LOW POWER HIGH GROWTH RATE DEPOSITION OF MICROCRYSTALLINE SILICON

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ABSTRACT: Microcrystalline growth regimes and solar cells obtained in different pressure and silane depletion conditions are studied in a large area KAI-S plasma reactor. The microcrystalline material quality is systematically investigated by Fourier Transform Photocurrent Spectroscopy (FTPS) to evaluate the defect density. It is shown that higher pressure and silane depletion positively affect the material quality. A clear correlation between FTPS measurements and cell efficiency is established, showing that the limiting factor is the material quality of the intrinsic microcrystalline layers. The highest efficiency achieved so far is 8.2% for a 1.2 μm thick microcrystalline solar cell deposited at ~3 Å/s on glass coated with ZnO deposited by low pressure chemical vapor deposition. The efficiency drops to 6.4% for solar cells deposited at 9 Å/s in conditions where silane powder is present in the plasma. Upon modifying the reactor geometry in order to suppress powder formation, solar cells achieve 7.0% efficiency at 12 Å/s. The results can be described by pressure and silane depletion dependent ion bombardment. Transition curves from amorphous to microcrystalline are studied, revealing ion bombardment induced amorphization of the layer at low pressure and low silane depletion. Modeling of the ion energy bombarding the substrate supports this interpretation.

Keywords: Thin Film Solar Cell, Micro Crystalline Si, High Deposition Rate

1 INTRODUCTION

Microcrystalline silicon is a composite material embedding silicon nanocrystals in an amorphous matrix [1]. It has attracted much research efforts in the photovoltaic domain [2], because of its potential for integration in a tandem cell concept as bottom cell with an amorphous silicon top cell. Efficiencies of micromorph tandem cells and modules well above 10% have thus been demonstrated [3]. However, many efforts have still to be made in order to improve the overall comprehension of the μc-Si:H growth by plasma-enhanced chemical vapor deposition (PECVD). For instance, because of its thick active layer requirement (between 1.5 and 2.5 μm), μc-Si:H material has to be grown at high deposition rates while retaining high material quality. As of today, this seems to be the main concern for lowering industrial manufacturing costs.

A wide range of parameters have to be taken into account for this problem, such as hardware parameters: electrode geometry or shape, inter-electrode distance, operating frequency, etc. and process parameters, easily adjustable for a given reactor: power density, pressure, substrate temperature and gas flows.

Thus, because of the complex structure of the material that depends on deposition conditions [1, 4] and substrate properties [5], and due to the difficulty of characterizing plasma deposition regimes, the impact of all these parameters on the microcrystalline material quality is still an open field of research.

In this paper, microcrystalline silicon thin films are deposited in different conditions of pressure and silane depletion and following a recent publication [6, 7] a novel low power regime for high rate deposition is investigated. It is shown that by increasing the pressure and reducing the hydrogen flow, the microcrystalline material quality can be greatly improved. Structural material characterization of deposited μc-Si:H layers is presented and solar cells are prepared. The material quality (i.e. defect density and Urbach tail) in different deposition regimes is evaluated systematically by Fourier Transform Photocurrent Spectroscopy (FTPS) [8]. A significant correlation of the intrinsic material quality with the solar cell efficiency is observed, and an interpretation in terms of ion bombardment energy is proposed.

2 EXPERIMENTAL

Microcrystalline silicon layers were deposited by very high frequency (VHF) PECVD at 40.68 MHz in large area KAI-S and KAI-M reactors (0.16 m² and 0.25 m² substrate size, respectively) based on the plasmabox concept [9], using silane and hydrogen as gas precursors. During deposition, the peak to peak voltage V_{pp} was measured on the RF driven electrode using a calibrated high impedance capacitive gauge connected to an oscilloscope. The samples were analyzed by micro Raman spectroscopy [10]. Solar cells were deposited in the p-i-n configuration in the same reactor in a single chamber process on ZnO coated glass substrates [11]. The ZnO layers were obtained by low pressure chemical vapor deposition. The same doped layers and a 100 nm thin intrinsic buffer layer at the p/i interface were used in all depositions and only the 1.1 μm thick bulk intrinsic layers were varied. The solar cell surface was 0.25 cm² and the solar cells were characterized by I-V measurements using a WACOM sun simulator and by spectral response measurements to determine the external quantum efficiency. The short-circuit current density is calculated from the measurement of the external quantum efficiency (EQE) curve, by integrating, over the wavelength range from 350 to 1000 nm, the product of EQE times the incoming spectral density of photon flux of the solar spectrum.

The material quality of the absorbing μc-Si:H layer incorporated in each cell was evaluated through FTPS measurements. The absorption coefficient of low-energy (sub-gap) photons gives important information on the electronic quality of the material: concentration of dangling bonds, i.e. defect density or recombination centers have a significant impact on the Urbach tail, and the signal at 0.8 eV gives an estimation of the midgap defect density. The measurement being very sensitive to the type of ZnO used (variations of light diffusion and level of free carrier absorption) particular attention was
given to make sure that all cells were prepared using the same type of contacts. Calibration of the absorption curves was performed at 1.35 eV at the corresponding absorption coefficient of crystalline silicon.

3 RESULTS AND DISCUSSION

Fig. 1 displays the I(V) characteristics of three solar cells deposited in different pressure and silane depletion conditions. High depletion is achieved by increasing the residence time of the gas molecules in the reactor (i.e. decreasing the hydrogen flow). All cells were deposited with the intrinsic layer near the transition region at roughly 60% Raman crystallinity. Two intrinsic layers deposited at 1.2 mbar and at 3.5 mbar are in low silane depletion regimes whereas the third intrinsic layer deposited at 1.2 mbar is in the high depletion regime. The efficiency of the cells is 8.2% at 3.5 mbar, 6.6% at 1.2 mbar (high depletion) and 3.6% at 1.2 mbar (low depletion).

Remarkable improvements are observed for the cells prepared at higher pressure or silane depletion. Both the open-circuit voltage ($V_{oc}$) and fill-factor (FF) are increased significantly, going from 0.34 V to 0.52 V and from 52% to 72%.

In order to understand this improvement, further tests were carried out to analyze the material defect density. This was done through FTPS measurements, and the results can be seen in Fig. 2. The solar cell with its intrinsic layer prepared in low depletion conditions at 3.5 mbar shows a sub-gap absorption coefficient way below the 1.2 mbar one. At 0.8 eV a difference larger than one order of magnitude is observed, indicating that the defect density of the material is indeed significantly lower when deposited at higher pressure. The cell prepared at 1.2 mbar but in high depletion conditions shows an intermediate value in agreement with the cell result. The correlation with the overall electrical cell performances is straightforward, leading to higher FF and $V_{oc}$ for lower mid-gap defect density material.

We interpret the difference of material quality observed with varying pressure and silane depletion as an indication that ion bombardment energy plays an important role in the deposition process.

As the deposition pressure is lowered, the capacitive sheaths become less collisional, allowing more energetic ions to impinge on the substrate, which in return is detrimental to the material quality. In the case of higher silane depletion, the plasma potential, deduced from measurements with the voltage probe, decreases and reduces the ion energy (see Fig. 3). A reduction of the DC bias voltage can be observed in the same figure as well. The two cells at 1.2 mbar in Fig. 1 were deposited with hydrogen flows corresponding at the extremum of the points plotted in Fig. 3. For comparison, the plasma potential for the cell deposited at 3.5 mbar is 115 V.

In order to validate our interpretation transition curves from amorphous to microcrystalline were measured as a function of RF input power. The results are given in Fig. 4. As the power density is increased, the three regimes exhibit quite different behaviors. At 3.5 mbar and at 1.2 mbar in the high depletion regime, the increase in power density of the discharge results in a monotonous increase of the crystallinity, going from a complete amorphous phase at low power to a highly crystalline material at high power. The width of the transition is different and depends on the plasma conditions [12]. In the low pressure, low depletion regime instead, the crystallinity...
fraction increases slowly and even decreases for power densities higher than 0.14 W/cm².

![Raman crystallinity as a function of input RF power prepared in different pressure and silane depletion conditions. The lines are a guide to the eye.](image)

Fig. 4: Raman crystallinity as a function of input RF power prepared in different pressure and silane depletion conditions. The lines are a guide to the eye.

A decrease in crystallinity cannot be easily explained as higher RF power should favor the growth of material with a higher crystalline fraction. It has been proposed in the past that ion bombardment is an important factor determining the microcrystalline material quality [1,13,14] and that it affects the crystallinity as well [1]. The average ion energy $e_i$ impinging the surface can be estimated from the $V_{pp}$ probe and is depicted in Fig. 4. It is calculated in the case of collisional sheaths as [15]:

$$e_i = 0.62 \frac{\lambda_i}{s_m} \bar{V}.$$  

$\lambda_i$ is the mean free path, $s_m$ the sheath length and $\bar{V}$ the time averaged voltage across the sheath. It can be seen that the ion bombardment energy is in the same range on which crystallinity is significantly affected [1], thus further supporting our interpretation.

![Solar cell efficiencies as a function of the deposition pressure and silane depletion (black). The mean ion energy was calculated for each deposition regime (red). The lines are a guide to the eye.](image)

Fig. 5: Solar cell efficiencies as a function of the deposition pressure and silane depletion (black). The mean ion energy was calculated for each deposition regime (red). The lines are a guide to the eye.

A summary for all solar cell depositions is displayed in Fig. 5. As can be seen, there is a clear trend indicating that deposition of intrinsic $\mu$-Si:H at higher pressure is beneficial for cell performances. Increasing silane depletion at a given pressure improves as well the solar cell efficiency in conditions where powder formation is not important. At higher pressures, around 2.0 mbar, powder formation becomes an issue and modifications to the reactor are necessary in order to reduce it and to further improve cell efficiency and deposition rate to 7.0% and 12 Â/s. The black dots on the line are solar cell efficiencies obtained in low depletion conditions at different pressures, whereas the black dots off the line are efficiencies obtained in high depletion conditions. The same holds for the mean ion energy (red dots). As can be seen high depletion deposition conditions are characterized by lower ion energies.

4 CONCLUSIONS

Single junction microcrystalline $p$-$i$-$n$ cells were prepared with an intrinsic layer deposited in different pressure and silane depletion conditions. It is observed that solar cells made at higher pressures and depletion exhibit significantly higher performances. FTPS measurements of $\mu$-Si:H intrinsic layers included in the solar cells concur with this observation: with increasing pressure the defect density is significantly lowered, which is an indication of improved electronic material quality. $\mu$-Si:H transition curves measured as a function of RF power and calculations of the average ion energy impinging on the substrate suggest that ion bombardment is responsible for these differences.

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6 REFERENCES