



Analysis of amorphous-nanocrystalline silicon thin films by time-of-flight elastic recoil detection analysis and high-resolution electron microscopy

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ABSTRACT

The in-depth distribution of hydrogen atoms in 100 nm-thick, amorphous-nanocrystalline, silicon films (a-nc-Si:H) was estimated by time-of-flight elastic recoil detection analysis (TOF-ERDA) using a previously described set-up. The layer with nanocrystals was deposited on a 50 nm amorphous layer by plasma-enhanced chemical vapor deposition (PECVD), using silane gas that was diluted with hydrogen. High-resolution transmission electron microscopy (HRTEM) showed that the films contained nanocrystals of silicon embedded in an amorphous Si:H matrix. The size of the nanocrystals and the crystal-to-amorphous ratio increased in the direction from the substrate toward the surface of the film. The amorphous matrix appeared uniform, except for the area close to the a-Si:H/a-nc-Si:H interface, where spots that were brighter than average appeared. These areas can be attributed to the presence of less-dense material, presumably voids. It is assumed that the surface of the voids is “decorated” with hydrogen that saturates the silicon “dangling bonds”. This is why the distribution of hydrogen should indicate a density fluctuation in the material. Consistent with this assumption, the TOF-ERDA showed a non-uniform distribution of hydrogen across the depth, with a maximum value close to the a-Si:H/a-nc-Si:H interface that coincides with the less-dense material seen by the HRTEM. This supports the idea about the important influence of voids on crystal formation, particularly in the nucleation phase. After a heat treatment at 400 °C, the distribution of hydrogen remained the same, while the total hydrogen concentration decreased. This indicated that the type of hydrogen bonding was the same across the amorphous network and assumed that the areas of less-dense material are agglomerates of smaller voids.

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1. Introduction

Amorphous-nanocrystalline silicon (a-nc-Si:H) is a promising material for thin-film solar cells. It could be a satisfactory replacement for pure amorphous silicon due to it suffering from much less degradation during exposure to light. Furthermore, nanocrystals, 2–10 nm in size, show quantum size-effects and offer further possibilities for tailoring the optical gap and the increased use of such material in multilayer solar cells [1–3]. An additional interesting fact is that the material can be obtained in a highly crystalline form (a crystal fraction of 70% and above) by plasma-enhanced chemical vapor deposition in silane that is diluted with hydrogen gas on a substrate heated to 200–300 °C. In the modeling of the nanocrystals formation the most important role has been ascribed to the atomic hydrogen formed in the glow discharge. In contact with the surface of the growing film, the hydrogen atoms etch

away the less-well-bonded silicon in less-ordered domains and in this way promote the formation of a more-ordered material. The diffusivity of the atomic hydrogen is large, and that is why the near-surface layer becomes enriched with hydrogen, presumably in voids, so increasing the high compressive stresses. The consequence of such stresses is the generation of strained Si–Si bonds, which accelerates the nucleation of crystallites. As a result, the crystals grow in a highly strained and void-rich a-Si layer [4–7].

According to the above-mentioned model, the initial layer should contain voids and a larger concentration of hydrogen than the average for the film. In order to check this assumption, we deposited an amorphous-nanocrystalline silicon layer on a 50 nm amorphous layer. The a-Si:H/a-nc-Si:H interface was studied with High-Resolution Electron Microscopy (HRTEM), while the distribution of hydrogen in the bi-layer was measured with time-of-flight elastic recoil detection analysis (TOF-ERDA). The growth of the a-nc-Si:H layer was selected to be relatively slow (2 nm/min), leaving enough time for the process of hydrogen incorporation. The results obtained from this experiment should be valid for all other depositions of this kind under a variety of conditions.

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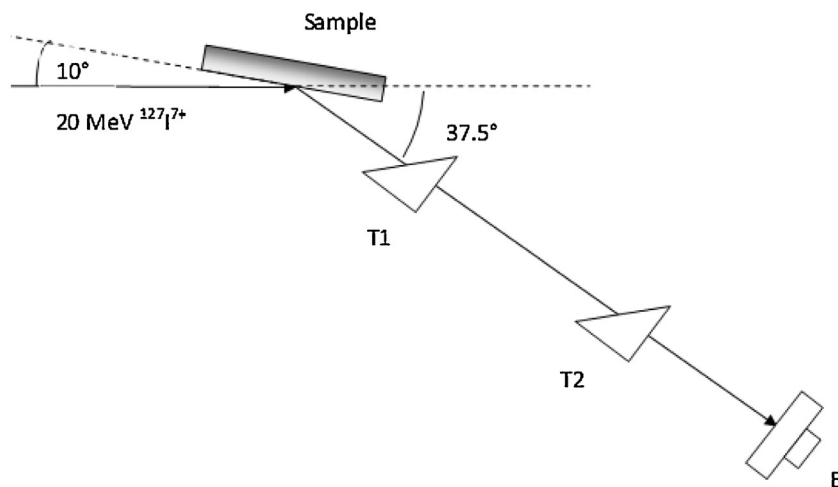


Fig. 1. TOF-ERDA experimental setup.

2. Experimental

The samples were deposited by plasma-enhanced chemical vapor deposition using a radio-frequency discharge in a gas mixture of silane (90%) and hydrogen (10%) for the amorphous layer, while the dilution was increased to 94% hydrogen in a gas mixture for the formation of a-nc-Si:H [8]. The substrate was glass and glass covered with a SnO₂ thin film. The power density during the formation of the a-nc-Si:H layer was 20 mW/cm², resulting in a film growth rate of 2 nm/min. The sample thickness was 60 nm. The thermal treatment was conducted in a vacuum at 400 °C for 1 h. The crystallinity of the deposited layers was estimated using Raman spectroscopy [9]. The typical values were between 30 and 40% of crystal phase. The HRTEM measurements were performed using a JEOL JEM 2010F transmission electron microscope. Details of the HRTEM experiment and the sample preparation are given in Ref. [9]. The HRTEM images were filtered with a FFT filter using a Bragg mask in order to emphasize the ordered (crystalline) domains of the sample. The size of the nanocrystals was taken as the diameter of the circle with the area of the nanocrystal taken from a micrograph [10].

The atomic content and the depth profiles of the hydrogen and silicon in the samples were determined using TOF-ERDA. The TOF-ERDA measurements were performed on the 6-MV Tandem Van de Graaff accelerator located at the Ruđer Bošković Institute. As shown in Fig. 1, 20 MeV ¹²⁷I⁷⁺ ions with a 10° incidence angle, with respect to the sample surface, were used. The TOF-ERDA spectrometer was positioned at an angle of 37.5° to the beam direction. T1 and T2 are the timing stations for measuring the time of flight and E is the energy detector. More details about the TOF-ERDA spectrometer and the method can be found in Refs. [11,12].

3. Results and discussion

3.1. HRTEM

A characteristic micrograph of the a-nc-Si:H sample is shown in Fig. 2. It is clear that the nanocrystals exhibit various sizes and orientations, and are isolated and immersed in the amorphous silicon matrix. The mean size of the crystals was about 7 nm, while the distribution was log-normal, indicating random nucleation (Fig. 3). The number of nanocrystals formed close to the interface was much smaller than the number formed close to the surface of the film.

The micrographs in Fig. 4 show a cross-section of the a-nc-Si:H deposited on a-Si:H for the TCO layer. The square indicates the area

where the film appears less dense than the a-Si:H and a-nc-Si:H. These areas extend close to the interface between the two layers and appear at the beginning of the a-nc-Si:H formation. After the formation of the a-Si:H layer, the film growth continued in the silane diluted with up to 94% of hydrogen in the gas mixture. As a consequence of the dilution the plasma that came into contact with the surface of the growing film contained a lot of neutral and ionized hydrogen atoms that impinged on the surface of the grown film. Part of this flux was spent on chemical etching of the less-ordered material, while part of the hydrogen penetrated below the surface, into the grown film, creating the defects that enable faster diffusion of the atoms. As a consequence of this hydrogen incorporation, it is also possible that the larger voids appeared and filled up with hydrogen. Such defects could enhance the formation of a strained Si–Si bond and the formation of nucleation centers for the crystallization. Besides nanocrystal growth on the top of the amorphous layer, incorporated hydrogen also creates a favorable situation for the formation of nanocrystals in the already-formed a-Si:H matrix. One such crystal is visible in the micrograph of the a-Si:H/a-nc-Si:H interface shown in Fig. 5. The amorphous phase

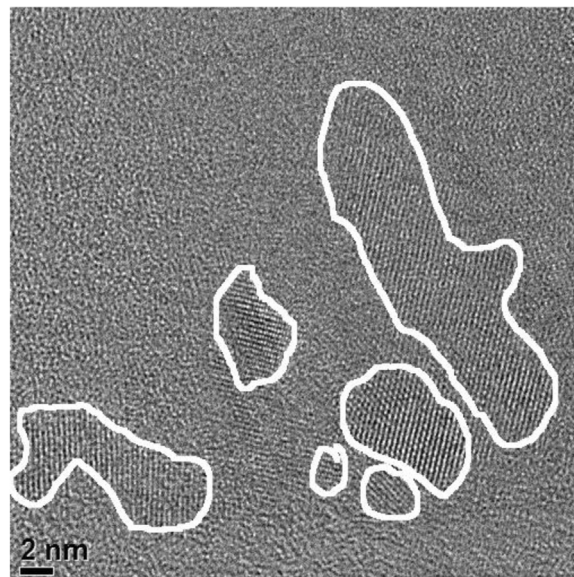


Fig. 2. HRTEM micrograph of a-nc-Si:H sample (as deposited). The boundaries of several nanocrystals are highlighted.

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