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Film Growth

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Crystallinity Uniformity of Microcrystalline Silicon Thin Films Deposited in Large Area Radio Frequency Capacitively-coupled Reactors

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ABSTRACT

The microcrystalline silicon (μc-Si:H) intrinsic layer for application in micromorph tandem photovoltaic solar cells has to be optimized in order to achieve cost-effective mass production of solar cells in large area, radio frequency, capacitively-coupled PECVD reactors. The optimization has to be performed with regard to the deposition rate as well as to the crystallinity uniformity over the substrate area. The latter condition is difficult to achieve since the optimal solar grade μc-Si:H is deposited at the limit between a-Si:H and μc-Si:H material, where the film crystallinity is very sensitive to the plasma process. In this work, a controlled RF power nonuniformity was generated in a large area industrial reactor. The resulting film uniformity was studied as a function of the deposition regimes. Results show that the higher the input silane concentration, the more the uniformity of the crystallinity is sensitive to the RF power nonuniformity for films deposited at the limit between a-Si:H and μc-Si:H. The effect of the input silane concentration on the microstructure uniformity could be explained on the basis of an analytical plasma chemistry model. This result is important for reactor design. In reactors generating nonuniform plasma the input silane concentration has to be limited to low values in order to deposit films with uniform microstructure. To benefit from the high silane flow rate utilization fraction encountered only for higher input silane concentration, the RF power distribution has to be as uniform as possible over the whole substrate area.

INTRODUCTION

Plasma enhanced chemical vapour deposition of silicon for large area microelectronics has to fulfil various objectives to achieve a successful production of devices such as TFT displays or low cost thin film photovoltaic solar cells. High deposition rate (≈10 Å/s) of silicon film, especially of microcrystalline silicon (μc-Si:H), is one of these objectives which for many years has been the centre of interest of research groups all around the world. The quality of the deposited films is of course also one of the major concerns to reach cost effective production of high-efficiency solar cells. Therefore, properties such as the crystalline fraction or the hydrogen content of the film have to be as uniform as possible (less than ± 10 %) over the whole substrate area, similarly for the film thickness uniformity. The film uniformity becomes a crucial issue when processing large area devices that nowadays can reach sizes of several square meters [1, 2]. Up to now, studies on the uniformity are mainly performed by industrial companies due to the scarcity of large area equipment in academic research laboratories. Moreover, these generally empirical studies are mainly focused on the uniformity of the deposition rate, i.e. uniformity of the film thickness, because generally it is assumed that to achieve a film with uniform properties one has to have a uniform deposition rate over, i.e. a uniform thickness.

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The present work is a study of the effect of an RF voltage perturbation in a large area radio-frequency PECVD reactor on both the film thickness and the film crystallinity. Two typical conditions for the deposition of microcrystalline silicon are compared. One is from a low silane input concentration (1 %) with a low RF power density, and the other is from a high silane input concentration (7 %) with a high RF power density. These two experiments show that the film thickness uniformity alone is not sufficient to obtain a uniform microstructure and that the crystallinity uniformity depends strongly on the deposition parameters. These results are interpreted on the basis of a simple analytical plasma chemistry model introduced in earlier work [3-5], and it is demonstrated that the higher the input silane concentration, the more the microstructure uniformity is sensitive to RF voltage nonuniformity.

EXPERIMENTAL ARRANGEMENT

Experiments presented in this work were performed in a modified version of a KAI-S (47 x 57 cm^2), radio-frequency (40.68 MHz) capacitively-coupled parallel plate reactor manufactured by Oerlikon AG. This reactor is not as large as actual production devices which are generally larger than 1 m^2. However, this reactor is much larger than parallel plate reactors conventionally used in research laboratories which are often cylindrical with diameter about 20 cm. The use of a large area reactor permits the study of film nonuniformities caused by sources other than edge effects such as the telegraph effect [6, 7] or the silane back-diffusion from the surrounding vacuum chamber [5, 8]. In the case of small open laboratory reactors, these effects are dominant and most of the plasma volume is dominated by edge effects, which makes it difficult to study the deposition uniformity in a controlled manner.

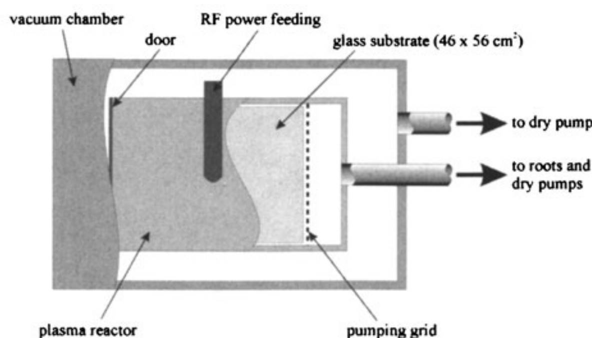

Figure 1: Top view of the KAI-S reactor based on the Plasma-Box™ concept with a unilateral pumping of the plasma reactor.

The reactor consists of a closed, grounded box with unilateral pumping as shown in Fig. 1. The 40.68 MHz RF power feeding is connected to a RF electrode suspended in the box (see Fig. 2b). This RF electrode acts also as a gas showerhead providing a uniform gas (SiH_4 and H_2) density distribution over the whole deposition area even with unilateral pumping [9].

In order to have a well-defined and controlled plasma nonuniformity, a non constant interelectrode distance was set across the width of the reactor, as shown in Fig. 2. The resulting

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variation in interelectrode distance is 3 mm (from 19 (left) to 22 mm (right)). The 46 x 56 cm^2 3 mm thick glass substrate, which covers almost the whole electrode area, was placed horizontally by using an insulator strip as shown in Fig. 2b. This precaution was taken in order to guarantee a constant gas residence time (constant plasma height of 16 mm) across the width of the reactor. This configuration results in a capacitive division of the interelectrode voltage as schematized in Fig. 2a, making the RF voltage amplitude across the plasma, U_p, higher for narrower interelectrode distance. The relative variation of U_p across the width of the reactor (Fig. 2b) can be estimated by using the model presented in Fig. 2a assuming two constant capacitive sheaths (width=3 mm) in series with a variable capacitance due to the vacuum under the glass substrate. Assuming a relation $P_{RF} \propto (U_p)^2$ between the RF power, P_{RF}, and U_p, the distribution of the RF power across the width of the reactor is almost linear with a total relative variation of ≈70 % as shown in Fig. 2b.

Two depositions were performed during 60 minutes with the following parameters:

- 500 W, 1 mbar, 1 % of silane, 20 sccm of silane, 1980 sccm of H_2, 230 °C and,
- 1000 W, 1 mbar, 7 % of silane, 20 sccm of silane, 265 sccm of H_2, 230 °C.

The crystalline volume fraction of the resulting films was estimated by micro-Raman spectroscopy. The Raman crystallinity was defined as the ratio of the area of the peaks associated with crystalline phase at 518 and 510 cm^{-1} to the sum of all Raman peaks including the peak associated with amorphous phase at 480 cm^{-1} [10]:

$$\phi_c = \frac{A_{518} + A_{510}}{A_{518} + A_{510} + A_{480}}.$$

This method is described in more detail elsewhere [4].

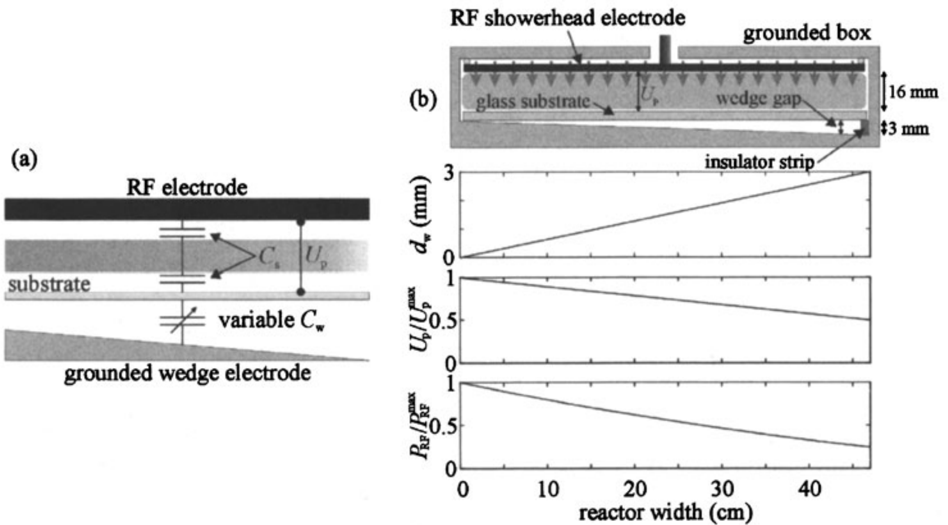

Figure 2: Lateral view of the wedge electrode design: (a) corresponding electrical circuit used to determine (b) the RF power relative distribution across the width of the reactor.

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The thickness uniformity was determined by light interferometry techniques. Two-dimensional interferograms of the whole substrate area were obtained using a diffuse white light source behind the coated glass substrate. The resulting light was then filtered at 720 nm before the interferogram acquisition with a highly sensitive camera. The thickness of the film was determined by white light reflectometry using a commercial reflectometer (NanoCalc2000).

RESULTS AND DISCUSSION

The two sets of deposition parameters were chosen in order to deposit films with microstructure at the transition from amorphous to microcrystalline silicon. This was chosen because the best PV cells are obtained when films are deposited in such conditions [11]. The film deposited with a 1 % input silane concentration was performed at low power (500 W) and high total flow rate (2000 sccm) in order to have a low silane depletion. On the other hand, for the film deposited from a high input silane concentration (7 %), the RF power has been increased to 1000 W and the total flow rate decreased to 285 sccm in order to obtain a high fraction of depleted silane necessary to achieve microcrystalline silicon. These two parameter sets correspond to two different regimes, named Regime 1 and Regime 2 in previous work [4].

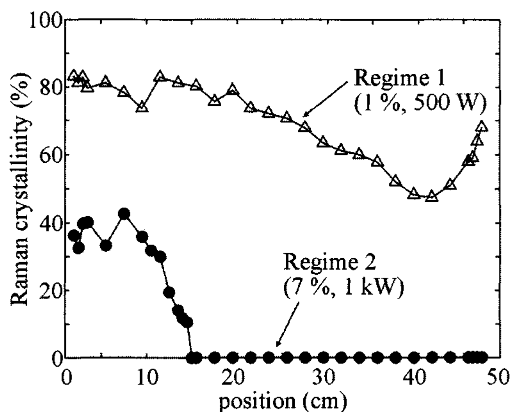

Figure 3: Raman crystallinity across the width of the reactor for two conditions: Regime 1 with a silane concentration of 1 % and a RF power of 500 W, and Regime 2 with a silane concentration of 7 % and a RF power of 1 kW.

Figure 3 presents the results of the Raman crystallinity measured across the width of the reactor in the central part of the substrate for the two different regimes. It shows that, depending on the deposition regime, the effect of the given RF power distribution is very different. In the case of Regime 1 at low silane concentration and RF power, the crystallinity is everywhere higher than 50 % and decreases only a little from the high plasma density side to the low plasma density side of the wedge reactor. However, the variation of the Raman crystallinity is small compared to the 70 % variation of the RF power across the reactor.

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On the other hand, for the film deposited in Regime 2 at high silane concentration and RF power, the Raman crystallinity falls abruptly from 40 % to 0 % at 10 cm from the reactor edge. The conclusion is that the RF power nonuniformity created by the wedge electrode has a very different effect depending on the deposition regime.

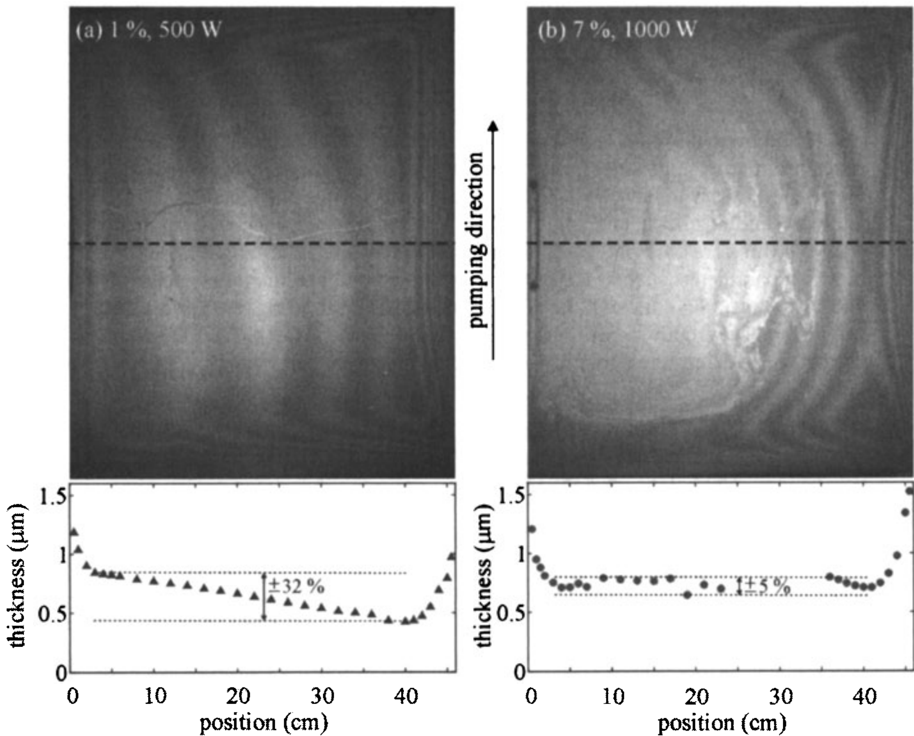

Figure 4: Thickness uniformity determined by (top) 2D monochromatic (720 nm) light interferometry and (bottom) white light interferometry across the width of the substrate following the dashed lines on the interferograms.

The transition from microcrystalline to amorphous silicon cannot be attributed to a difference in deposition rate as shown by thickness uniformity measurements presented in Fig. 4. Indeed, the zone where the microstructure transition occurs is almost flat (± 5 %). Neither can it be attributed to the amorphous incubation layer thickness generally observed before the growth of microcrystals, because the films are everywhere thicker than 400 nm, which is larger than amorphous incubation layer thickness generally observed. Moreover, in Plasma-Box™ type reactors, i.e. a closed and directly pumped reactor, the plasma chemistry transient at ignition is only about 1 second and cannot be at the origin of a thick incubation layer [5]. The thickness profiles presented in Fig. 4 also confirm the fact that nonuniformities due to edge effects are restricted to a 5 cm strip from the edge of the reactor. There, the increase of thickness on the substrate at the wall has two different sources: (i) the telegraph effect induced by the asymmetry

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between the RF and the grounded electrodes, and (ii) more intense plasma at the wall due to the geometrical edge of the RF electrode.

The absence of thickness measurements between 25 and 35 cm in the case of Regime 2 is due to film peeling off the substrate making the optical measurement inapplicable. However, micro-Raman spectroscopy is still able to determine the crystallinity because spectra can be acquired even from peeled films.

Plasma composition

In previous work [4], it was shown that the plasma composition, i.e. the silane concentration in the plasma, is a determining parameter for the film microstructure. It was shown that it is necessary to have a silane concentration in the plasma lower than 0.5 % to obtain microcrystalline silicon, and that for silane concentration in the plasma higher than 1.2 % the resulting films are amorphous. These two microstructure zones are separated by a transition zone in which parameters such as the pressure or the ion bombardment may determine the final microstructure. Nevertheless, the silane concentration in the plasma principally determines the two different crystallinity profiles presented in the present work. The silane concentration in the plasma, c_p, is determined not only by the input silane concentration, but by the relation

$$c_\mathrm{p} = c \cdot (1 - D),$$

between the input silane concentration, c, and the fractional silane depletion in the plasma, D, defined as the ratio

$$D = \frac{p^0_{\mathrm{SiH_4}} - p_{\mathrm{SiH_4}}}{p^0_{\mathrm{SiH_4}}},$$

where $p^0_{\mathrm{SiH_4}}$ and $p_{\mathrm{SiH_4}}$ are the silane partial pressure in the gas before plasma ignition and in the plasma, respectively. The RF power distribution in Fig. 2 causes a variation of the silane depletion across the width of the reactor, and hence the silane concentration in the plasma increases from the left-hand-side to the right-hand-side of the reactor (neglecting edge effects). However, this alone is not sufficient to explain the different behaviour between the two experiments presented here.

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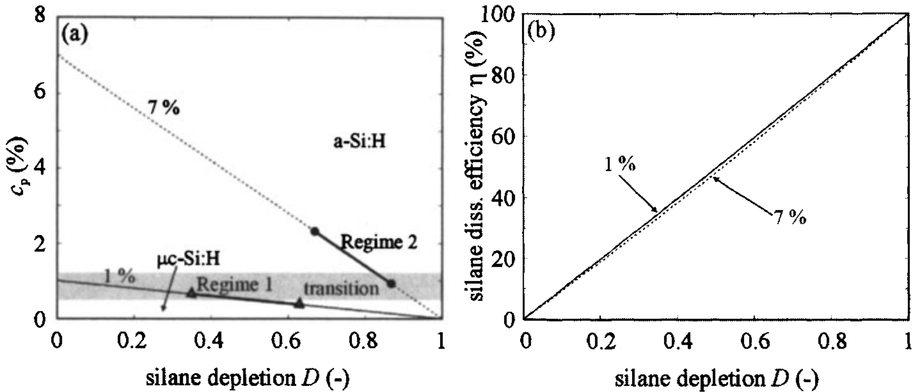

Figure 5: (a) Silane concentration in the plasma, c_p, and (b) silane dissociation efficiency, η, as a function of the silane depletion for the two experimental conditions Regimes 1 and 2, with corresponding estimated silane depletion range of 0.35-0.63 and 0.67-0.87, respectively.

Figure 5a presents the silane concentration in the plasma as a function of the silane depletion fraction for the two present cases: Regime 1 (1 %) and Regime 2 (7 %). The difference in slope of the two regimes shows clearly that they have a different impact on the plasma composition for a nonuniform silane depletion as in the present case. With an input silane concentration of 1 %, the deposition is everywhere – i.e. independently of the silane depletion - in the microcrystalline zone ($c_p < 0.5$ % in Fig. 5a) or at least in the transition zone between μc-Si:H and a-Si:H (0.5 % < c_p < 1.2 % in Fig. 5a). For higher concentration, this is no longer the case. The strong gradient of the silane concentration in the plasma as a function of the silane depletion makes the microstructure of the deposited film nonuniform for film deposited at the limit between a-Si:H and μc-Si:H, where the PV cells show the best performances [11]. This explains why in Fig. 3 the microstructure uniformity between the two Regimes is so different for the used parameters, i.e. at the transition between a-Si:H and μc-Si:H.

However, even if the uniformity of the plasma composition varies strongly from one case to the other, the silane dissociation efficiency, η, defined as the ratio between the silane dissociation rate ($kn_e n_{SiH_4}$) to the silane flow rate (Φ_{SiH_4}) [3, 4]

$$\eta = \frac{kn_e n_{SiH_4}}{\Phi_{SiH_4}} = \frac{D}{1+(1-D)c}$$

is almost independent of the input silane concentration, as shown in Fig. 5b. The silane dissociation efficiency is mostly determined by the silane depletion fraction and depends only little on the input silane concentration. This explains why even with a strong plasma composition nonuniformity, the thickness profiles of the two Regimes are similar in Fig. 4. Moreover, it shows that having a uniform thickness does not guarantee a uniform microstructure.

However, for the case of Regime 2 (7 %) the thickness profile is more uniform (± 5 %) in the central region which is not affected by edge effects than the case at lower silane concentration (± 32 %). This effect may be attributed to the different range in silane depletion fraction between the two experiments. In the case of Regime 1, the parameters are a low RF

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power (500 W) and a high total flow rate (2000 sccm). This corresponds respectively to a low electron density, n_e, and a high pumping rate, a. Therefore, the dissociation rate over the pumping rate ratio is low, making the silane depletion fraction also low, i.e. about 0.35 to 0.63 (± 28 %), since it depends on kn_e/a, where k is the silane dissociation constant, following the expression [4]

$$D = \left(1 + \frac{a/kn_e}{(1+c)}\right)^{-1}.$$

This dependence is plotted in Fig. 6, and it shows that for low kn_e/a ratio corresponding to the Regime 1, a given variation of the electron density such as the one resulting from the wedge electrode design of the reactor used in the present study (here 70 %), induces a strong variation of the silane depletion fraction. On the other hand, for deposition in the microstructure transition zone with higher input silane concentration, i.e. higher kn_e/a ratio, the silane depletion fraction is less sensitive to electron density variation because of the asymptotic behaviour of $D=D(kn_e/a)$. The silane depletion variation induced by the 70 % variation of n_e is estimated from Fig. 6 to be lower than 0.2 (± 12 %) in the Regime 2. Consequently, the silane dissociation efficiency is more uniform across the reactor, making the film thickness more uniform as shown in the central part of Fig. 4 where edge effects such as intense plasma due to the proximity of ground and RF electrodes have no influence on the plasma. This is not in contradiction with the strong nonuniformity in microstructure observed in Fig. 3 since for films deposited at the limit between a-Si:H and μc-Si:H, even a silane depletion fraction variation as low as 0.1 may induce a change in microstructure.

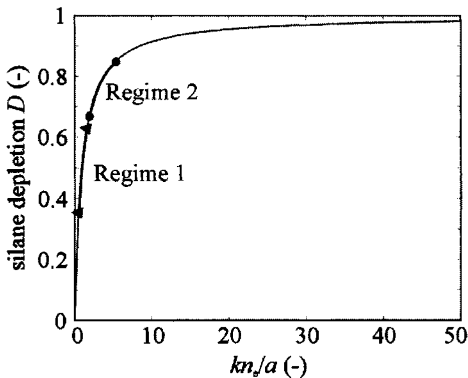

Figure 6: Silane depletion fraction as a function of the ratio of the dissociation rate (kn_e) to the pumping rate (a). The two regimes corresponds to a 70 % variation of the electron density n_e.

Impact on large area production reactor design and manufacturing

Up to now, only an intentional nonuniform voltage across the plasma has been discussed. However, even in parallel plate reactors, i.e. without wedge electrode, nonuniform voltage

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