hotplates, electrode arrays, cantilever arrays

(Some figures in this article are in colour only in the electronic version)

Introduction

The aim of this paper is to present the concept of using MEMS tools for combinatorial materials science, and to review work related to this idea. Combinatorial synthesis of materials libraries, combined with high-throughput measurement techniques, are technologies which enable the efficient investigation and production of new functional devices based on micro- or nanostructured thin films [1]. The aim of this methodology is to accelerate discovery and optimization of advanced materials. Micro-fabrication is a mature technology for producing micron-sized structures and microsystems (e.g., sensor and actuator arrays with integrated electronics) which have characteristic dimensions in the micrometre scale and have unique properties resulting from their small dimensions (e.g. surface/volume ratio) [2]. Combinatorial techniques and MEMS technologies share the concept of producing well-controlled materials and devices in the form of arrays. In the field of MEMS, fabrication of sensor/actuator arrays gives rise to improved functionality (e.g. selectivity) [3] and redundancy, and it facilitates error checking by reference measurements within the array. In combinatorial materials science, the arrays are called ‘materials libraries’ [4]. Advantages of materials libraries, compared to conventional preparation of samples, are that a broad range of different or continuously graded materials can be deposited in one experiment, and coverage of

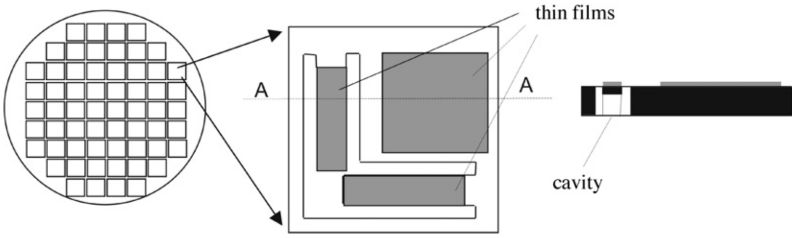


Figure 1. Schematic illustration of a micro-fabricated Si substrate on which a thin film material library is deposited. The substrate incorporates cantilevers and electrodes (not shown) used for the screening of a library. For the fabrication of such substrate/materials libraries with micro-sized features the use of micro-shadow masks is proposed (see section 1.1).

a large parameter space becomes possible. This facilitates rapid exploration of materials with enhanced properties. Occurrence of measurement errors due to limited sampling can be reduced.

Another important aspect is that the materials and device applications in MEMS and thin film combinatorial materials science are of the same length scale. Advanced MEMS technology increasingly requires new tailor-made materials: tailored with respect to composition, nanostructure, stress state, etc. In fact, with increased complexity of microsystems, mixed-material systems are being developed that include silicon, metals, polymers and other organic substances. As technologies in these fields advance, materials and structures will be more and more integrated: this will make the differentiation between material and structure obsolete as a final consequence. A development goal of materials science will therefore be the integration of multiple functionalities into the used material itself in order to achieve a high density of functions on the smallest scale. Such new, multi-functional materials and material combinations at the micron scale can be efficiently developed and optimized by the combinatorial materials science methodologies.

There are also other common features in MEMS and combinatorial technologies which will not be discussed in this paper. Generally, MEMS enable new actuation and sensing technologies which can be used for materials fabrication and characterization. The very broad field of scanning probe microscopy relies on microfabricated structures and systems [5]. At the interface between organic and inorganic materials, direct-write methods based on the atomic force microscope (AFM) cantilever principle are emerging: e.g. dip-pen lithography [6] uses a special ‘ink’ on the tip of an AFM cantilever to deposit nanostructured arrays [7]. Nanoscale dispensing (NADIS, [8]) uses micrometre sized fluidic reservoirs near AFM tips to deliver molecules onto surfaces locally. Such technologies enable combinatorial surface chemistry at micron and nanometre scales. The idea of using parallel cantilevers for high-throughput micro/nanodot fabrication is becoming feasible with growing possibilities in MEMS. The concept of miniaturization helps to perform efficient research using only very small quantities of materials. High-throughput experimentation in bio-chemistry takes advantage of microsystems such as lab-on-chip [9]. Furthermore, there are microsystems such as micro-reactors which can be used for combinatorial chemistry [10], or micro-actuators needed for combinatorial ink-jet printing [11].

The use of MEMS tools for combinatorial materials investigation is proposed in order to improve both quality and quantity, in terms of resolution and throughput, for the synthesis and analysis of new materials and new material combinations at micron and sub-micron scales. Therefore, this paper illustrates the utility of MEMS tools for combinatorial materials research and highlights some recent results in these areas. First, MEMS tools are discussed, which enable improved fabrication processes for discrete materials libraries in terms of material properties, quality, throughput and fabrication cost. It is important to mention that the obtainable accuracy of the synthesis of materials libraries determines the quality and feasibility of the high-throughput measurements. Examples for such MEMS tools are micro-machined shadow masks. In particular, fabrication of materials libraries directly on micro-machined sensor/actuator arrays without the use of photolithography is very promising. This is illustrated in figures 1 and 2. Other examples are active microsystems such as micro-hotplates for (post-)processing of materials. Second, the use of MEMS in high-throughput materials characterization in such cases as electrode and cantilever arrays is discussed.

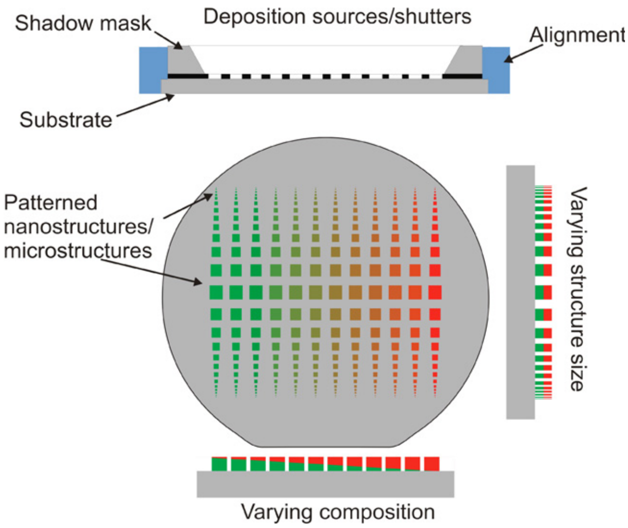


Figure 2. Schematic illustration of a shadow masking process for fabrication of thin film materials libraries. Materials are deposited through micro- or nano-sized apertures. The shadow masks can be designed in a way to allow varying lateral structure size over the substrate. By combinatorial deposition methods (e.g. opposed wedge type films [14]) a varying composition can be achieved in a direction orthogonal to the size variation.

1. Micro-machined structures and microsystems for the fabrication and processing of materials libraries

The way materials libraries are fabricated determines to a large extent how effectively high-throughput measurements can be performed. Materials libraries can be deposited as continuous composition spreads or as discrete arrays [1]. Using micro- or nanostructuring technologies, discrete materials libraries can be fabricated which consist of hundreds to thousands (in the case of nanoscale spots even millions) of different materials on a single substrate. However, the density and size of the addressable spots on a materials library have to be compatible with those of the applied screening method, which determines the resolution of the analysis. As measurement technologies advance by miniaturization, and sensor dimensions reach the micron scale, similarly-sized dimensions of materials spots on high-density materials libraries can be realized.

Requirements for the fabrication of materials libraries include accuracy of the desired chemical compositions and correctness of the lateral dimensions in the case of discrete materials libraries. These aspects are interlinked when one is performing multiple depositions through masks which have to be aligned with respect to each other. It is expected that the most reliable results can be obtained when fabricating and processing as much as possible *in situ* during one experiment in order to avoid contamination which inevitably occurs when breaking vacuum.

1.1. Passive MEMS for patterning: micro-fabricated shadow masks (micro-, nanostencils)

In order to fabricate discrete materials libraries with micrometre or sub-micrometre resolution, one can use standard photolithographic surface patterning methods. The structuring of thin film layers however involves a series of processing steps and sub-steps: thin film deposition, photoresist spinning, exposure, development, etching and finally resist removal. These steps need to be performed for each layer in the process. A further drawback is the potential contamination of surfaces with organic materials (photoresist, developer). In addition, the use of photoresist masking structures is restricted to low temperatures and an in-vacuum change of the mask orientation is not possible. However, several re-orientations of shadow masks with respect to previously deposited layers are necessary for producing high-quality materials libraries. Therefore, surface micro-patterning methods based on photolithography for the creation of large materials libraries consisting of multi-component arrays are not suitable.

A promising alternative to overcome these problems is to perform thin film patterning based on the shadow mask principle, which allows for an *in situ* (i.e. in vacuum) application including several re-orientations of the mask with respect to the substrate. A major advantage of the shadow mask patterning method is that unconventional surfaces such as chemically modified surfaces and mechanically fragile substrates, e.g. cantilever arrays, and non-flat substrates can be patterned by local deposition [12]. Micro-fabricated shadow masks (micro- or nanostencils (i.e. solid-state membranes with (sub-)micron apertures) [13]) confine the deposition of a thin film to a well-defined surface area, thus eliminating the need for other processing steps, such as etching. They allow for rapid, clean and direct patterning of laterally confined layers of a thin film on a large variety of surfaces. Using stencil masks, laterally structured films can be fabricated in a single processing step. Figure 2 shows a schematic diagram of a micro-fabricated micro/nanostencil, as well as resulting patterned structures. The combination of micro/nanostructured shadow masking technology with combinatorial material deposition methodologies, as illustrated in figure 2, could lead the way to a new direct fabrication or optimization of novel sensors and actuators based on nanoscale materials without the use of photolithography. In particular, the combination of these two technologies allows the variation of composition (e.g. by opposing wedge type multilayer films) and nanostructure (by the nanostencil) in one experiment (see figure 2). Thus, screening for nanoscale effects, or generally the study of materials properties depending on the length scale, in thin films can be facilitated.

A MEMS-made shadow mask typically consists of a thin solid-state membrane attached to a silicon chip as a frame. The size of a thin membrane can reach several millimetres, whereas the membrane apertures can be fabricated with a possible length scale ranging from millimetre scale down to sub-micron dimensions (a few tens of nanometres in the case of high-resolution nanofabrication with a focused ion beam (FIB)). The smallest, single, metal structure fabricated up to now to our knowledge is about 10 nm in lateral dimension, although it is limited to micrometre areas only [15]. The membrane material usually consists of low-stress silicon nitride (SiN) or single-crystal silicon (Si) made in silicon-on-insulator (SOI) wafers. Photo-structurable polymers, such as SU-8, have also been used, which offer the advantage of a simplified stencil fabrication process [16].

There are several limitations of micro/nanostencils, one is mechanical stability, another is aperture clogging. The three parameters of pattern size, pattern density and overall area of patterning determine the performance of shadow masks. Structures with well-defined edges (<50 nm edge roughness) can only be fabricated by depositing through ultra-thin (about 100 nm) shadow mask membranes. Dense pattern structures require membrane apertures to be in close vicinity to the neighbouring apertures. Large areas require large membranes. From a mechanical point of view, an optimum can be found to satisfy two out of the three above parameters, but not all three simultaneously [17]. A novel DUV-MEMS stencil has provided further technological improvement in density and throughput [18]. Another critical issue, especially when working with stencils having sub-micron scale apertures, is their re-use. Nanoscale apertures are easily clogged during the deposition process as the deposited film also grows on the aperture's sidewall. Stencil masks can be cleaned by wet-chemical etching of the deposited material, provided a selective removal of the deposited film with respect to the stencil material is available. Alternatively, dry plasma cleaning is also feasible. Another possibility is to reduce the adhesion of the deposited materials on the apertures by coating the stencil with a functional layer, such as self-assembled monolayers (SAM) to reduce adhesion [19]. From the viewpoint of

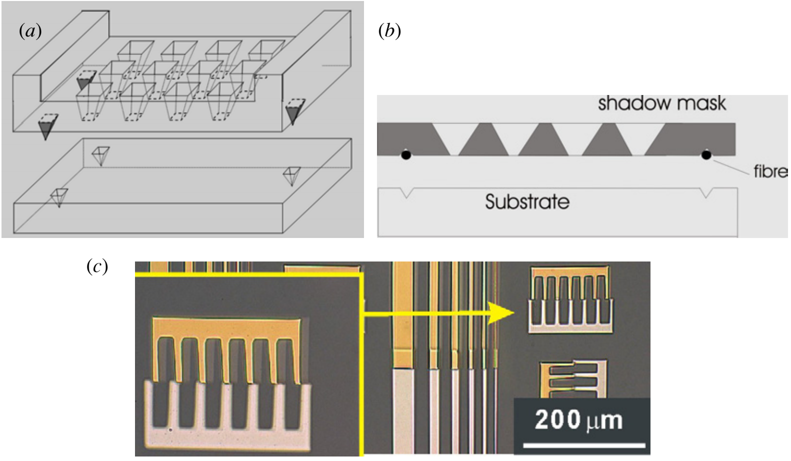


Figure 3. Schematic of possible alignment methods for micro-machined shadow masks: (*a*) alignment pins using pyramids, (*b*) alignment using wires in etched V-grooves. (*c*) Results for alignment test structures in two different metal layers (Al and Au) [16]. The pattern was deposited using a micromechanical jig alignment scheme. A precision of $<2\ \mu$m was achieved in the x- and y-directions.

substrate contamination by the stencil at higher temperatures, the use of thermally stable Si/SiN stencils is preferable compared to polymeric SU-8 stencils.

1.1.1. Alignment of shadow masks. In the case of depositing combinatorial materials libraries using the precursor deposition method [20], multiple shadow masking steps are necessary. This is also true for depositing materials on pre-structured wafers (e.g. cantilever, electrode arrays, see figure 1). Therefore, an alignment of the masks with respect to pre-deposited films or microstructures is necessary. This can either be performed by using external mechanical alignment devices (figure 2) or by using microstructured features on the mask and the substrate (figure 3). Especially interesting is the use of the intrinsic accuracy of Si single crystal substrates. By anisotropic etching, V-grooves and pyramidal structures can be fabricated which can be used for alignment. Micro-stencils with *in situ* mechanical alignment, or self-alignment based on silicon micro-pins [12], photoplastic jig and V-groove structures [16], as well as {111} silicon planes [21], have been demonstrated.

1.1.2. Comparison of evaporation, sputtering and PLD through nanostencils. Local deposition through shadow masks or stencils is not limited to methods based on thermal evaporation, but can also be used with sputtering, epitaxy and pulsed laser deposition (PLD). The possibilities of sub-micron patterning by means of microstencils using PLD have been investigated by one of the authors [22]. Stencils with circular and elliptical patterns were used, with apertures ranging from 1 μm down to 500 nm. $SrTiO_3$, Si and self-assembled monolayers (SAM) on Au were used as substrate materials to deposit Ni, NiO and Au. The results show that the chosen deposition set-up presents an easy and fast method for high-quality pattern creation. Figure 4 shows a result obtained by magnetron sputtering of Cu through a nanostencil.

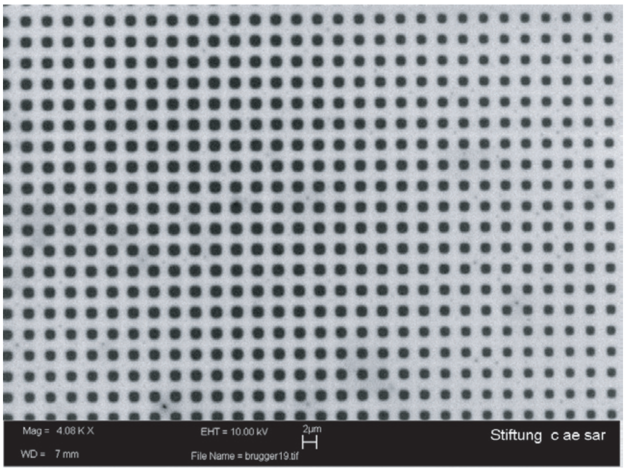


Figure 4. SEM picture of a Cu film (thickness: 5 nm) sputter-deposited through a nanostencil. The complete array contains 10 000 spots (each about 2 μm diameter) in an area of about 0.076 mm^2.

1.2. MEMS tools for local processing

1.2.1. Electrode arrays. Electrode arrays can be used for electrochemical combinatorial material deposition [23] as the electrodes can be addressed individually using a multiplexer or a switching matrix. They can easily be manufactured by photolithography, deposition and patterning of films. Furthermore, electrode arrays can be used also for sensing applications, as discussed in 2.2.

1.2.2. Micro-hotplates. Micro-hotplate arrays (figure 5(*a*)) can be described as a special form of electrode arrays. They can be used for *in situ* or *ex situ* combinatorial thermal material processing and parallel testing of materials properties. A detailed description of micro-hotplates can be found in [24]. A micro-hotplate consists of several thin films on a (micro-machined) substrate. The individual micro-hotplates should be thermally isolated which can be achieved by suspending the micro-hotplate over an etch-pit by arms with low thermal conductivity which also carry the electrical lines. These lines connect the resistive heater and probing electrodes for on-chip measurements such as temperature and electrical resistance. The electrical lines are insulated by e.g. SiO_2.

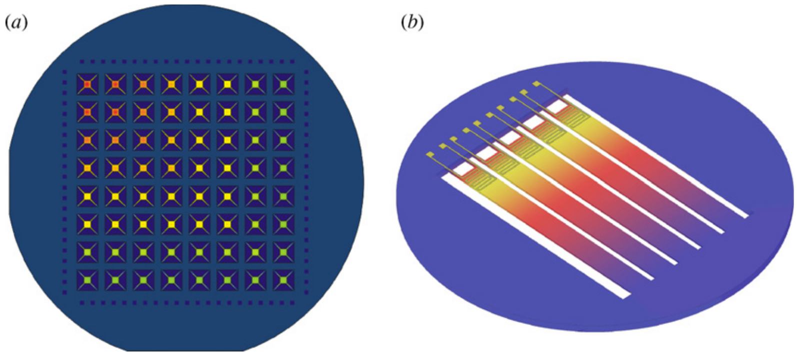


Figure 5. Schematic of (*a*) discrete array of micro-hotplates and (*b*) concept for micro-machined gradient heaters.

A metal plate can be deposited to ensure a uniform temperature distribution over the micro-hotplate. Temperatures of up to 1000 °C can be achieved. Due to their low mass, heating and cooling can be performed rapidly, allowing for novel thermal processing routines such as rapid change of temperature during deposition [24].

Depositing thin films locally on micro-hotplates can be realized by different approaches [24]. As the hotplate areas are typically on the order of 100 μm × 100 μm, adequate deposition processes have to be applied, when the hotplates are to be coated with different materials. Semancik [24] discusses thermally activated chemical vapour deposition, localized electrochemical deposition, thermal drying and lithography. Finally, shadow masking is proposed for processes such as evaporation and sputtering.

Due to individual addressability of the micro-hotplates, one can perform experiments with a local control of substrate temperature. Using only one thin film deposition on a single substrate with locally controlled temperature variation ranging from e.g. 150 °C to 800 °C, it becomes possible to rapidly identify optimized deposition temperatures.

Figure 5(*b*) shows the concept of a micro-machined gradient annealing experiment. A homogeneous film can be deposited on a substrate with a continuously varying temperature. With this method one can rapidly study diffusion, crystallization temperatures, phase formation temperatures, etc in multilayers.

1.2.3. Active shadow masks. The use of passive shadow masks has been described in section 1.1. It would be of high technological interest if active shadow masking could be realized, i.e. shadow masks which would be addressable to open or close apertures on demand, or move from one position to another without re-orienting the whole mask. Luethi *et al* [25] have presented an active scanning stencil based on a combination of shadow masks and scanning probe methods. The method represents a resistless lithography technique, i.e. a local and variable direct patterning of thin film structures on wafers. Here, the sample is moved underneath a cantilever with an aperture during the deposition of the material, thus arbitrary patterns can be written on the surface, such as rings, wires and intersecting lines with dimensions of 100 nm. Another advantage of this technique is that tapered thin film structures can be realized by varying the scan speed during the deposition. After deposition, the thin film structures can be characterized using the same AFM tip. Thus, this technology is highly interesting for depositing nanoscale combinatorial libraries. A related method has been presented recently for forming nanometre-scale metal features based on evaporation onto a substrate through a stencil mask. The stencil mask is laterally translated by a piezoflexure stage, between evaporations of different metals. The metals are chosen based on their etch chemistry to allow one material to be lifted off with respect to another. In this way, sidewall features are formed with dimensions and spacing controlled by moving the translation stage with 1 nm resolution [26].

2. Micro-machined structures and microsystems for the high-throughput characterization of materials libraries

Due to the small size of MEMS sensors, this technology is enabling new methods for faster and better local materials characterization: the whole field of scanning probe microscopy is based on micro-structured probes [5]. Another example is microstructured four-point probes for electrical conductivity measurements at (sub-)micron scale [27, 28]. In the following section, cantilever and electrode arrays for the high-throughput measurement of materials properties are discussed.

2.1. Cantilever arrays

The cantilever is a basic design component for MEMS which can be directly used to optimize thin film materials used for actuation and sensing in MEMS. Perhaps the most successful application of a micromachined cantilever is in atomic force microscopy including all its derivatives (scanning probe microscopy, e.g. magnetic force microscopy). Furthermore, the idea of using cantilevers in array form is very promising for new parallel versions of AFM [29], and also for new possibilities of data storage [30] and for gas- [31] or bio-sensing [32].

Accelerated thin film material characterization using micro-machined cantilevers or cantilever arrays is another interesting approach. Cantilever techniques, either static or dynamically driven, have been used for the measurement of thin film materials properties such as mechanical properties [33], internal friction [34], stress state [35, 36], bimetal effect [39], magnetostriction [37–39] and ΔE effect [40], piezoelectric effect [39], and phase transitions like shape (*a*) (*b*)

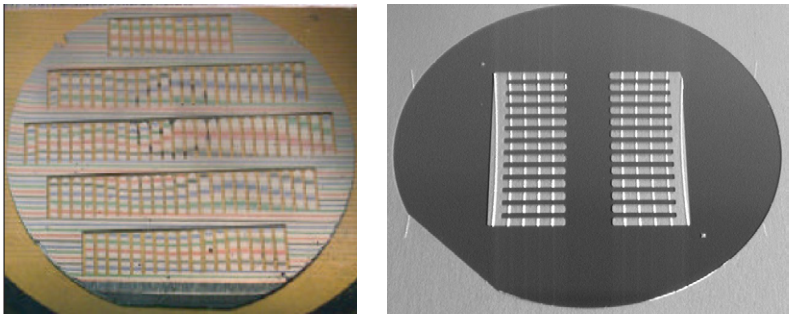


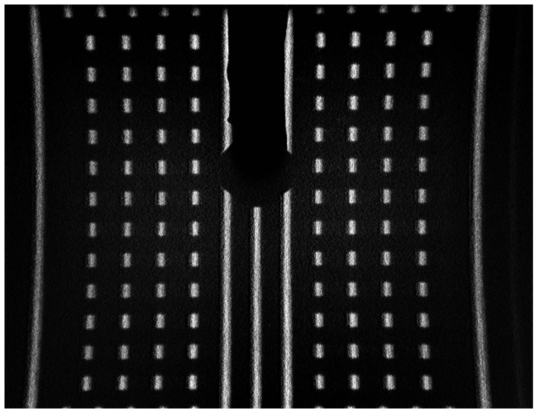
Figure 6. Arrays of Si cantilevers fabricated by bulk silicon micromachining used for screening of thin film materials properties. Typical cantilever dimensions are 2 mm $\times$ 1 cm, thickness 60 to 100 μm. The lines in (*a*) are a reflection of an image with coloured lines held over the wafer [41]. The shifts in the positions of the lines as a function of temperature are used to detect small changes in the local curvature of the cantilever; (*b*) shows a photograph of a cantilever array where laser lines can be seen which are reflected by the cantilevers.

memory effect [39]. Furthermore, structural changes in thin films occurring e.g. during crystallization can be monitored by coated cantilevers.

The first examples of the use of micromachined cantilever arrays for combinatorial materials science are published in [41, 42]. Materials libraries prepared by a co-sputtering method were screened for the (ferromagnetic) shape memory effect. By monitoring the reversible thermally induced actuation of the shape memory alloy film/Si cantilever bimorphs, martensitic transformation temperatures can be detected [43]. For individual cantilevers, actuation is typically measured using the capacitance formed between the end of the cantilever and a separate electrode. In order to map the regions of shape memory alloys and their transition temperatures for the entire spread, micromachined arrays of cantilevers were used, and the composition spreads were deposited directly on the array wafers (figure 6(*a*)) [41]. In order to study thermally induced actuation of the entire cantilever array simultaneously by visual inspection, a method was developed which works on the simple principle that individual cantilevers with metallic films deposited on them behave as concave mirrors. During a transition, stress-induced actuation on a cantilever results in a sudden change in radius of the 'mirror', and an image reflected off the cantilevers responds very sensitively as the curvature of the mirrors changes. By monitoring the change in the image as a function of temperature, composition regions undergoing a transition can readily be discerned. In this manner, a cantilever array serves as a 'self-reporting' combinatorial library for detection of the structural phase transition. All transitions observed were found to be reversible. As a result of this measurement, a large new region in the Ni–Mn–Ga thin film phase diagram which transforms martensitically was discovered.

A parallel measurement of the bi-metal effect of a Pd film on Si cantilevers is shown in figure 7. A laser with an optic generating a line array is used to monitor the curvature of the cantilevers. The four reflections from each cantilever on a screen are captured by a CCD camera. The movement of the spots is measured as a function of temperature using automated image analysis. Generally, the preparation of materials libraries or composition spreads on a cantilever array should be in such a way that there is no gradient in composition along the cantilever.

(*a*)



(*b*)

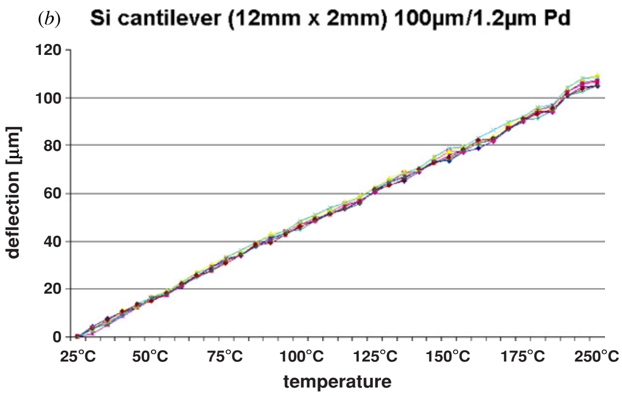


Figure 7. (*a*) CCD camera image of laser lines reflected from the cantilevers (see figure 6(*b*)). (*b*) Measurement result of the bi-metal effect derived by automated picture analysis from images taken at different temperatures.

2.2. Electrode arrays

Electrode arrays can be used for *in situ* or *ex situ* high-throughput measurements of the electrical resistance of films which are deposited on the arrays. If such an electrode array materials library is brought into a magnetic field, magnetoresistive effects such as anisotropic or giant magnetoresistance (AMR, GMR) can be measured effectively. Furthermore by heating or cooling such materials libraries, the temperature dependence of (magneto)electric properties can be screened.

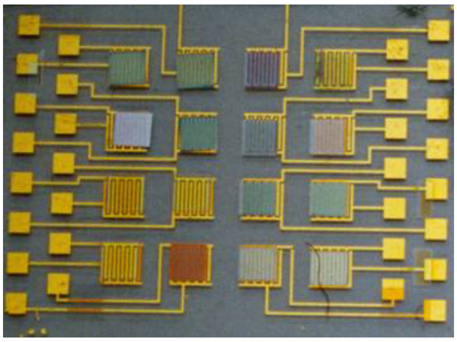


Figure 8. An inorganic electronic nose chip (1 inch × 1 inch) fabricated by combinatorial pulsed laser deposition [45].

Surface acoustic wave (SAW) devices consist of interdigitated electrodes on piezoelectric substrates. SAWs can be applied in combinatorial materials screening [44]. These devices are sensitive to a range of properties and can be miniaturized by standard photolithography, film deposition and etching processes.

There is a close link between materials and devices in microsystems. An example is an 'electronic nose' chip fabricated by one of the authors, figure 8 [45]. An electronic nose is an instrument comprised of an array of different, semi-selective gas sensors and signal multiplexing electronics, capable of recognizing individual or mixtures of analytes through pattern recognition.

There is a continuing need to improve the sensitivity and selectivity of inorganic gas sensors. In particular, selectivity is a critical figure of merit, and ideal sensors would respond differently to different gas species. One strategy in pursuing the development of improved sensors is to systematically study a large number of compositionally varying sensor materials simultaneously by using the combinatorial approach.

The advantage of combinatorial libraries is two-fold: one is to search and optimize the compositions for high sensitivity and selectivity of gases, and the other is to make use of the natural array geometry of the libraries with different sensor elements for electronic noses.

For fabricating gas sensor array chips, a combinatorial PLD was used, which allows spatially selective deposition of compositionally varying discrete samples with arbitrary layout designs on 1 inch × 1 inch substrates using computer controlled two-dimensional physical shadow masks. 50 nm thick sensor films of different compositions were deposited on selected sites (each with 2 mm × 2 mm area) on two-terminal Au electrode patterns on Al_2O_3 (c-plane) substrates (figure 8). The Au patterns were fabricated using a photolithographic lift-off process prior to the sensor film deposition. Various semiconductor films were deposited at 550 °C with an oxygen partial pressure of 2×10^{-3} Torr. Each sensor array consisted of 16 different compositions where SnO_2 was the host material and ZnO, WO_3, In_2O_3, Pt and Pd were the dopants. The testing of the chips was performed in a cylindrical gas flow chamber, and all sensors were connected to the outside electronics to monitor their resistance change. The ability of the sensor arrays to distinguish different gas species through multi-channel pattern recognition was demonstrated. Response patterns for different gases (chloroform, formaldehyde and benzene) were obtained down to 12.5 ppm.

3. Conclusion

The use of MEMS tools such as micro-fabricated shadow masks, micro-hotplates as well as cantilever and electrode arrays or combinations thereof for combinatorial materials processing and high-throughput characterization was proposed. The combination of these technologies could lead the way to a more efficient fabrication of materials libraries and allow for new screening technologies based on micromechanical structures.

References

[1] Xiang X D and Takeuchi I 2003 *Combinatorial Materials synthesis* (New York: Dekker)

[2] Madou M J 2002 *Fundamentals of microfabrication* 2nd edn (Boca Raton, FL: CRC Press)

[3] Menz W, Mohr J and Paul O 2001 *Microsystem Technology* (New York: Wiley) pp 10–11

[4] Xiang X D, Sun X, Briceño G, Lou Y, Wang K A, Chang H, Wallace-Freedman W G, Chen S W and Schultz P G 1995 A combinatorial approach to materials discovery *Science* **268** 1738–40

[5] Binnig G, Gerber Ch, Stoll E, Albrecht T R and Quate C F 1987 Atomic resolution with atomic force microscope *Europhys. Lett.* **3** 1281–6

[6] Piner R D, Zhu J, Xu F, Hong S H and Mirkin C A 1999 'Dip-pen' nanolithography *Science* **283** 661–3

[7] Ginger D S, Zhang H and Mirkin C A 2004 The evolution of dip-pen nanolithography *Angew. Chem. Int. Ed.* **43** 30–45

[8] Meister A, Jeney S, Liley M, Akiyama T, Staufer U, de Rooij N F and Heinzelmann H 2003 Nanoscale dispensing of liquids through cantilevered probes *Microelectron. Eng.* **67–68** 644–50

[9] Baba Y, Shoji S and van den Berg A 2002 *Micro Total Analysis Systems* (Dordrecht: Kluwer)

[10] Kikutani Y and Kitamori T 2004 Micro-flow reaction systems for combinatorial syntheses *Macromol. Rapid Commun.* **25** 158–68

Jähnisch K, Hessel V, Löwe H and Baerns M 2004 Chemistry in microstructured reactors *Angew. Chem. Int.* **43** 406–46

Watts P and Haswell S J 2003 Microfluidic combinatorial chemistry *Curr. Opin. Chem. Biol.* **7** 380–7

[11] Wallace D B and Grove M E 2003 Ink-jet methods in combinatorial synthesis *High-Throughput Analysis* ed R A Potyrailo and E J Amis (Dordrecht: Kluwer) pp 469–90

[12] Tixier A, Mita Y, Gouy J P and Fujita H 2000 A silicon shadow mask for deposition on isolated areas *J. Micromech. Microeng.* **10** 157–62

[13] Brugger J, Berenschot J W, Kuiper S, Nijdam W, Otter B and Elwenspoek M 2000 Resistless patterning of sub-micron structures by evaporation through nanostencils *Microelectron. Eng.* **53** 403–5

[14] Ludwig A 2004 Combinatorial fabrication of magnetic multilayer films *Appl. Surf. Sci.* **223** 78–83

[15] Champagne A R, Couture A J, Kuemmeth F and Ralph D C 2003 Nanometer-scale scanning sensors fabricated using stencil lithography *Appl. Phys. Lett* **82** 1111–3

[16] Kim G, Kim B and Brugger J 2003 All-photoplastic microstencil with self-alignment for multiple layer shadow-mask patterning *Sensors Actuators A* **107** 132–6

[17] Kim G M, van den Boogaart M A F and Brugger J 2003 Fabrication and application of a full wafer size micro/nanostencil for multiple length-scale surface patterning *Microelectron. Eng.* **67–68** 609–14

[18] van den Boogaart M A F, Kim G M, Pellens R, van den Heuvel J-P and Brugger J 2004 DUV-MEMS stencils for high-throughput resistless patterning of mesoscopic structures, *J. Vac. Sci. Technol.* B at press
[19] Koelbel M, Tjerkstra R W, Kim G M, Brugger J, van Rijn C J M, Nijdam W, Huskens J and Reinhoudt D N 2003 Self-assembled monolayer coatings on nanostencils for the reduction of materials adhesion *Adv. Funct. Mater.* **13** 219–24
[20] Wang J, Yoo Y, Gao C, Takeuchi I, Sun X, Chang H, Xiang X D and Schultz P G 1998 Identification of a blue photoluminescent composite material from a combinatorial library *Science* **279** 1712–4
[21] Brugger J, Andreoli C, Despont M, Drechsler U, Rothuizen H and Vettiger P 1999 Self-aligned 3D shadow mask technique for patterning deeply recessed surfaces of micro-electro-mechanical systems devices *Sensors Actuators* **76** 329–34
[22] Vroegindeweij F, Speets E A, Steen J A J, Brugger J and Blank D H A 2004 Exploring microstencils for sub-micron patterning using pulsed laser deposition *Appl. Phys.* A **79** 743–5
[23] Mirsky V M, Kulikov V, Hao Q and Wolfbeis O S 2004 Application of combinatorial electropolymerization to the development of chemical sensors *MRS Proc.* **804** JJ4.1.1
[24] Semancik S 2003 Temperature dependent materials research with micromachined array platforms *Combinatorial Materials Synthesis* ed X D Xiang and I Takeuchi (New York: Dekker) pp 263–95
[25] Luethi R, Schlittler R R, Brugger J, Vettiger P, Welland M E and Gimzewski J K 1999 Parallel nanodevice fabrication using a combination of shadow mask and scanning probe methods *Appl. Phys. Lett.* **75** 1314–6
[26] Racz Z, He J, Srinivasan S, Zhao W, Seabaugh A, Han K, Ruchhoeft P and Wolfe J 2004 Nanofabrication using nanotranslated stencil masks and lift off *J. Vac. Sci. Technol.* B **22** 74–6
[27] Petersen C L, Hansen T M, Bøggild P, Boisen A, Hansen O, Hassenkam T and Grey F 2002 Scanning microscopic four-point conductivity probes *Sensors Actuators* A **96** 53–8
[28] Nagase M, Takahashi H, Shirakawabe Y and Namatsu H 2003 Nano-four point probes on microcantilever system fabricated by focused ion beam *Japan. J. Appl. Phys.* **42** 4856–60
[29] Kim Y S, Nam H J, Cho S M, Hong J W, Kim D C and Bu J U 2003 PZT cantilever array integrated with piezoresistor for high speed parallel operation of AFM *Sensors Actuators* A **103** 122–9
[30] Vettiger P, Despont M, Drechsler U, Dürig U, Häberle W, Lutwyche M I, Rothuizen H E, Stutz R, Widmer R and Binnig G K 2000 The 'Millipede'—more than one thousand tips for future AFM data storage *IBM J. Res. Dev.* **44** 323–40
[31] Baselt D R, Fruhberger B, Klaassen E, Cemalovic S, Britton C L Jr, Patel S V, Mlsna T E, McCorkle D and Warmack B 2003 Design and performance of a microcantilever-based hydrogen sensor *Sensors Actuators* B **88** 120–31
[32] Berger R, Delamarche E, Lang H P, Gerber C, Gimzewski J K, Meyer E and Guntherodt H J 1997 Surface stress in the self-assembly of alkanethiols on gold *Science* **276** 2021–4
[33] Weihs T P, Hong S, Bravman J C and Nix W D 1988 Mechanical deflection of cantilever microbeams: a new technique for testing the mechanical properties of thin films *J. Mater. Res.* **3** 931–42
[34] Berry B S and Pritchet W C 1975 Vibrating reed internal friction apparatus for films and foils *IBM J. Res. Dev.* 334–43
[35] Hou M T K and Chen R 2004 A new residual stress measurement method using ultra-wide micromachined bilayer cantilevers *J. Micromech. Microeng.* **14** 490–6
[36] Keatch R P and Lawrenson B 1994 A microstructure for detecting the stress distribution in thin coatings deposited on to silicon substrates *Microelectron. J.* **25** 393–400
[37] du Trémolet de Lacheisserie E and Peuzin J C 1994 Magnetostriction and internal stresses in thin films: the cantilever method revisted *J. Magn. Magn. Mater.* **136** 189–96
[38] Klokholm E 1976 Measurement of magnetostriction in ferromagnetic thin-films *IEEE Trans. Magn.* **12** 819–21
[39] Quandt E and Holleck H 1995 Materials development for thin film actuators *Microsyst. Technol.* **1** 178–84
[40] Ludwig A and Quandt E 2002 Optimization of the ΔE-effect in thin films and multilayers by magnetic field annealing *IEEE Trans. Magn.* **38** 2829–31
[41] Takeuchi I, Famodu O O, Read J C, Aronova M A, Chang K S, Craciunescu C, Lofland S E, Muttig M, Wellstood F C, Knauss L and Orozco A 2003 Identification of novel compositions of ferromagnetic shape-memory alloys using composition spreads *Nature Mater.* **2** 180–4
[42] Famodu O O *et al* 2004 Combinatorial investigation of ferromagnetic shape-memory alloys in the Ni–Mn–Al ternary system using a composition spread technique *Mater. Trans.* **45** 173–7
[43] Wuttig M, Craciunescu C and Li J 2000 Phase transformations in ferromagnetic NiMnGa shape memory films *Mater. Trans. JIM* **41** 933–7
[44] Potyrailo R A, Morris W G and Wroczynski R J 2003 Acoustic wave sensors for high-throughput screening of materials *High-Throughput Analysis* ed R A Potyrailo and E J Amis (Dordrecht: Kluwer) 219–46
[45] Aronova M A, Chang K S, Takeuchi I, Jabs H, Westerheim D, Gonzalez-Martin A, Kim J and Lewis B 2003 Combinatorial libraries of semiconductor gas sensors as inorganic electronic noses *Appl. Phys. Lett.* **83** 1255–7