

SUBSTRATE EFFECT ON CRYSTALLINITY DEVELOPMENT IN THIN FILM NANOCRYSTALLINE SILICON

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In this work a simple approach by which it is possible to probe crystallinity development in thin film nanocrystalline silicon (nc-Si:H) using depth-profile Raman measurement is presented. Crystalline mass fraction f , is used as a measure of crystallinity and growth phases and varies in growth direction. Each growth phase is identified by certain range of crystalline mass fraction extracted from the phase material. Investigation shows that radio frequency plasma enhanced chemical vapour deposition (rf PECVD) growth of nc-Si:H evolves through various material phases from an initial amorphous incubation layer (ASIL) through other phases into the full nanocrystalline regime. It is found that f increases gradually in growth direction and saturates at the full nanocrystalline regime. By means of seeding, it is shown that the growth process can be modified such that nc-Si:H evolution is more rapid, more uniform, less dependent on substrate and begins nearly directly from the crystalline phase hence omitting the amorphous and other intermediate phases.

(Received November 30, 2012; Accepted December 20, 2012)

Keywords: Thin film nanocrystalline silicon, crystalline mass fraction, growth substrate, seed layers

1. Introduction

Thin film nanocrystalline silicon is an attractive material for thin film photovoltaic application. It is known to suffer less degradation than amorphous silicon. The growth mechanism is such that it is deposited under a high hydrogen dilution and the as-deposited film often is composed of micro crystals and voids embedded in an amorphous matrix. Thin film nanocrystalline silicon is a complex material with the mass fraction of each of the components varying for different nc-Si:H films depending on the deposition condition. The growth of rf PECVD nc-Si:H at fixed hydrogen dilution begins with the amorphous incubation layer (ASIL) and evolves through the crystal nucleation into the so-called proto-crystalline phase. From the proto-crystalline phase there is a transition to the mixed phase regime consisting of amorphous and nanocrystalline materials [1, 2]. Beyond the amorphous-nanocrystalline (a-Si/nc-Si) transition film growth evolves into the fully nanocrystalline regime.

To probe the structural changes in mixed phase silicon film various techniques are employed. Transmission electron microscopy (TEM) [3, 4] and Real time spectroscopic ellipsometry [5, 6] are commonly used. These methods are limited in that they do not give details about the quantitative crystallinity structure of the mixed phase material. More so, TEM is a destructive method. By monitoring the changes in the open circuit voltage of hydrogenated mixed-phase silicon solar cells, amorphous materials have been distinguished from materials deposited at the a-Si/nc-Si transition and beyond [7,8]. The main drawback of this method is the fact that the open circuit voltage of the cells can be affected by other parameters, which are not filtered out in this case. Furthermore, this approach limits investigation to only devices.

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The structural properties of mixed-phase nc-Si:H is dependent on its crystallinity and is quantitatively expressed in terms of the crystalline mass fraction. To determine the crystalline mass fraction, Raman measurements are carried out and the spectrum reflecting the amorphous and crystalline peaks are shown. By fitting these peaks to appropriate models, the crystalline mass fraction is extracted [9]. Raman is a fast and non-destructive technique for probing the structure of thin film silicon. Its accuracy is mainly depth-limited due to absorption losses in the material as the laser propagates. This makes it difficult to fully understand the structural changes in the entire probed material in growth direction especially for nanocrystalline silicon whose structural properties are known to be depth-dependent. The commonly used approach to Raman measurements of thick films only probes the top layers.

Reducing the ASIL layer such that the developing crystal size and mass yields a device quality nc-Si:H material has been a major research challenge till date. By means of seeding, we have demonstrated that the nucleation process is modified as the film growth begins on an underlying crystalline background [10]. The use of hydrochloric acid to suppress the ASIL has equally been reported [11].

Nanocrystalline silicon is usually deposited directly on glass substrate especially for material characterization. In either substrate or superstrate configuration, nc-Si:H solar cell active films are deposited on glass with either a transparent conductive oxide or another silicon layer. For infrared spectroscopy measurement films are deposited directly on crystalline silicon wafers. Finding a correlation between the different substrates and the structural profile of the deposited layer is still an open question.

In this work, we investigate the effect of nature of underlying substrate on the crystallinity development profile of nc-Si:H. Phase changes at different depths in nc-Si:H are linked to changes in crystallinity in growth direction. It is shown that the underlying substrates affect the crystallinity development profile. With the use of nc-Si:H seed layers deposited first on the substrate to facilitate crystal nucleation, the growth profile of the overlying nc-Si:H layer is modified. In this paper, we shall show that the substrate effect can also be favourably manipulated during film growth.

2. Experimental details

Films reported here are intrinsic nc-Si:H grown using the rf PECVD set-up at the photovoltaic materials and devices (PVMD) laboratory at the Delft University of Technology. In the first deposition series, one run ~ 500 nm thick layers on three different substrates was deposited. The substrates are Corning glass (E2000), Corning glass with 15-nm thick p-type nc-Si:H and Corning glass with 40 s etched aluminium doped zinc oxide. For this deposition, the H₂ and SiH₄ flows were fixed at 150 and 2.2 sccm respectively. The deposition pressure and the substrate temperature were kept constant at 9 mbar and 180°C, respectively while the deposition power was maintained at 78 W. In another deposition run, seed layers were first deposited on the substrates using SiH₄ flow of 0.7 sccm for 5 minutes while keeping all the other parameters constant. Afterwards, nc-Si:H layers were grown using same conditions as in the first deposition run hence the only difference in this second run being the introduction of seed layers. The films were characterized using X-ray diffraction and Raman spectroscopy.

The Raman spectra were measured using a Raman microscope (Renishaw-Gloucestershire, UK) Ramascope system 2000, grating 1800 lines/mm) in a back scattering geometry with a 2 mW Ar laser at a wavelength of 514.5 nm focused on a spot of about 1μm. The phase change investigation was done by a depth-profile Raman measurement on the layers. For this purpose, a reactive ion etching system (Alcatel CL GIR 300) was used to etch through the depths of the materials followed by the Raman measurements. The depths were determined using Dektak step profiler. Full details of this approach are presented in Agbo et al [12].

3. Results and discussion

3.1 Crystallinity development of nc-Si:H on different substrates

The crystallinity development profile in growth direction of intrinsic nanocrystalline silicon layers deposited on Corning glass, Corning glass with nc-p-layer and Corning glass with 40 s etched ZnO:Al is presented in figure 1 (a). Here the indicated phase materials are distinguished using the specified f ranges for ease of understanding of the structural and phase-change evolution in growth process. The crystalline mass fraction generally increases in growth direction in all the substrates. The changing crystallinity is an indication of a phase transition in growth direction beginning from the amorphous incubation layer into the proto-crystalline regime as assigned in figure 1. From the amorphous-to-nanocrystalline transition structural changes evolve further into the full nanocrystalline regime. It has been shown earlier [10] that this phase change evolution occurs within the first 500 nm of a 1300 nm thick intrinsic layer. After this 500 nm transition point the crystallinity saturates. At saturation of crystallinity, the film growth attains steady-state condition at the full nanocrystalline regime hence no further increase in crystallinity if observed after this stage in line with earlier investigation [13]. From figure 1(a) it is seen that the layer grown on a nanocrystalline background gives a higher crystallinity relative to the other substrates hence implying that there is a substrate-dependent effect in this case.

3.2 Effect of seeding on nc-Si:H crystallinity development

In figure 1(b) the crystallinity depth profile of the test layers are shown with the layers deposited on the same substrates as in figure 1(a) under the same deposition conditions except that a 40-nm thick nc-Si:H seed layer was first deposited on the substrates before main test layers. Here, a modification in the growth profile is observed in all the substrates. The crystalline mass fraction, f , evolves rapidly ($f \sim 60\%$) from the onset of growth, which leads to an initial higher crystalline mass fraction and a more homogenous layer. This trend is a reverse of what is usually obtained in conventional rf PECVD nanocrystalline layers without an underlying seed layer as in figure 1(a). This way it is possible to make nanocrystalline films with high crystallinity with the growth evolving directly from the nanocrystalline regime and bypassing all the other intermediate growth phases as shown. This further implies that high crystalline nc-Si:H can be obtained for even much thinner layers. Notice that there is a limited dependence of the crystallinity development on the substrate in this case. This possibility of manipulating the growth process from the substrate can be a vital approach in controlling the growth mechanisms of nc-Si:H, which are quite sensitive to often-erratic plasma and deposition conditions. The similar crystallinity depth profile of all the substrate implies that seeding reduces the substrate effect on the growth mechanisms of nc-Si:H.

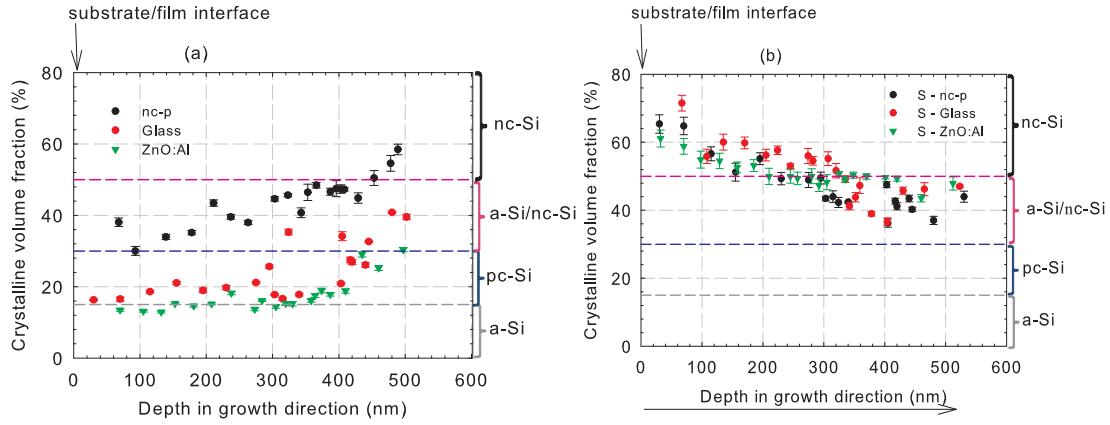


Fig. 1. Crystallinity depth profile of rf PECVD thin film nanocrystalline silicon deposited directly on glass, glass with nc-Si:H p-layer and glass with etched ZnO:Al (a) without a seed layer and (b) with a seed layer. The legends represent the substrates.

3.3 Bi-facial Raman profile of seeded/unseeded nc-Si:H

In order to investigate further how the substrates and seed layers affect the crystallinity evolution at the onset and at the end of film growth a bi-facial Raman measurement was carried out. This implies measuring the Raman profile of the films with the laser from the glass side in one instance and from the film side on the second instance [8, 14]. Results of this investigation are presented in figures 2 and 3 for the unseeded and the seeded cases respectively. In figure 2(a) the glass-side Raman profile shows an initial growth that is dominated by the ASIL given the broad peaks around the 480 cm^{-1} typical of amorphous material in all the substrates used. Figure 2(b) gives the facial Raman profile with obvious crystalline peak at 520 cm^{-1} especially for the film deposited on nc-Si:H p-layer and on glass. A clear dependence on substrate especially at onset of growth is observed. The Raman profile of nc-Si:H layer deposited on glass/nc-Si:H substrate shows a stronger crystalline peak at around 520 cm^{-1} which can be linked to the already-crystalline growth background.

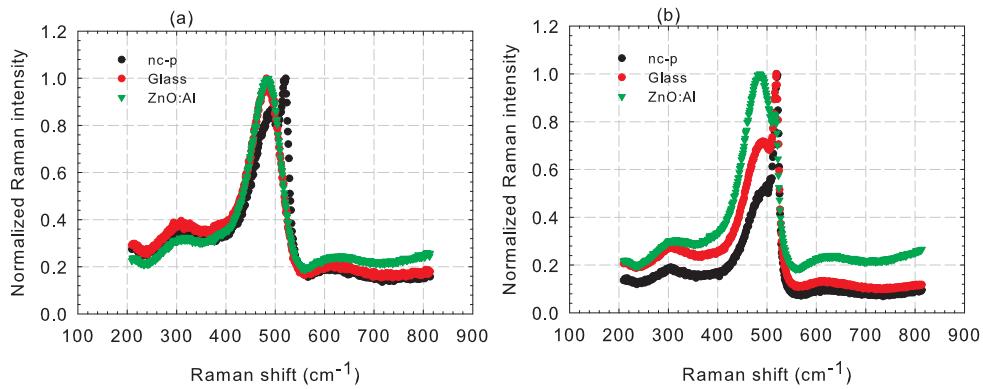


Fig. 2. Bi-facial Raman spectra of unseeded nc-Si:H films on different substrates with measurements taken (a) from the glass side and (b) from the film side.

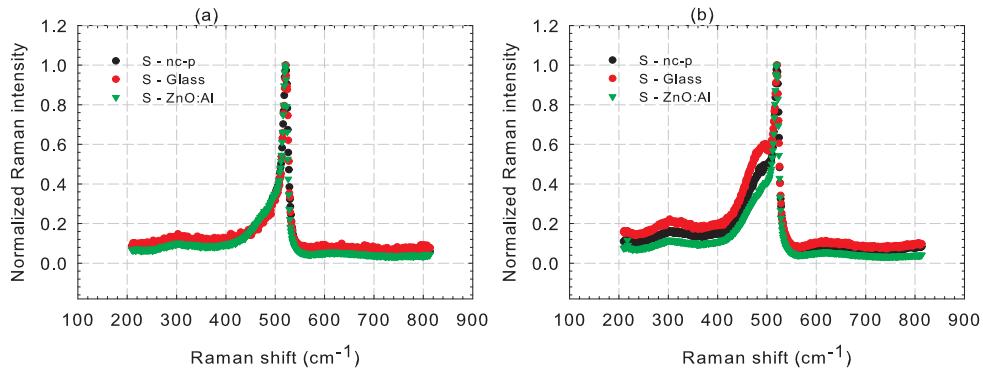


Fig. 3. Bi-facial Raman spectra of seeded nc-Si:H films on different substrates with Raman measurement taken (a) from the glass side and (b) from the film side.

The bi-facial Raman profiles of the seeded layers are presented in figure 3. The back-side profile (figure 3(a)) shows that the nc-Si:H films evolved without the ASIL and this further corroborates the results in figure 1(b). The seed layer here not only facilitates nucleation by eliminating ASIL but also suppresses effects of underlying substrate hence the similar Raman spectrum obtained for the three substrates. The facial Raman profile represented in figure 3(b) indicates pronounced crystalline peaks in all the films with slight differences in their amorphous shoulder. In downplaying the substrate effect, seed layers provide a background that promotes uniform silicon nuclei distribution on the substrate at onset of growth. This way, they serve as ‘cap’ to the substrates hence suppressing possible interferences to crystallinity development that may arise as a result of the nature of substrate.

4. Conclusion

Thin film nanocrystalline silicon is a mixed-phase and complex hydrogenated material comprising the amorphous tissue, crystals and voids. Its growth evolves through a number of intermediate phase changes. Phase changes in the growth of nc-Si:H represent different crystallinity levels in the material and as such the crystalline mass fraction can be an indicator of phase transitions. In the work reported here it has been demonstrated that ex-situ investigation of phase-change profiles in nc-Si:H is possible by means of depth-profile Raman measurement. The results show that when using rf PECVD the nc-Si:H growth begins with the amorphous incubation layer with gradual increase in crystallinity until saturation at the full nanocrystalline regime. Applying a seed layer reverses this order and makes it possible to grow nc-Si:H from onset of deposition without the intermediate phases. These effects were investigated for different underlying substrates and were found to still hold independent of the substrate. However, we observed that without seed layer the crystallinity development profile is substrate-dependent. Underlying substrate effect on crystallinity depth profile of nc-Si:H can be eliminated using seed layers.

Acknowledgements

The PVMD group of Delft University of Technology is acknowledged for the facilities used for this research.

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