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Large-Area Deposition of Amorphous, Photovoltaic Silicon

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CONTENTS

1) PROJECT AIM AND INTRODUCTION

Successful mass production of silicon photovoltaic solar cells requires high throughput and yield of good quality, uniform, large-area silicon thin films. The CRPP, in collaboration with BALZERS AG, has adapted an industrial plasma reactor to investigate the implementation of Very High Frequency operation along with suitable plasma diagnostics and process monitoring.

Photovoltaic solar cell production using high quality amorphous silicon deposited at elevated rates by the Very High Frequency (VHF) technique was pioneered by the group of Professor Shah at IMT Neuchâtel. Other demonstrated advantages of Very High Frequency plasma operation are minimal ion bombardment damage, low material stress, reduced particle contamination, and favourable conditions for micro-crystalline silicon deposition. Until now, these investigations have been confined to laboratory-scale reactors with solar cell areas of around 10 x 10 cm. The principal aim of this current project is to test the feasibility and usefulness of VHF operation in large-area (at least 35 cm x 45 cm) industrial reactors suitable for volume production of solar cell panels, particularly with regard to impedance matching, film uniformity, powder formation and the understanding of the high deposition rate. Following the successful demonstration of VHF implementation and uniform deposition in an industrial reactor, the project was prolonged to optimise micro-crystalline silicon deposition for the new generation of IMT Neuchâtel 'micromorph' solar cells.

The report is structured as follows: Reactor and diagnostic development are described in Section 2, results in Section 3, collaborations and transfer in Section 4, summary and conclusions in Section 5.

2) REACTOR AND DIAGNOSTICS DEVELOPMENT

Reactor Modifications for Diagnostic Access

The core of the experiment is a Plasma-Box reactor Type KAI-1S developed and supplied by Balzers AG. The original reactor as supplied to industry was a completely-enclosed 'black box'. The substrate size was 45 cm x 35 cm and subsequent Balzers reactors will shortly reach substrate areas of $1m^2$ using the same reactor principle.

Special care was taken to ensure that apertures for diagnostic access did not disturb the electrical, thermal and leak-tight continuity of the reactor, since this could artificially degrade the deposited film quality and uniformity. This was achieved by using specially-designed grids (to avoid hollow cathode parasitic discharges) and sapphire windows (for resistance to the plasma cleaning process) at the end of stand-off tubes. The design and construction of modifications were carried out at the CRPP workshops (Table 1 and Fig. 1).

Reactor type	Plasma-Box; substrate size 35 x 45 cm
Excitation frequency	13 - 90 MHz
RF power	200W maximum
Substrate temperature	up to 250°C
Gases	Silane, Argon, Hydrogen, Helium, Sulphur Hexafluoride, Oxygen
Gas flow	up to 500 sccm per gas, through uniform showerhead. Special input for "pusher gas"
Vacuum pumps	Turbopump for high vacuum ($<10^{-6}$ mbar) Roots pump with butterfly valve pressure control + Dry primary pump
Working pressure	< 1.2 mbar
Process-Control	SEAL Processor + Computer

Table 1: Plasma-Box Reactor parameters for large area deposition at the CRPP.

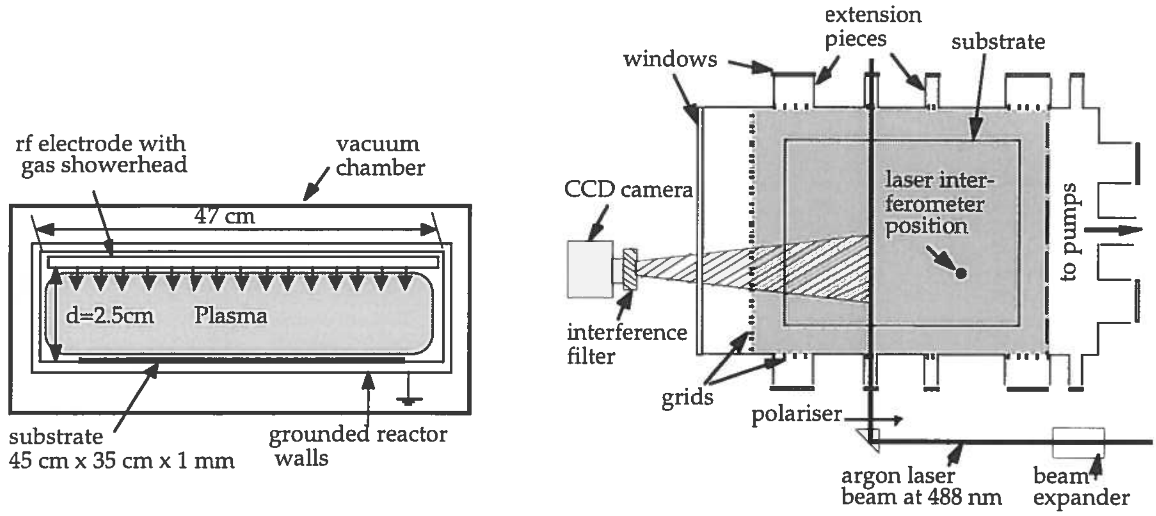


Fig. 1: *Schematic front and plan view of the plasma box reactor with implementation of the powder diagnostic.*

In addition to the demounting, removal and installation of the reactor and its sub-systems, the following improvements have been carried out to facilitate the implantation of the new diagnostics mentioned above: Installation of a butterfly valve for rapid, precise feedback control of the pressure, without suffering from electrical interference due to Roots pump variable speed control; Design, fabrication and installation of special flanges for the ZnSe windows (FTIR diagnostic), the inclined flanges for ellipsometer access, and the microwave guide inserts; Substrate elevation mechanism and switching system for replacing the matching box connection by the galvanometer for the substrate charge measurements; Design and construction of a central RF electrode connection and feedthrough to allow uniform film deposition during VHF operation. The computerised process- and security-control system (SEAL) installed at the CRPP has allowed continuous trouble-free operation. This system also permitted significant economies in basic measurement and control apparatus.

Reactor Cleaning

A plasma etch method for reactor cleaning was introduced from Balzers AG. A plasma in a Helium/Oxygen/Sulphur (10/10/100 sccm) gas mixture at 0.1 mbar was sufficient to clean up the reactor in between successive deposition experiments. This practical technique removes any need for laborious mechanical and/or acid scrubbing.

Diagnostics

Laser Interferometry

A diode laser interferometer was installed to measure thin film interference fringes through a hole in the ground electrode from outside the vacuum chamber. The fringe period during plasma deposition gives an in situ measurement of deposition rate (Fig. 2a: deposition rate 6 A/s with 200 sccm pure silane, 150 W 0.4 mbar). Similarly, the etch rate during plasma etching can be monitored as in Fig. 2b (3 A/s etch rate). An oblique reflectance He-Ne laser interferometer was also used to test for anisotropic refractive indices in certain films.

Whole Surface Interferograms

In addition to the in situ laser diode thin-film interferometer for on-line deposition rate measured at a point on the substrate, a large scale illumination source with CCD and interference filter was developed to display ex-situ interferograms of the whole substrate area.

By this method, the thickness uniformity to within a fraction of the wavelength of light is instantaneously visualised over the entire film surface. In combination with white-light interferometry (by an Optical Multichannel Analyser and monochromator), a film thickness map is reconstructed over all of the deposited film. This diagnostic technique is invaluable for evaluating the outcome of large-area deposition experiments.

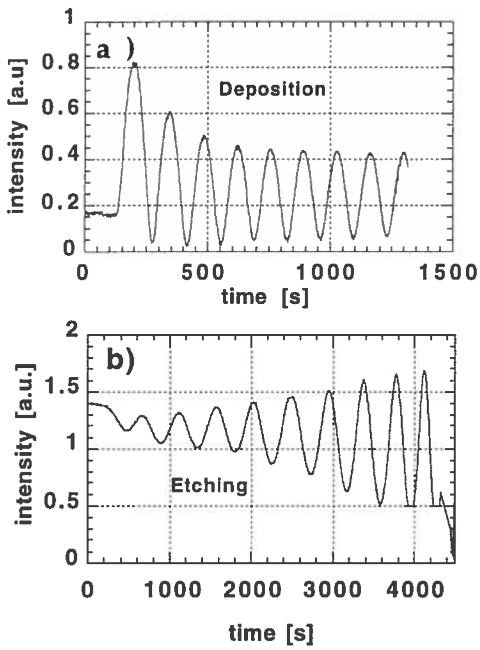


Fig. 2: In situ film thickness measurement in: a) silane plasma deposition; b) an etching plasma.

Powder measurements by light scattering

Beam-expanded polarised light from an Argon ion laser is scattered from particles and monitored by a CCD camera via an interference filter. Video or computer acquisition thus provides real-time imaging of powder formation in the plasma. Plasma emission spatial profiles give an indication of plasma uniformity both laterally and vertically across the electrode gap. Special attention was paid to the CCD image deconvolution necessary for the depth-of-field and finite-angle corrections for large-area emission sources. Detailed analysis of the extinction and diffusion of the laser light using Mie theory can also be used to estimate the particle refractive index, size and number density.

Electrode RF voltage probe

Our previous experience has consistently proved the value of rf voltage measurements made directly at the rf electrode: other probes mounted outside the vacuum chamber introduce intolerable voltage errors, especially at VHF frequencies. However, commercial probes are incompatible with the internal environment of the Balzers reactor. A novel rf voltage probe was therefore designed and installed directly on the large area rf electrode; it can withstand the elevated reactor temperatures (250 °C) without corrupting the high vacuum and includes an rf buffer to provide reliable measurements at several metres from the point of measurement. This probe monitors several important plasma parameters such as plasma effective power, plasma and electrode potentials (from which the substrate surface potentials can be deduced).

Fourier Transform Infrared Absorption Spectroscopy

Infrared absorption spectroscopy has been applied to measure the silane fractional depletion in the plasma during the deposition process, as a function of excitation frequency. This powerful technique is highly specific, sensitive, non-perturbative, and is likely to become a universally-used diagnostic for reactive plasmas throughout research groups and industry. The convenient single-pass line-of-sight arrangement is compatible with industrial design requirements; it uses an external infrared detector to measure the absorption spectrum, through the plasma volume via ZnSe and sapphire windows, of an infrared source beam of a commercial Fourier Transform spectrometer. Quantitative results are described in detail below.

Neutral and Ion Mass Spectrometry

The Hiden Plasma Monitor has been successfully applied throughout the OFEN projects at the CRPP. In recognition of the accrued reputation for high quality of the instrument during this work, the manufacturers Hiden Analytical Ltd have offered a complete revision, free of charge, of the specrometer. This includes the latest electronics and software versions, and an extended mass range option to 1000 amu from the previous 500 amu maximum. This plasma monitor was also the first of its kind to be equipped with an attachment mass spectroscopy option, as proposed by us. Using this, the attachment cross-section of neutral hydrogenated-silicon clusters was measured for the first time. The charge-sign discrimination of the channeltron detector has also been studied - this is of general importance for the field of ion mass spectroscopy. The data obtained will help to ascertain the relative importance of neutral and negative ion clustering reactions in silane plasmas which can be responsible for the particulate contamination of films deposited during solar cell manufacture.

Microwave Diagnostics for Plasma Density Measurements

Microwave interferometery in the range 7 to 12 GHz (Band X), developed on the small PADEX reactor, is a reliable, sensitive and rapid absolute measurement of the free electron density. However, multiple reflections within the KAI-1 prohibit interferometry on the large reactor. The classical technique in such a case is to construct a plasma reactor in the form of a resonant cavity in which a single mode frequency can be tracked, but in the case of industrial reactors, the reactor shape is dictated by other requirements such as deposition uniformity. The KAI-1 represents a strongly over-moded cuboid cavity in which the high wavenumber density of modes would seem to preclude identification and tracking of a single eigenmode. Fortunately, imperfections in the reactor cavity such as windows, pump ports etc. mean that the higher modes are strongly damped and in practice, individual modes can be identified. Since the plasma density profile varies significantly only across the electrode gap, the plasma acts as a uniform dielectric over the electrode surface and hence all modes with the same mode number across the electrode gap will be shifted by the same frequency, proportional to the plasma density. The measurement consists in measuring the shift in mode spectrum obtained by frequency-sweeping the microwave source. This diagnostic (Fig. 3) has been used to measure the electron density dependence on excitation frequency as described below.

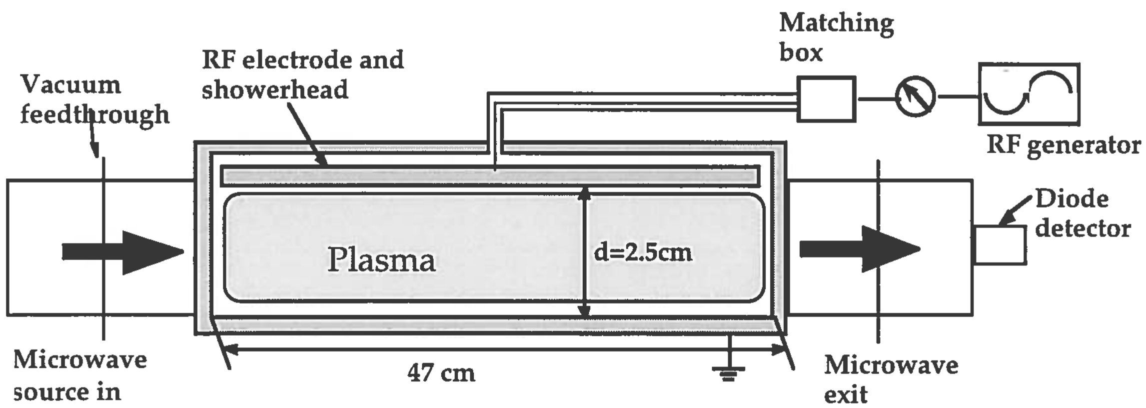


Fig. 3: *Schematic of microwave cavity measurement and central RF connection*

Visible-UV Spectroscopic Ellipsometry

Ellipsometry consists in measuring the alteration in polarisation degree on reflection from a surface, from which the dielectric constant can be deduced along with various other properties (roughness, crystallinity...) according to the model used for interpretation. A Visible-UV spectroscopic ellipsometer, obtained with OFEN, Balzers SA and CRPP co-funding, has been installed on the PADEX reactor so as to permit in situ measurements of the growing silicon film during plasma deposition. A fundamental parameter in the deposition of micro-crystalline films is the degree of crystallinity. In situ ellipsometry and several other ex situ diagnostics, such as Raman scattering, X-Ray diffraction and electron microscopy, each provide an estimate of crystalline fraction, but the values often differ widely. A commonly-used method for ellipsometric data assumes that micro-crystalline silicon can be represented by an effective medium composed of single-crystal silicon, amorphous silicon, and voids. However, the measured spectra of relative permittivity do not reproduce the sharp variation at the Critical Point peaks of single-crystal silicon and the micro-crystalline fraction is therefore strongly underestimated. Another technique of interpretation has been developed whereby the second and third derivatives of the permittivity spectrum are compared with a Critical Point equation in which the peak broadening characteristic of micro- and nano-crystals can be accounted for. The technique was initially tested on micro-crystalline samples furnished by IMT Neuchâtel and compared with their previous measurements. The crystalline fractions obtained with the improved ellipsometric interpretation are in much closer agreement with other diagnostics, which increases confidence in the ellipsometric data. It is interesting to note that the measured relative permittivity of micro-crystalline samples is much reduced with respect to the commonly-known values for amorphous and single-crystal silicon; this is habitually attributed in the literature to extreme film porosity, but the films are mechanically rigid and appear to be compact by electron microscopy. We are currently searching a more reasonable physical explanation of this ellipsometric observation, which may well reveal unique properties of plasma-deposited micro-crystalline silicon.

Substrate Charge Measurements: Avoiding Electrostatic Discharge Damage

At the end of a plasma processing step, an electrically-isolating film can be left with an electrostatic charge. This poses a serious problem for industrial production because of irreversible film damage due to electric breakdown during further substrate handling. Electrostatic discharge damage can cause pinholes which destroy segments of the final solar cell array which reduces yield and the overall efficiency of the final solar panel.

In order to anticipate this problem *before* damage occurs, and to test the effectiveness of solutions proposed to eliminate the charge, a novel diagnostic has been invented by which the residual charge can be measured in situ before substrate removal takes place. The technique uses an galvanometer connected in parallel with the matching box circuit just at the end of a plasma process. A displacement current is measured as the substrate is raised for removal from the ground electrode; this current is proportional to the residual charge and substrate velocity (the method takes advantage of the substrate lifting mechanism in the Balzers KAI-1). The sensitivity is more than adequate to detect charge levels liable to cause electric breakdown in subsequent handling.

Depending on the plasma process parameters when the plasma is extinguished, the charge level can vary very widely and even change polarity. Using this novel diagnostic, various solutions have been identified to avoid film damage and thereby increase production yields and decrease overall costs. This new technique is currently being installed for use in an industrial production environment.

3) RESULTS

Very High Frequency Impedance Matching

First and foremost, it was necessary to match the impedance of the large reactor to the rf amplifier supply for the Very High Frequency range. A 4-pole network analysis, developed for the small reactor Padex during the previous project, showed that the original Balzers automatic 'T' matching box for 13.56 MHz could not be adapted for VHF use. However, the Balzers reactor impedance, measured and modelled for 1 - 110 MHz, was found to qualitatively resemble the equivalent circuit of the small reactor. A 'π' network, based on the former IMT Neuchâtel design, was therefore constructed and provides very good high power (> 200 W) coupling from 30 to 100 MHz. Using the model, a complete identification of the parasitic circuit elements has enabled an accurate estimation of the capacitor values as a function of frequency as shown in Fig. 4. Supplementary variable vacuum capacitors could cover the whole 13 - 100 MHz range with a unique matching box if required. *We find that VHF rf power coupling to industrial-size reactors is no more problematic than for the conventional 13.56 MHz frequency.*

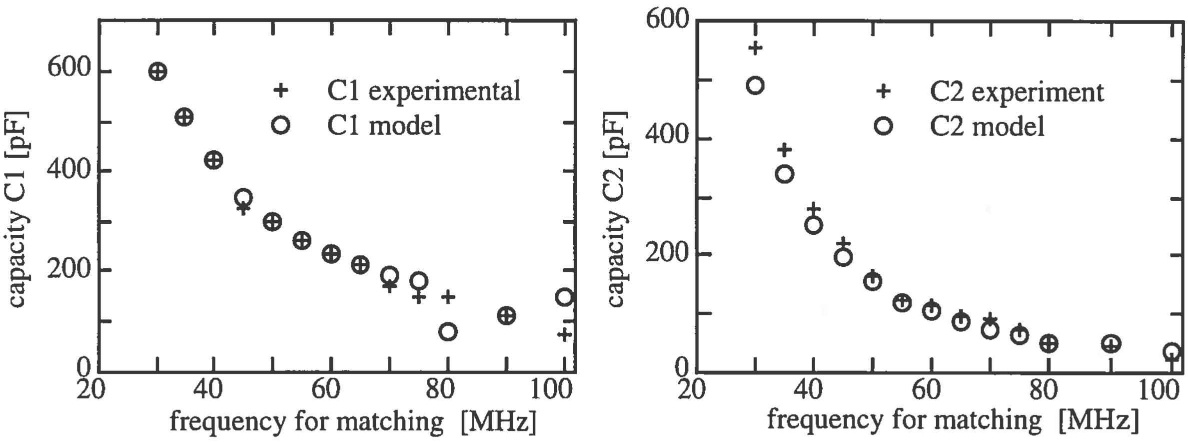


Fig. 4 : *Comparison between calculated and experimental capacitor values for VHF matching.*

Powder Investigations

Particle contamination is a major problem for large area reactor plasma deposition since the enclosed geometry results in long confinement times for polymerisation of the reactive gas radicals. Pinholes caused by powder particles incorporated in a film cause short circuits and the affected solar cells are rejected. Powder clouds suspended in the plasma above the growing film can cause inhomogeneous deposition by locally changing the plasma power dissipation. Powder formation was monitored over the rf power, pressure, flowrate, and temperature ranges currently used in industry, and several demonstration videos were produced.

Particles grow to 200-250 nm and may be charged with several hundred electrons, behaving like a 'floating potential' probe in the plasma. Their presence can strongly affect the plasma electron density and energy distribution. Supplementary studies comparing powder spatial distribution and 2D plasma numerical simulation (from Professor Boeuf at Toulouse) show that particles arrange themselves in the neighbourhood of local, time-averaged potential wells. Critical zones for particle formation were shown to be localised at the reactor edges; this is also associated with shallow potential traps and film thickness gradients as will be discussed below). A 'pusher gas' (an inert gas introduced at the reactor mouth) was observed to efficiently empty the plasma of suspended particles before plasma extinction by sweeping them into the exhaust throat. Powder can also be reduced by square wave rf power modulation at

~500 Hz, which also confines the particles nearer to the reactor walls and away from the deposited film. Finally, we note that large area VHF deposition shows no visible powder at deposition rates (5 Å/s) where 13.56 MHz operation already incurs serious powder contamination problems, thereby confirming that this reported advantage of VHF deposition in the small Padex reactor remains valid in large area industrial reactors.

Thickness Uniformity of the Deposited Amorphous Silicon: Improvements in the Reactor Configuration

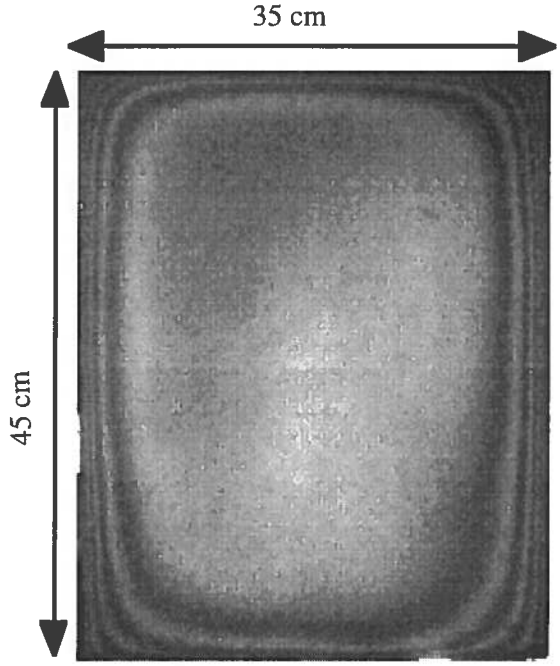
Good homogeneity over large area films is a prerequisite for successful mass production of solar cells. Thickness gradients appear especially around the substrate edge, so much so that in conventional industrial production, the outer few cm have to be rejected. It was necessary, therefore, to thoroughly investigate the non-uniformity at 13.56 MHz to provide a reference for VHF deposition: clearly, the voltage distribution effect at VHF (mentioned below) is not responsible for any intrinsic non-uniformity at 13.56 MHz. The gas flow through the rf electrode showerhead was sufficiently well-distributed, as tested by comparing reactors with different showerhead widths, and is not the cause of the problem. In fact, we have proven that a uniform showerhead gas distribution, for a uniform plasma, is the necessary and sufficient configuration for depositing uniform films. Other industrial models cannot yield satisfactory films except in exceptional special cases. At 13.56 MHz with low rf power and deposition rate (< 2 Å/s) uniform films (< 4% inhomogeneity) can be obtained, but higher powers and deposition rates cause a drastic deterioration of the film homogeneity (> 25%).

Two phenomena, separately or together, may be responsible for non-uniform plasma depostion at low (13.56 MHz) frequencies: i) Time-averaged potential wells near to the reactor walls; and ii) The discontinuity of the dielectric at the junction between the insulating substrate and the exposed metal ground electrode. Both of these effects may perturb the uniformity of the plasma power dissipation directly, or indirectly via powder trapping. These were investigated in turn:

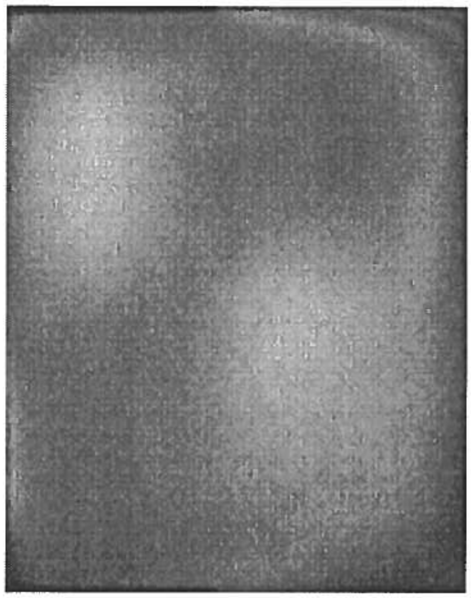
i) Time-averaged potential wells have been shown to trap powder particles in the plasma near to the edges of electrodes. In an empirical attempt to smooth out the transition from rf to ground potentials at the reactor corners, a special rf electrode with an electrically-floating surrounding frame was furnished by Balzers for testing at the CRPP: measured profiles of plasma emission and laser-light scattering from powder, however, showed no clear improvement. Our next step is to exploit a 2-D plasma fluid code, successully applied to the Padex reactor, but adapted for the large-area reactor. An appropriate electrode topology could then be searched by means of the code before any future construction. We note in passing that rf power modulation improves uniformity.

ii) The dielectric discontinuity effect was investigated by placing a frame of glass plates around the glass substrate. The non-uniform part of the deposition was then displaced away from the substrate area onto the sacrificial glass frame, leaving a highly-uniform a-Si:H layer as shown in Figure 5. For 3 Å/s deposition rate (which is rapid for conventional 13.56 MHz plasmas), *the non-uniformity passed from worse than 20% to better than 5% over the entire substrate area.*

This suggests that the dielectric discontinuity is a major cause of poor uniformity, and not the plasma/reactor geometry, since the latter was the same in each case. Moreover, a gap between a glass plate and the substrate reintroduced thickness gradients on the substrate, as did a poor physical contact between the substrate and the ground electrode; all these observations suggest that *suitable dielectric matching across the substrate-electrode boundary has great potential for improving a-Si:H film uniformity.* A practical implementation for industry would be to implant alumina shims into the ground electrode surface: these shims resist the etching plasma and so can be permanently mounted in the reactor, and the flat electrode profile facilitates robotic insertion of the substrates. Suitable, economically-priced alumina plates have now been obtained ready for testing.



a) Without topology modification



b) With topology modification

Fig. 5: *nterferograms of amorphous silicon films deposited at 13.56 MHz; the deposition conditions are identical except for a glass frame placed around substrate b). The films are ~1 μm thick, and each fringe corresponds to 80 nm. 100 sccm silane, 0.5 Torr, 100 W, 4 Å/s.*

The junction between insulating substrate and conducting electrode surface might be expected to greatly perturb the plasma, but has largely been ignored hitherto by the plasma deposition community. In fact, to a first approximation, the plasma rf capacitive sheath tends to isolate the plasma from differences in the electrode surface material. However, we have shown that rf current continuity imposes *a residual dc and ac potential at the substrate surface which modifies the sheath voltage with respect to the neighbouring exposed metal surface.* This is confirmed by good agreement between an analytical model and experiments with various substrate thicknesses using the novel voltage probe for reliable electrode voltage measurements. These residual potentials probably cause the deposition non-uniformity at the substrate/electrode junction, which explains why the dielectric plates are effective.

Voltage Uniformity in Large Area Reactors for VHF operation

An anticipated technical difficulty with large area reactors at VHF frequencies is that the vacuum quarter-wavelength (1 m at 70 MHz) of the rf excitation becomes comparable to the electrode dimensions, giving rf voltage amplitude variations across the electrode surface. The rf voltage was directly measured between the plates over the whole electrode area without plasma using a modified internal voltage probe. Figure 6 clearly shows the effect of rf frequency on the distribution of rf voltage for the present configuration of a single rf input connection. Indeed, the plasma emission at low rf powers shows that the plasma is sustained only over part of the electrode surface (furthest from the rf feedthrough). Note that the plasma does not short out the voltage variations, despite being equipotential due to the capacitive sheaths which absorb the differences in inter-electrode voltage. The plasma power is however locally determined by the sheath RF voltage amplitude, which in turn determines the plasma power dissipation and directly, the deposition rate and film thickness. It is important to have a reliable model because time and expense prohibit empirical testing of several different reactor constructions.

With the assistance of the theory department, an analytical model was developed which accurately reproduced the measurements and numerical results by means of an expansion in Green functions (see Fig. 6). The physical understanding afforded by the analytical approach shows that *the principal non-uniformity is due to a logarithmic singularity in the vicinity of the RF connection* (and similarly, at the ground connection) as demonstrated in Fig. 6a). This effect dominates the intuitive 'standing wave' image of voltage distribution obtained from transmission line theory. In fact, this singularity is a property of the two dimensional case and has no physical analogue in one dimension. The depth of a singularity can be reduced by using a distributed RF connection.

A further important phenomenon is that of the skin effect: the RF current is confined to a surface layer which in our case is much thinner than the RF electrode itself. The RF electrode is therefore effectively a double-skinned electrode in which continuity of the RF current in the top and bottom surfaces is via the edges of the RF electrode. The complex geometry of the real reactor was reproduced by introducing image source currents into an equivalent unfolded two-dimensional geometry in the analytical model. The importance of this effect is that *the RF contact singularity can be separated from the plasma zone by displacing the RF connection to the back face of the RF electrode.* The optimal situation for a single RF connection is in the centre of the back face as shown by voltage measurement and calculation in Fig. 6b). The resulting film homogeneity is greatly improved since only the relatively small free-space standing wave amplitude variation remains (and this for an effective width which is double the width of the RF electrode). A custom-built RF passage and central back-face connector was designed, constructed and installed at the CRPP. It is now routinely used to produce films at 70 MHz with a homogeneity well within the tolerance limits required for integral 35 cm x 45 cm solar cell substrates, as shown in Figs. 7 and 8. The original main goal of uniform, industrial-scale VHF plasma deposition has therefore been achieved.

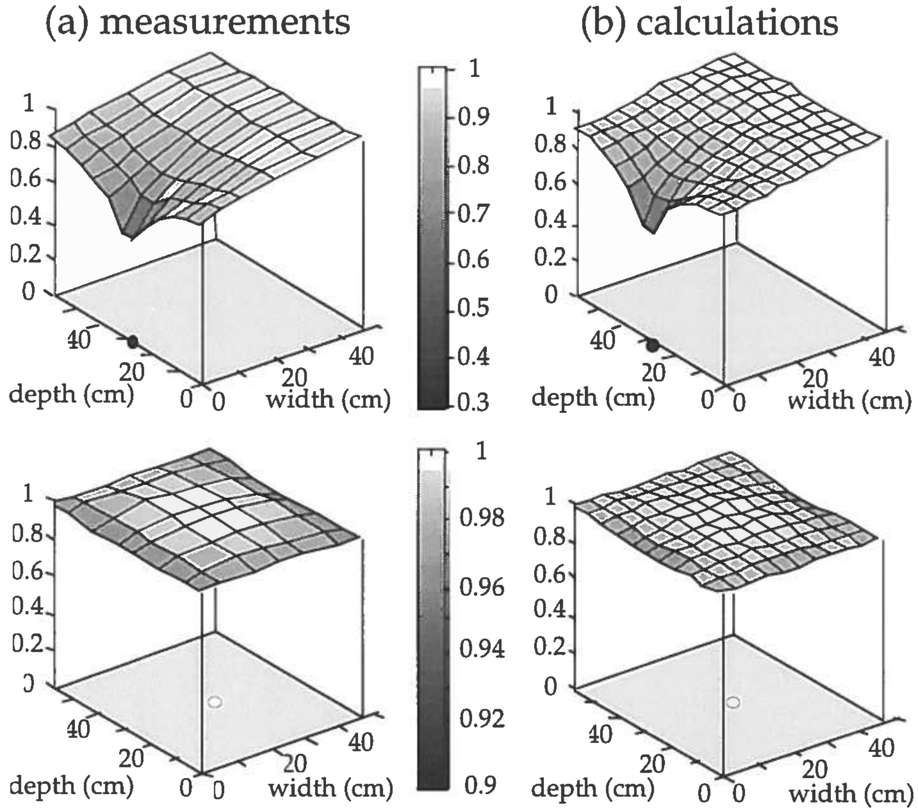


Fig. 6: *Comparison of a) voltage distribution measurements and b) analytical calculations. The upper figures correspond to a single RF edge connection; the lower figures correspond to the optimal configuration of a single RF and ground connection at the centre of the electrode back face. All data obtained for 70 MHz excitation frequency.*

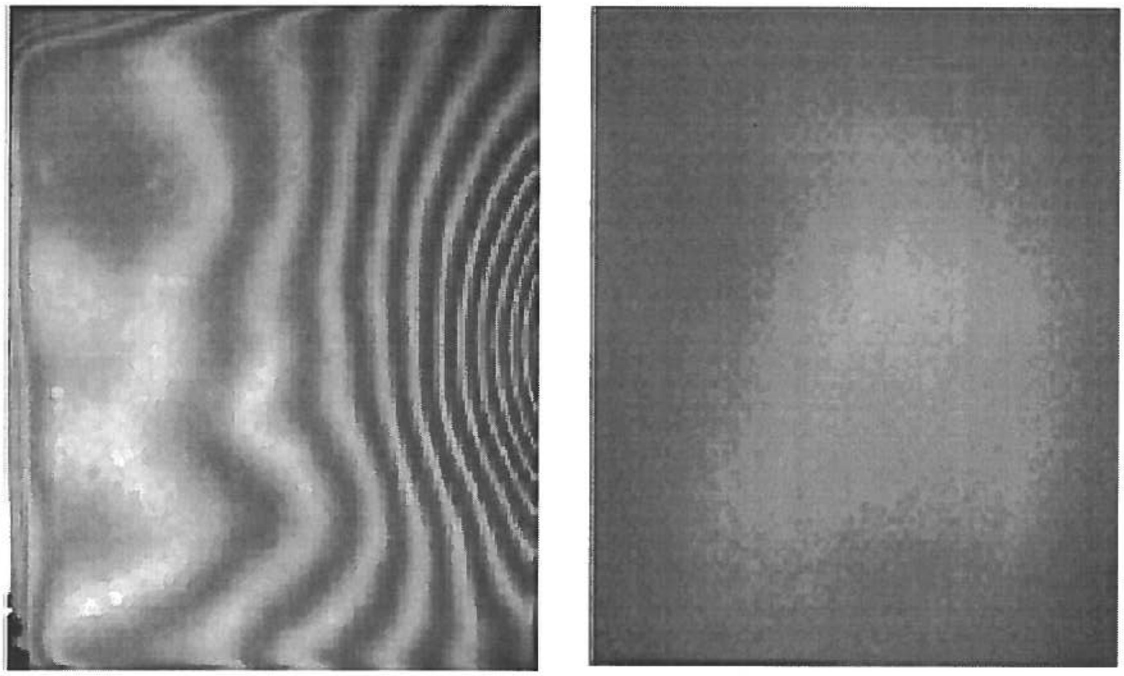


Fig. 7: *Whole film interferograms of amorphous silicon films, 35 cm x 45 cm. The fringes indicate regions of non-uniform film thickness. Left: with a single RF and ground connection at the right hand edge; Right: the improved film homogeneity obtained with a central back-face RF and ground connection.*

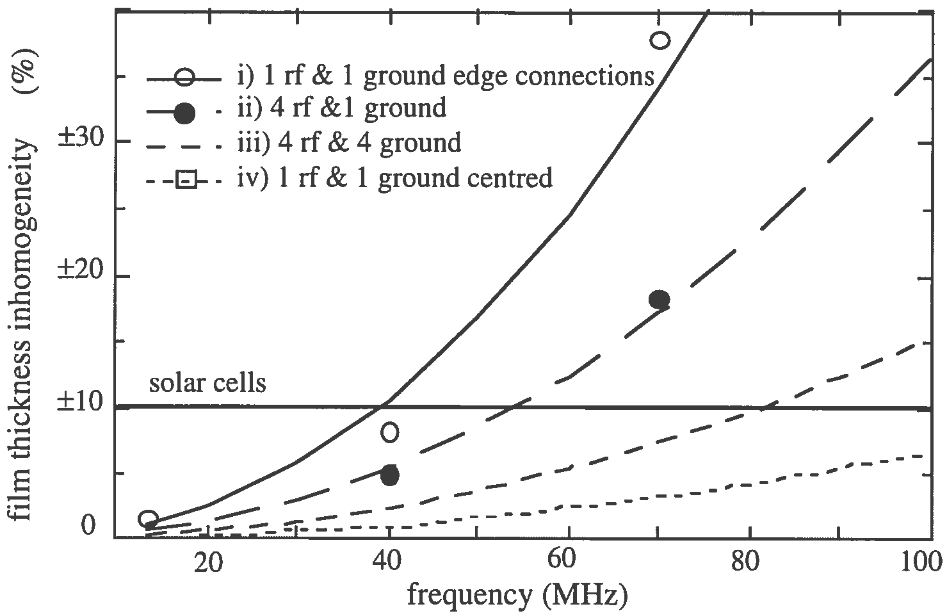


Fig. 8: *Measurements and model calculations of the film inhomogeneity as a function of RF frequency. With the optimal configuration of one centred RF and ground connection, VHF operation is well within the tolerance limits for industrial scale solar cell manufacture.*

Very High Frequency Efficiency and Deposition Rate: Silane Depletion Measurements

Using Fourier Transform Infrared Absorption Spectroscopy (FTIR) it was possible, for the first time, to *directly measure the efficiency of VHF plasmas in converting the silane working gas into radicals.* This step is clearly a mechanism of primary importance for initiating the deposition process.

The technique employed is as follows: the infrared source beam of the FTIR excites a silane molecule at its characteristic ro-vibrational frequencies, giving an absorption spectrum which is a 'fingerprint' of the molecule. The attenuation of the infrared intensity after crossing the plasma is a direct measurement, after calibration, of the concentration of silane molecules. Figure 9 shows a part of the silane transmission spectrum (the 'Q branch') for several conditions: With no plasma, the absorption is due to the silane supply gas. When the plasma is on, the absorption decreases (the transmission increases) because a fraction of the silane gas

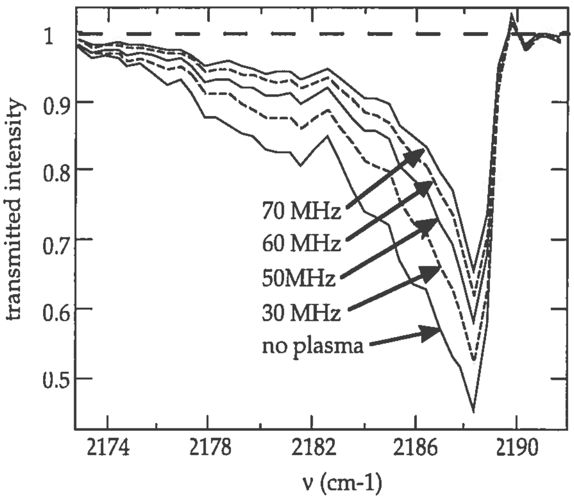


Fig. 9: *Infrared transmission spectra of silane (Q branch only) for different RF frequencies, and the deduced silane depletion fraction compared with the concomitant deposition rates. The VHF plasma is significantly more efficient in converting the silane to active radicals.*

has been converted into reactive radicals (which have other absorption frequencies) by electron collisions - the supply gas has been 'depleted'. These novel measurements were performed at constant process pressure, plasma power, and silane flowrate. It is clear from this raw data that the *VHF plasma is more efficient at converting the silane into reactive radicals* during its passage in the plasma. Figure 10 compares the deduced silane depletion fraction with the concomitant deposition rate of amorphous silicon. The elevated deposition rate of VHF plamas would appear to be due to a higher production rate of active radicals.

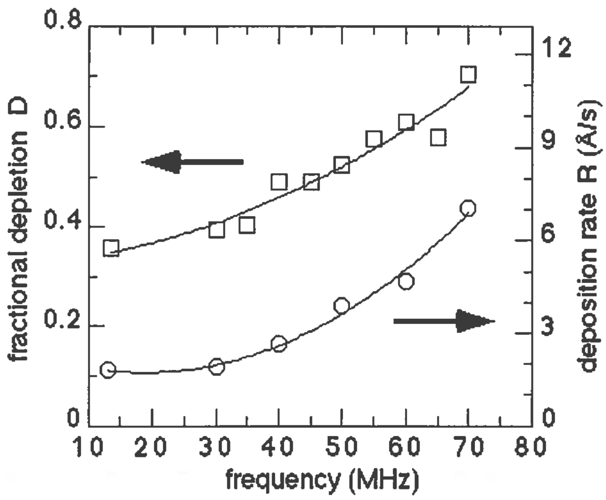


Fig. 10: *Dependence on the frequency of the silane fractional depletion and corresponding amorphous silicon deposition rate for a pure silane plasma at 0.2 Torr, 100 sccm, 80 W and 200 degrees C.*

A simple model based on gas phase density continuity equations shows that this increase in fractional depletion is due to *a factor four improvement in the electron impact dissociation rate at 70 MHz* compared with the conventional 13.56 MHz (see Fig. 11). This is largely responsible for the observed increase in the deposition rate with the frequency in VHF plasmas.

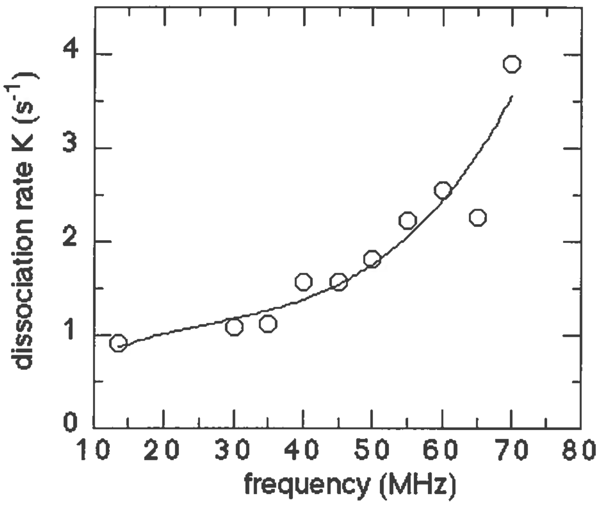


Fig. 11: Dependence on the frequency of the dissociation rate calculated from the fractional depletion measurements in Fig. 10.

These FTIR results were complemented by simultaneous measurements of the emission intensity and the electron density with the newly-developed microwave cavity diagnostic described above. The result is that *the improved dissociation rate is principally due to a concomitant increase in electron density in VHF plasmas* and not the electron temperature. Although such an increase has previously been proposed on theoretical grounds, along with various other theories, this is the first experimental demonstration of the VHF effect on electron density and dissociation rate. It is important to note that these unambiguous results were made possible because of the well-defined geometry and uniform plasma of the Balzers plasma box reactor, which proves the advantages of directly studying the final, industrial-scale reactor.

Finally, the FTIR method also gives a measurement of the silane gas utilisation efficiency by determining the fraction of undissociated gas and gaseous radicals which are removed by the pumping system instead of contributing to film growth; in this way the overall silane economy can be estimated and optimised.

Microcrystalline Silicon Deposition

Micro-crystalline silicon has been shown to be a useful material for solar energy in the novel 'micromorph' cells developed at IMT Neuchâtel. The CRPP aims to contribute to the optimisation of micro-crystalline deposition rates which are generally lower than for amorphous silicon. The newly-developed ellipsometric analysis was invaluable for determining the degree of crystallinity of the films deposited at the CRPP during this campaign.

A broad experimental investigation of plasma parameters clearly showed that a *necessary* condition for micro-crystalline silicon production is the complete depletion of silane gas (as measured using the FTIR diagnostic). Given our observation that VHF plasmas are more efficient in dissociating silane, this explains why it is that *VHF operation is naturally more effective for micro-crystalline deposition* than conventional frequencies, as borne out by empirical observation by IMT Neuchâtel and subsequently in other laboratories.

Further work confirmed that a copious source of atomic hydrogen is also necessary, probably for silicon atom 'rearrangement' mechanisms, for example by selective etching of disordered material. These observations led to a simple description in terms of gas continuity equations which graphically illustrate that the key factor is the *gas composition within the plasma*, which is generally not the same as the relative composition of the input gas flowrates, because of plasma dissociation and radical deposition. A corollary of this 'obvious' but often overlooked result is that it is not possible to define a universal recipe for micro-crystalline silicon deposition in terms of flowrates etc because factors which vary from reactor to reactor such as different pumping speeds for different gases must first be taken into account.

This understanding led us into unsuspected regions of parameter space where micro-crystalline silicon could still be deposited, such as in pure silane plasmas, which at first sight seem contrary to traditional recipes of highly-diluted silane/hydrogen plasmas. It reasonable to expect that novel operation régimes will eventually result in even more rapid deposition of good quality micro-crystalline material. Furthermore, a study of the dependence of deposition rates on fundamental control parameters such as flow rates, pressure, RF power and RF frequency demonstrates that optimal deposition rates are to be obtained from parameter scans by simultaneously changing more than one control variable - thus guaranteeing that the deposition rate is not unnecessarily reduced by neglecting to compensate, for example, for silane gas depletion by using insufficient flow during a power scan.

These micro-crystalline experiments are performed on the small PADEX reactor (substrate size 8 by 8 cm) and on the Balzers KAI-1 reactor (substrate size 35 by 45 cm). High RF power densities are advantageous for high rate micro-crystalline deposition, and this can be achieved in PADEX with our existing 200 W amplifier purchased at the very beginning of the project. A specific interest in the KAI-1 work is that large area uniformity of micro-crystalline films can be directly studied in an industrial environment thereby avoiding any uncertainty of future scale-up problems. However, to reach equivalent power densities, a 1 - 2 kW power amplifier will be necessary, and special attention will have to be paid to parasitic hollow cathode discharges and RF matching and feedthrough overheating due to the scaled-up currents. Nevertheless, we can already conclude that micro-crystalline films are as uniform as amorphous films and so present no particular difficulty for industrial applications from this point of view.

Numerical Simulation of Plasmas

Comparisons between polarisation-sensitive laser light scattering experiments in a small reactor and a plasma fluid numerical simulation have demonstrated the capability of the code to predict dust trap regions for various reactor geometries and substrate positions. Thanks to CRPP's contact, via the Brite-Euram project, with Dr. J.-P. Boeuf at Toulouse, this technique will shortly be applied to the large-area geometry of the Balzers reactor to map out the expected powder-trapping potentials for our reactor configuration. New electrode topologies to reduce powder trapping and deposition inhomogeneities can then be explored by the simulation before selecting a design for construction.

The physical origin of substrate residual charge after plasma extinction is as yet unknown; it may be due to stray self-bias potentials which persist momentarily during the post discharge. The two-dimensional RF plasma fluid numerical simulation, including dielectric substrates, could also be employed to investigate substrate potentials and charges during and after the plasma.

Alternative Plasma Sources for Amorphous and Micro-crystalline Silicon Deposition

Pilot studies were carried out to compare VHF deposition with alternative plasma sources, namely: inductively-coupled plasmas, hollow cathode arrays, and DC Arcs. Thermal expanding arcs produce sufficient quality a-Si:H at very high rates, and information was exchanged with the leading group in this domain (Professor Schram at the Eindhoven Technical Institute). The CRPP is particularly well-situated to study DC arcs through its experience with a parallel Balzers project on High Current DC Arcs for diamond deposition, since micro-crystalline silicon and diamond deposition both require copious atomic hydrogen production. The installation of silane for this experiment at the site in Ecublens was expressly to test the feasibility of the new DC arc method for high deposition rates of micro-crystalline silicon.

4) COLLABORATIONS, CONTACTS WITH INDUSTRY etc

Our group has benefited from excellent relations with Balzers SA in Liechtenstein and Palaiseau, France (Drs J. Schmitt, J. Perrin, E. Turlot, A. Galdos and J. Dutta), both materially and through gaining industrial expertise. The material aid from Balzers SA in terms of hardware, servicing and advice cannot be overestimated. The current phase of VHF film optimisation for micro-crystalline silicon is being pursued within the framework of our long-standing collaboration with the IMT Neuchâtel, especially regarding expert advice and provision of micro-crystalline samples for calibration and testing of the ellipsometer.

Fourier Transform Infrared spectroscopy was made possible by a collaboration with Eindhoven Technical Institute; an ellipsometer was acquired thanks to OFEN, Balzers SA and CRPP co-funding; Hiden Analytical Ltd offered a major revision and upgrade of our mass spectrometer; and Balzers SA loaned their plasma monitor to CRPP during 1996.

Our complementary Brite-Euram project improved our knowledge of powder formation in plasma reactors. Our contacts in this European task, which include the Ecole Polytechnique of Palaiseau (Drs. J. Perrin and P. Roca i Cabarrocas) and the Universites of Orleans (Prof. A. Bouchoule), Toulouse (Dr. J.-P. Boeuf), Eindhoven (Dr. G. Kroesen), Barcelona (Prof. E. Bertran) and Lisbon (Prof. R. Martins), allowed us to participate in an extended range of disciplines which we apply to the physics of the large-area reactor.

International interest in this work outside Europe is witnessed by invitations to several conferences in the USA and Japan and contacts have been established with, for example, Drs Selwyn (IBM), Shima (Sanyo Electric), Boswell (Australian National University), and Anelva Corporation (Japan).

The CRPP has profited from the assistance of several visitors to the laboratory. These include Dr. V. Nosenko from the Physics Institute in Kiev, Ukraine via a Schweizerische Akademie der Technischen Wissenschaften (SATW) exchange, who has launched and innovated our ellipsometer programme; and C. Monard via a 'stage' from the GREMI laboratory in Orleans, who carried out numerous measurements on FTIR and electron density etc; and several diploma students within the EPFL. A return exchange visit to CRPP funded by the COST programme and an EPFL diploma project at Eindhoven was organised with the leading group in thermal cascaded arcs for rapid a-Si:H deposition (group of Professor Schram at Eindhoven Technical University).

5) SUMMARY

Results

The crucial question of large area deposition uniformity with Very High Frequency plasma reactors has been solved both analytically and practically and is now published. The implementation of VHF plasma deposition on industrial scale reactors has been demonstrated and large area uniform films of amorphous and micro-crystalline silicon at VHF frequencies are now routinely produced using the newly-designed optimal electrode configuration.

Any remaining film inhomogeneity due to powder accumulation at the reactor edges can be eliminated by placing dielectric shims surrounding the substrate/electrode junction. RF power pulsing also reduces the deleterious effects of powder. The uniform showerhead has been proven to be the correct gas flow system for obtaining uniform plasma composition and deposition.

The underlying mechanism explaining the high rate of VHF plasma deposition has been clearly shown to be an enhanced dissociation rate due to increased electron density. These experimental results represent a breakthrough in the international plasma community concerning the efficiency and comprehension of the VHF technique. The data were obtained by the novel adaptation to an industrial reactor of infrared absorption and microwave resonant cavity methods. The technique can also be used to optimise deposition rate and silane economy.

It was found that the deposition of micro-crystalline silicon (μc-Si:H) occurs in conditions beyond complete depletion of silane in the plasma - this fixes the plasma parameters which are the most promising for rapid deposition. By virtue of its high dissociation rate, VHF is therefore particularly suitable for μc-Si:H production.

A range of diagnostic techniques and reactor modifications have been brought to the industrial environment. For the plasma: powder and light emission measurements, VHF matching and voltage distribution, ionic mass spectrometry, gas depletion and electron density measurements. For the silicon film: large area interferometry, estimation of micro-crystalline fraction by spectroscopic ellipsometry, and a diagnostic for substrate charge.

Infrastructure

This project has seen a major upgrade in the infrastructure of the laboratory following the CRPP's move to its new EPFL site in Ecublens.

The new laboratory is furnished with the latest industrial-standard gas handling, security and toxic gas elimination equipment (Gas Reactor Columns) financed by the Construction Fédérale, the EPFL and the CRPP. Importantly, the available range of semiconductor-industry reactive gases has been expanded six-fold, which will allow us to test alternative deposition chemistries such as SiF_4 addition. A possible upgrade of the industrial reactor VHF power amplifier to 1 or 2 kW is under consideration with CRPP funding, which represents a considerable investment on their part towards our OFEN project. Innovative plasma sources, for comparison with the proven VHF technique, were also made available for testing.

Conclusions

Volume production of solar cells in today's large plasma reactors is a complex, high-technology business which demands continuous developments in diagnostics and process control in order to guarantee sufficient yields of defect-free, economical solar panels. In this project, large area uniform film VHF deposition has been demonstrated and advanced diagnostics invented and implemented on an industrial prototype reactor (depletion, electron density, ellipsometry and electron attachment mass spectroscopy). Industrial awareness and interest for VHF processes has thus been stimulated, and the CRPP continues to acquire further expertise and know-how of industrial manufacturing methods. Our experience is that university laboratories are able to investigate new concepts in depth without the short-term distractions which habitually plague industry research programmes. This symbiosis of industry and university ultimately helps to improve the reactor and process; at the same time, diploma and doctoral students can profit from familiarisation with an industrial environment. It should be noted that production involving such technologies can only be envisaged with heavy industrial backing in view of the large-scale resources required. This end would be most effectively reached by the nurturing of mutual confidence between laboratory and industry as exemplified by the current style of this project. CRPP's experience with large-area reactors and the solar cell technology of IMT Neuchâtel promises well for a future production of amorphous solar cell panels by the VHF technique.

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