Solar-Cell Suitable µc-Si Films Grown by ECR-CVD

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ABSTRACT

The preparation of µc-Si films from SiH_4-H_2 mixtures by electron-cyclotron resonance (ECR) CVD at deposition temperatures ≤ 400°C on foreign substrates is reported. Deposition conditions were identified for which Si films with a high degree of crystallinity were grown as was confirmed by Raman spectroscopy. A factorial analysis was carried out, for which the influence of deposition temperature, microwave power, hydrogen dilution and total pressure on film growth were investigated. Samples of optimized crystallinity were prepared in a low-pressure and high-hydrogen dilution regime. In-plane grain sizes were measured by TEM and found to be on the order of 10 - 12 nm. Next to the optimization of crystallinity several sources of impurity contamination during film deposition were identified and eliminated. Intrinsic µc-Si layers could be prepared under these conditions that exhibited a dark conductivity σ_d of 2×10^{-7} S/cm and photosensitivity σ_{ph}/σ_d of 150. It is concluded that ECR CVD is capable of producing intrinsic layers with electronic properties as necessary for use in state-of-the-art *n-i-p* µc-Si solar cells.

INTRODUCTION

One of the key issues for a large scale production of thin-film silicon solar cells is to find deposition techniques that allow high deposition rates and at the same time yield material of high crystallinity. In addition, low-cost substrates such as glass limit the deposition temperature to range up to a few hundred °C at maximum. One technique that seems to fulfill most of the requirements is plasma-enhanced electron-cyclotron resonance (ECR) chemical vapor deposition. The plasma is generated in the ECR process via resonant absorption of a microwave by electrons in a magnetic field and gas ionization via subsequent electron-atom collisions. By the application of this plasma-generating principle, the total process pressure may typically lie in the mTorr range, which is 1-2 orders of magnitude lower than in the usual parallel-plate plasma-enhanced CVD (PECVD). Because the average mean free path of particles in the gas-plasma phase exceeds the thickness of the plasma sheath, the generated ions are not affected by collisions on their way to the substrate, and they impinge with a rather sharp and well defined energy distribution. Thus, ECR CVD enables an improved control of the deposition process. Moreover, the high plasma density achieved by the ECR techniques also results in high deposition rates. The advantages of ECR have mainly been demonstrated in the field of anisotropic etching so far [1]. Here, we will demonstrate that with ECR CVD it is also possible to deposit undoped microcrystalline silicon films (µc-Si) which are suitable as absorber layers in µc-Si *n-i-p* solar cells. The aim of our work was to find optimized deposition parameters through a factorial analysis resulting in a high degree of crystallinity of the µc-Si films. It will be shown that µc-Si films can be prepared with dark conductivities in the range of 10^{-7} S/cm and a photoresponse exceeding the dark conductivity by more than a factor of 100 under AM1.5 illumination.

DEPOSITION SYSTEM

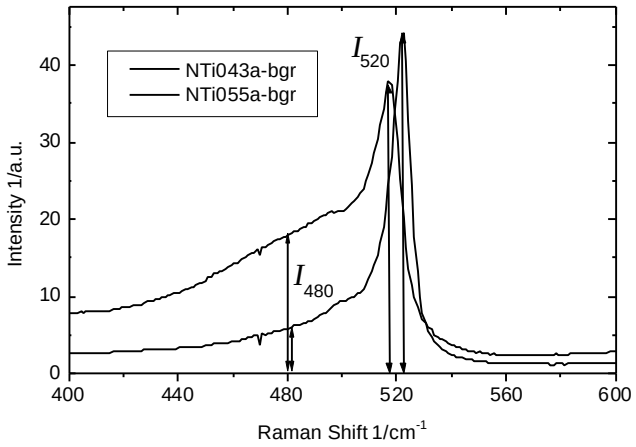
An ECR system that has been described previously [2] was employed for the depositions. The plasma is excited within an ASTex ECR plasma source, into which a 2.45 GHz microwave is coupled via a quartz glass window. The deposition chamber of 40 cm diameter is situated underneath the cylindrical ECR source. The chamber walls were water cooled during most depositions. The 8" susceptor upon which substrates were placed rests on a heatable chuck and the distance between the center of the plasma region and the susceptor can be varied from 58 to 70 cm. The total volume of the system amounts to 90 L while the internal surface area is about 1.4 m^2. Evacuation of the chamber down to high-vacuum regime is performed by an oil-free 1000 L min^{-1} turbomolecular pump providing a residual gas pressure between 5 and 50×10^{-8} Torr. The outgassing rate was determined by measuring the pressure rise with time to typically amount to 6×10^{-6} mbar L^{-1} s^{-1} for a chuck temperature of 400°C and cooled chamber walls. Gases are supplied via an inlet valve in the ECR region for the working gas H_2 and via a ring situated above the susceptor for the process gas SiH_4 in H_2. The total pressure was regulated via a throttle valve to 7 mTorr and the substrate temperature was set to 325°C (chuck 550°C) during most depositions presented in this work. A regular cleaning of the chamber was necessary to reduce the formation of flakes and to ensure that the quartz window through which the microwave is coupled into the plasma zone was uncoated. For this purpose a NF_3 plasma cleaning was employed which led to a continuos background of fluorine in the residual gas phase. The µc-Si films prepared in the chamber, therefore, contained fluorine in the range of some 0.1 %. But this contaminant turned out not to be deleterious to the electronic properties which is in accordance with other work where µc-Si films were prepared from F-containing precursors [3].

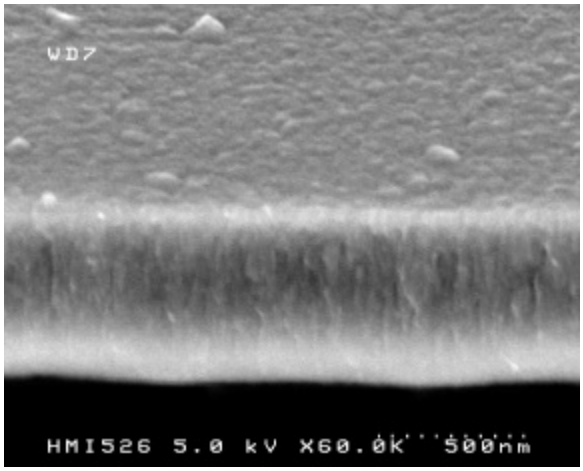
OPTIMIZATION OF µc-Si CRYSTALLINITY & GROWTH

In order to identify the optimum deposition conditions for thin films with a high degree of crystallinity a factorial analysis [4] was performed. The layers as prepared on fused silica substrates were investigated by Raman spectroscopy. As a figure of merit for the degree of crystallinity we used the Raman intensity ratio at 520 to 480 cm^{-1}, $I_{520}/I_{480} = y$, accounting for the Raman bands of crystalline silicon and amorphous silicon, respectively. The intensity ratio y served as response function. The deposition temperature T, the microwave power L, hydrogen dilution H, and the total pressure p_{tot}, which were considered as the most significant deposition parameters, served as independent variables x_i in the factorial analysis. The linear coefficients a_i and the first mixed coefficients a_{ij} can then be derived by expanding the response y into a Taylor series of independent variables x_i

$$y \cong a_0 + \sum_i a_i x_i + \sum_{ij} a_{ij} x_i x_j \qquad (1)$$

The linear expansion yields only an approximation of y. We assume it to serve as a practical description of the response within the limited range of investigated parameter space. All depositions were carried out with fixed values for the deposition time of one hour and a process gas mixture of 4 sccm SiH_4 in 10 sccm H_2. The corner points investigated were 250 and 325°C





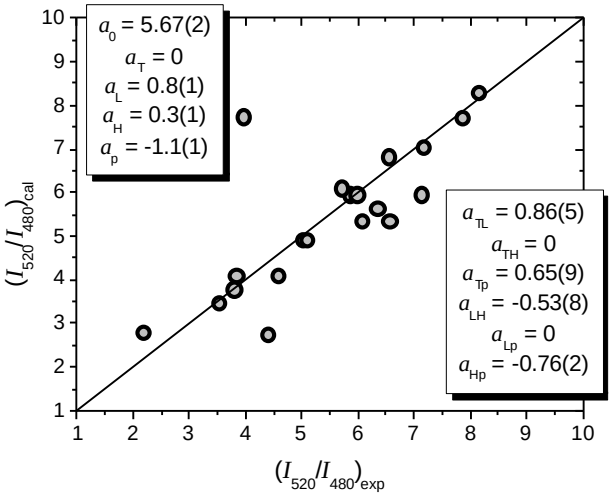
Figures

1. *Raman spectra of two samples as prepared within a factorial analysis of the ECR-CVD system, exhibiting the smallest, y = 2.4, and largest, 8.4, values for the intensity ratio I_{520}/I_{480}.*
2. *SEM micrograph of the sample having the largest Raman intensity ratio, I_{520}/I_{480} = 8.4. The picture was taken at an angle of inclination of 30°.*

for T_{dep} (x_1), 500 and 1000 W for L (x_2), 30 and 80 sccm for the flow of the H_2 working gas (x_3), and 7 and 10 mTorr for p_{tot} (x_4). In addition, some intermediate points in the four-dimensional parameter space have also been investigated. Corner points and intermediate points were normalized to x_i = -1, 0, 1, so that the significance of the system coefficients a_i and a_{ij} can directly compared by their magnitude. 24 depositions were performed in total.

Figure 1 displays the Raman spectra of those two depositions that yielded the smallest and the largest intensity ratio I_{520}/I_{480}, i.e. $y = 2.2$ and $y = 8.4$. The sample having $y = 8.4$ clearly exhibits a high degree of crystallinity, which is corroborated by the SEM picture given in Fig. 2. The system coefficients a_i and a_{ij} were determined by a multi-dimensional regression of the formula given above to the measured y values. Figure 3 displays the theoretical y values as calculated by substituting a_i and a_{ij} into the formula as a function of measured y values. In addition the coefficients a_i , a_{ij} are given in the figure. All values lie close to a line of slope 1, which indicates a perfect linear relation between y and x_i and a deposition system with ideal reproducibility. We conclude from the plot that the coefficients give a reliable description for the relation between deposition conditions and the obtained degree of crystallinity.

Regarding the deposition conditions of the sample with the highest degree of crystallinity, which were 325°C/7mTorr/1000W/80sccm, two of these parameter values might have been expected. The first one is that the highest y values were found for higher deposition temperature. It is interesting to note however, that a vanishing linear temperature coefficient, $a_T = 0$, was obtained. Accordingly, the deposition temperature does not directly enhance the crystallinity, but I_{520}/I_{480} increases due to the combined effect of temperature and microwave power or total pressure, which can be seen from a_{TL}, $a_{Tp} > 0$. This indicates a predominant influence of particle energy on the evolution of crystalline film growth, which is not yet understood in detail. Our



3. *$y = I_{520}/I_{480}$ values as calculated by the coefficients given in the plot versus experimental y values. The line of slope 1 would have been obtained for a perfect linear dependence of y on parameters x_i and a deposition system of ideal reproducibility.*

4. *In-plane TEM micrograph of an undoped µc-Si sample as prepared under standard conditions.*

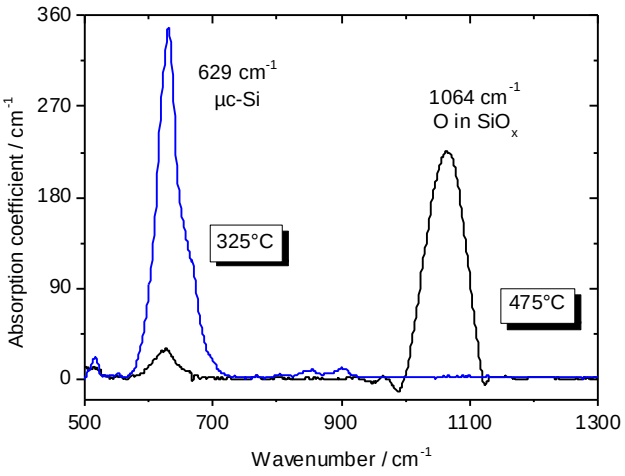
study also reveals that a high crystallinity is obtained for a high hydrogen dilution, x_4 = 80 sccm. This result is in accordance with many investigations of the microcrystalline-amorphous phase boundary of thin silicon films that have been prepared by other deposition techniques like PECVD for instance. The optimum values obtained for the two other parameters, i.e. that the highest degree of crystallinity is observed with the highest microwave power L and for the lowest total pressure p_{tot} may not as easily be understood from the present knowledge of µc-Si growth. These effects are probably due to complex interactions between the process parameters as can be seen from the large mixed coefficients a_{ij}. We conclude from the factorial analysis that µc-Si films with a high degree of crystallinity can be prepared by ECR. The optimum deposition parameters served as standard parameters for the following investigations.

A thickness series of samples was deposited under the optimized conditions in order to gain a deeper insight into the growth of ECR-prepared µc-Si films. Depositions were performed on molybdenum-coated Corning glass 1737F by setting the deposition time t to 15, 30, 60, 120 and 240 min. The structure of the samples was characterized by infra-red spectroscopy, X-ray diffraction (XRD) [5] and transmission electron microscopy (TEM). Thicknesses d were determined from interference maxima of FTIR spectra measured in the reflection mode. The five d values were found to follow a linear relation, $d(t) = a + bt$, where b accounts for the deposition rate having b = 12 nm/min. The growth of an initial phase distinct from µc-Si is indicated by the fact that a = 48(5) nm > 0 was found. We have shown that the initial growth of the films

yielded an amorphous layer [5]. This layer grows to a thickness of about 10 nm, where the growth of silicon crystallites begins and which continuously proceeds from thereon. Fig. 4 displays an in-plane TEM view of the second thickest sample. The TEM was performed using a Philips CM 300 UT microscope operated at 300 kV. The sample preparation was by conventional grinding and polishing techniques using diamond abresive paste. The finishing to electron transparency was obtained by ion milling at an angle of 13° and 4.5 kV in a cooling stage at liquid nitrogen temperature. The TEM picture reveals an average grain diameter of 10 - 12 nm. Between adjacent grains boundaries are visible in brighter contrast. These boundaries form a skin around the grains that might represent extremely defective areas or be even amorphous.

REDUCTION OF CONTAMINANTS

Various groups have pointed out that the reduction of contaminants is an essential pre-requisite to deposit µc-Si films with suitable properties for applications in large-area electronics [6, 7]. Therefore, a number of appropriate technical measures were taken to minimize the in-situ contamination of µc-Si films with undesired residual gas species. Firstly, a quartz glass tube (liner) was inserted into the cylindrical ECR source that should reduce plasma-wall interactions. A possible sputtering of transition metal atoms from the chamber wall by the plasma and their subsequent incorporation into the growing film was avoided by insertion of the liner. Secondly, the preparation of B- and P-doped µc-Si films in the same process chamber was terminated to avoid any unintended doping. Thirdly, the SiH_4 supply was changed from 5N material to higher-purity 6N gas. Finally, gas purifier systems (Millipore Mini XL) were built into the supply lines as close to the gas inlets of the chamber as possible, which should reduce the O_2 and H_2O content of the working gas and process gas. The inclusion of gas purifiers has been demonstrated by the Neuchâtel group to yield intrinsic material in case of undoped µc-Si films prepared under base pressures only in the high-vacuum range [6] and we consider this measure as the most effective one in reducing the oxygen content. FTIR spectra that were taken from samples prepared before the gas purifiers were built in, sometimes exhibited an absorption band at around 1070 cm^{-1}, where Si-O-Si asymmetric-bond-stretching vibrations in a SiO_x matrix would absorb [8, 9]. We attribute this foreign phase to the *in-situ* incorporation of oxygen during the process. Absorption bands around 1070 cm^{-1} could be observed for some samples, but vanished for others, see figure 5 - even if the samples were prepared under the same conditions. An oxygen concentration of some 10^{20} cm^{-3} is derived from the



5. FTIR reflection spectra of two µc-Si samples on Mo-coated glass prepared under standard conditions, but different deposition temperature, with and without SiO_x band.

absorption strength of the 475°C sample. We interpret the effect by outgassing of internal surfaces in the deposition chamber which acts as a difficult to control memory for residual gases. No FTIR absorption of SiO_x inclusions could be detected after installing the gas purifiers.

CONCLUSIONS AND OUTLOOK

The measures taken to reduce the contaminants turned out to improve the electronic properties of undoped films. While the dark conductivity was found in the beginning to range from 10^{-5} to 10^{-6} S/cm, it decreased into the 10^{-7} S/cm range afterwards. Also the ratio of photo-conductivity to dark conductivity increased from initial values of less than 10 to $\sigma_{ph}/\sigma_d > 10^2$ under AM1.5. These numbers correspond to the best values obtained with other deposition techniques like PECVD or hot-wire CVD [6, 10]. From these results we conclude that the preparation of highly-crystalline µc-Si films with state-of-the-art electronic properties is possible by ECR CVD. We are currently developing a two-step or profiled deposition process in order to avoid the initial amorphous growth. It has been shown by hot-wire and PE-CVD that the amorphous layer may be avoided with high hydrogen dilution and low deposition rate [10, 11]. This deposition scheme has been varied and applied to the ECR CVD process. The second deposition step can be done with a significantly higher rate, and a rate of 30 nm/min could be realized so far. By variation of the process conditions we optimistically expect the ECR to yield not only solar-cell suitable thin µc-Si films, but also in a high deposition rate regime.

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