Amorphous-nano-crystalline silicon thin films in next generation of solar cells

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Abstract

The optical properties of amorphous-nano-crystalline thin films deposited by Plasma Enhanced Chemical Vapor Deposition (PECVD) were studied in correlation with the size distribution of individual crystal sizes and the crystalline to amorphous fraction. A possible application as active part in solar cells was tested by integrating the actual Si layers in a typical p-i-n solar cell structure.

The nano-structural properties were examined by Grazing Incidence Small-Angle X-ray Scattering (GISAXS), Grazing Incidence Wide Angle X-ray scattering (GIWAXS) and High-Resolution Electron Microscopy (HRTEM). X-ray scattering measurements were done at the Austrian SAXS beam-line (Synchrotron Elettra, Trieste). The in-depth size distribution of the nano-crystals was found either uniform across the sample, or the crystals were slightly larger when located closer to the surface. Typical sizes were between 2 and 5 nm while the Raman crystal fraction varied from 15 to 30 vol. %. Measurements of the optical properties showed that the spectral distribution of the absorption coefficient in a whole range of crystal to amorphous fractions remained similar to pure amorphous silicon in the visible part of the spectrum and showed square dependence on the photon energy (Tauc gap). The average optical gap was larger for smaller nano-crystals and a higher crystal fraction just confirming the quantum size effects that correspond to quantum dots.

The spectral response of solar cells with the examined thin films as active elements showed a narrower spectral distribution and a blue shift comparing to pure amorphous solar cells. The effect was larger for samples with a higher nano-crystal fraction and smaller crystals suggesting a possible application in multi-layer solar cells.
1. Introduction

Nano-crystalline thin films are a promising candidate for producing high efficiency solar cells and hence electric power with the price competitive with conventional sources but without emission of "greenhouse gases" (CO2). Those high expectations are based on using quantum confinement effects connected with nano-meter sized objects in the form of ordered 3D domains, quantum dots (QD), called also nano-crystals. One of the proposed concepts is a high efficient cell composed of several active materials with various optical gaps stacked one on top of the other. Since a variation in the optical gap can be achieved by changing the size of the nanocrystals, multilayer solar cells can be obtained by using only one material but different crystal forms [1-3].

For a wide application of this concept, the material should be produced by the conventional method of deposition with the possibility of a simple up-scaling.

The PECVD method usually produces in-homogeneous samples, with a columnar structure which obscures the quantum size effects and hence benefits of using nano-materials in photovoltaic conversion. In this work we deposited the samples with a homogeneous distribution using the approach described earlier [1-3] and demonstrate that the QD effect can be used in multilayered solar cells.

Raman spectroscopy was used to estimate the ratio between crystal and amorphous fraction and average size of nano-crystals while GISAXS and GIWAXS was used for estimation the in depth homogeneity of deposited layers. The spectral response of test solar cells with active part made of pure amorphous Si films and films that contained 15 to 35% of nano-crystals embedded in amorphous matrix were compared with typical response of micro-crystalline thin films.

2. Experimental

Samples of amorphous and amorphous-nano-crystalline thin films with thickness between 100 and 200 nm were deposited by the PECVD method using radio frequency glow discharge in silane diluted with hydrogen as described in more details previously [4,5].

The optical properties of deposited films were determined by standard transmittance and reflectance measurements, and by ellipsometry [6].

GISAXS measurements were performed using the X-ray beam energy of 8 keV that corresponds to the wavelength $\lambda = 0.154$ nm. The grazing angle of incidence, $\alpha_i$, was selected in the range $0.2^\circ < \alpha_i < 0.5^\circ$. X-ray scattering intensity spectra were acquired by a two dimensional position sensitive charge-coupled device (CCD) detector, at a detector-to-sample distance $L = 2$ m. The depth distribution of the ‘particle’ sizes was obtained by changing the grazing incident angle, these measurements were described in more details in ref. [7].

Test solar cells of approximately 0.3 m$^2$ were deposited in p-i-n configuration, on the same glass substrate covered by thin oxide and with identical –p and –n layers.

3. Results and discussion

The structure of deposited materials was first tested with Raman spectroscopy. Typical spectra are shown in Fig.1. The lowest spectrum is amorphous material with a wide characteristic TO like peak around 480 cm$^{-1}$. In the other spectra appears an additional peak between 510 and 516 cm$^{-1}$ indicating crystals with a few nanometers in size. The data given in Fig.1 were estimated using eq. (1) and (2). The size of the crystals were estimated according to relation

$$\delta_{\text{Raman}} = 2\pi \sqrt{\frac{B}{\Delta \omega}}$$

(1)
where \( B = 2.24 \text{ cm}^{-1} \text{ nm}^2 \) and \( \Delta \omega \) is the peak shift of the TO mode in nc-Si toward lower wave numbers with respect to the peak of \( \mu \text{c-Si} \) (521 cm\(^{-1}\)) [8].

Since the samples contain both the amorphous and crystalline phase, the spectrum consists of two parts corresponding to the two phases which can be mathematically separated. The ratio of areas under the TO phonon related peaks that correspond to amorphous (\( A_{\text{amorph}} \)) and the crystalline phases (\( A_{\text{cyst.}} \)) defines the "Raman crystal fraction (cryst.fr.):"

\[
\text{cryst. fr.} = \frac{A_{\text{cyst.}}}{A_{\text{amorph}} + A_{\text{cyst.}}}
\]  

Figure 1. Raman spectra of a pure amorphous sample and samples with various nano-crystal fractions and individual crystal sizes (denoted in the graph).

Since the peak position in Raman depends on the strain in the material and does not give information about the in-depth distribution of the nano-crystals, the structure was further examined by GISAXS and GIWAXS. Characteristic GISAXS patterns taken at the grazing incidence angle and slightly above are given in Fig. 2.

Figure 2. 2D GISAXS patterns of a-nc-Si:H thin films as a function of the angle of incidence. The angle of grazing incidence are a) \( \alpha_{\text{critical}} \), b) \( \alpha_{\text{critical}} + 0.02 \) deg and c) \( \alpha_{\text{critical}} + 0.05 \), corresponding to the sample surface, and to 50 and 90 nm below the sample surface, respectively.
Since GISAXS intensity is a convolution of scattering contributions from different depths attenuated according to the incoming and scattering angle, an evaluation of the precise values is very demanding and time consuming. However, for a first approximation, the dominant contribution at the critical grazing incident angle comes from the near surface layer, while at the widest angles the contribution from the layer that is 100–200 nm below the surface becomes significant. The ‘particle’ sizes in the direction parallel to the surface and perpendicular to it were estimated by using the Guinier approximation for the analysis of the one-dimensional intensity distribution in characteristic directions. Both methods suggested almost spherical particles, consistent with the shape of quasi-3D patterns from Fig. 2.

The average sizes of the nano-particles were estimated from 1D vertical cuts (Fig.3) taken from the 2D SAXS pattern using a simple Guinier approximation [9]. The in-depth size distribution of the nano-crystals was found either uniform across the sample, or the crystals were slightly larger when located closer to the surface.

Figure 3. 1D vertical cuts taken from 2D GISAXS images (Figure 2) near the beam-stop area for different value of angle of incidence

GIWAXS spectra were taken simultaneously with the GISAXS spectra. One example for the samples A and B from fig. 1 and for a grazing incidence angle slightly above the critical angle is plotted in Fig.4 a.
Figure 4. a) GIWAXS patterns of samples A and B from Fig.1 and critical angle of incidence and b) GIWAXS of sample A at various incidence angles e.g. various penetration depth

The lines are broad as a consequence of the small crystal size, instrumental profile and strain. Since the crystal sizes were expected in the range of few nm, the contribution of eventual strain was neglected in the first approximation. The instrumental line broadening, $w_{\text{INSTR}}$, was estimated using NIST standard LaB6 powder. The crystal size is then estimated using the Scherrer formula [10]

$$D_{\text{GIWAXS}} = \frac{K \lambda}{(w_{\text{GIWAXS}} - w_{\text{instr}}) \cos(\theta)} \quad (3)$$

where $w_{\text{GIWAXS}}$ is the full width at half maximum of the peak at the corresponding angle $\theta$. One example for a GIWAXS spectrum of a sample with 35% crystal fraction is plotted in Fig.4b) around the Si (111) diffraction peak for various grazing incidence angles (critical angle, $+0.02$, $+0.05$ and $0.100$) that correspond to a sample depth of 50, 90 and 140 nm, respectively. The line width is almost the same, and since the width of the instrumental profile slightly decreases with the angle, the expression ($w_{\text{GIWAXS}} - w_{\text{INSTR}}$) from eq.1 remained constant resulting in a constant $D_{\text{GIWAXS}}$ size between 2 and 3 nm.

Comparing Raman with GISAXS and SAXS measured under various grazing angles confirms that the structure of the deposited films can be described as separated nano-crystals immersed in an amorphous matrix homogeneously distributed across the depth of the sample.

The spectral dependence of the absorption coefficients of the two nano-crystalline-amorphous layers from Fig.1. and the pure amorphous one are plotted in Fig.5. The layers containing nano-crystals have a slightly lower absorption coefficient than the pure amorphous in the visible part of the solar radiation. The blue shift of the absorption edge of the nano-crystalline samples and its dependence on the crystal size is clearly seen. The functional dependence of the absorption coefficient for direct optical transition, valid for pure amorphous material is described as

$$\left(\alpha E\right)^{1/2} = A(E - E_G) \quad (4)$$

where $\alpha$ represents absorption coefficient, $E$ the photon energy, $E_G$ the Tauc optical gap while $A$ is a constant. Since the distribution of the absorption coefficient is the same for nano-crystalline samples, it assumes direct optical transitions in samples with 35% of crystalline phase.

The shift in the optical gap with decreasing crystal size just confirms the quantum size effects present in the deposited material, described by relation

$$E_G = E_{G0} + \frac{C}{d^2} \quad (5)$$

where $E_{G0}$ is the optical gap of bulk material, $d$ is the size of the nano-crystals and $C$ is a constant.
A possible application of a-nc-Si:H layers with the examined structure as active part in solar cells was tested by integration in a typical p-i-n solar cell structure. The most important property, besides high absorption, reflects itself in the possibility of changing the spectral distribution of the opto-electrical response (Quantum efficiency, QE) with changing the crystals size in thin film. In Fig. 6 are compared a-Si, a-nc-Si:H and μc-Si solar cells. As can be seen, the QE of the solar cell with nano-crystals has a “blue shift” comparing to amorphous and microcrystalline cells which enable the use of this kind of material in multigap-multilayer solar cells where each the of individual cells covers a part of the solar spectrum, and thus stacked together increase the total efficiency of photovoltaic conversion.

Figure 5. Spectral distribution of the absorption coefficient for amorphous and nano-crystalline samples in the form of eq. (5), valid for the visible part of the spectra.

Figure 6. Quantum efficiency of solar cells with a-nc-Si:H, a-Si:H and μc-Si thin film as active material
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5. Summary

Thin film silicon samples with nano-crystals of 2 and 4 nano-meters and crystal fraction up to 35% were deposited by PECVD method. The particles size and crystal fraction was estimated by Raman spectroscopy while the uniformity across the sample depth was verified by GISAXS and GIWAXS. The spectral distribution of the absorption coefficient in the visible part showed a blue shift with respect to the amorphous layer consistent with quantum size effects associated with quantum dots. The spectral dependence of the quantum efficiency of solar cells containing such nano-crystalline layers shows a blue shift with respect to amorphous and micro-crystalline active layers that could be used in high efficiency multi gap multilayer solar cells.

6. Literature

7. K. Juraić at all, NIM (2010)