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Preparation of Nc-Si/A-Sio$_2$ Multi-Layer Thin Film Specimens for TEM Cross-Section Observation by Cryo Argon Ion Slicing

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Abstract

The nanocrystalline silicon (nc-Si) thin films have received a wide attention in the field of third generation solar cells. In this work, the amorphous hydrogenated a-Si: H/a-SiO_2 multi-layered films were deposited by plasma enhanced chemical vapour deposition (PECVD). Then the as-deposited thin film was annealed at 1100 °C to obtain nc-Si/a-SiO_2 multilayer. The structure of the as-deposited and annealed thin films was studied by X-ray diffraction (XRD) analysis. This article mainly reports about the Cryo Ar^+ ion slicing (milling) method for the preparation of ultrathin nanocrystalline silicon and silicon dioxide (nc-Si/a-SiO_2) multilayer specimen for cross-section transmission electron microscopy (XTEM) analyses. The Ar+ ion slicing method includes several initial preparation steps such as cutting, gluing and mechanical thinning. This slicing procedure results a minimum trial, high yield, and sufficiently thin cross-section without any artifacts for the high resolution transmission electron microscopy (HRTEM) observation. The textured multi-layers and the thickness of nc-Si/a-SiO_2 were analysed from TEM and HRTEM images. The nanocrystalline Si of dimension about 10nm was observed in the crystalline layer.

Keywords: Ar^+ ion slicing; Nc-Si/a-SiO_2 multi-layers; XTEM; XRD; Microstructure

Abbreviations: (nc-Si): Nanocrystalline Silicon; (PECVD): Plasma Enhanced Chemical Vapour Deposition; (XRD): X-ray Diffraction; (HRTEM): High Resolution Transmission Electron Microscopy

Introduction

Silicon multi-layered thin films are subject of the recent research to play a key role in solar cell technology. The morphological analyses of the textured nc-Si/a-SiO_2 multilayer semiconducting thin films are significant for the fabrication of solar cells. Besides the intrinsic properties, the structural properties have a great impact on the performance based on the quality of the interface between the layers. Also, the reproducibility is important for the commercial production and textured thin layer with high quality is needed for high efficiency. Hence, the analyses of size, structure and morphology of the thin layers are important to fulfil the above said requirements. Recently, large efforts have been put on the manufacturing of thin films to improve the efficiency of amorphous and micro-crystalline silicon based solar cells [1-6]. The main intention on the development of such materials in solar industry (3rd generation of solar cells) is to reduce the usage of materials and deposition costs, and also to increase the efficiency of the photovoltaic devices. The major issue to be solved is to shift the absorption in Si nanostructures to higher energies compared to the bulk material utilizing the quantum confinement effect, while ensuring an efficient charge carrier transport. The quantum confinement can be well controlled by the size of nanostructures and by the properties of the barrier material (SiO_2) [7-9]. Hence, the nc-Si/a-SiO_2 multi-layers of thin film were preferred for the investigation.

A crucial part of this research is the micro structural analysis of the multi-layer films, whereby the factors of interests are the grain distribution, texture, thickness of the layer and orientation of film structure [10,11]. For such characterization, cross-sectional transmission electron microscopy (XTEM) is a very essential tool enabling to study the structure, phase, defects and interfaces. The most convenient geometry to study the thin layers and their interfaces is to direct the electron beam perpendicular to the cross section of the film (layer). For such an analysis, it is necessary to make the film electron transparent in a direction perpendicular to the interfaces (film). The preparation of cross-sectional specimens is usually done by fabricating a sandwich structure (Si substrate/Thin film/Glue/Cover glass)

and subsequently thinning it in the direction perpendicular to its cross-section (perpendicular to film surface) to make transparent (thickness of the order of <50nm) for electrons. The preparation of cross-section specimens is time-consuming, specimen-dependent and consequently a trial-and-error method. However the features of XTEM observations are more informative compare with the observations of scratched samples of thin films. In this paper, a Cryo Ar^+ ion slicing (milling) procedure was successfully used for the preparation of (nc-Si/a-SiO_2) specimen for TEM analyses.

Experimental Details

Thin film fabrication

Initially, amorphous hydrogenated a-Si: H/a-SiO_2 multi-layered films were deposited in a radio frequency (13.56MHz) plasma enhanced chemical vapour deposition (PECVD) system (SAMCO 220N) using SiH_4 and N_2O as precursor gases. Samples with total thickness of 600 nm were prepared on Si (100) substrate in the form of multi-layers composed of alternating uniformly thick sub-layers (15nm a-SiO_2 and 10nm a-Si: H) followed by a final SiO_2 capping layer of the same thickness (Figure 1). First, always a thin a-SiO_2 sub-layer was obtained by decomposition of N_2O (120sccm) +SiH_4 (60sccm) gas mixture applying an RF power of about 50W. Then a sub-layer of a-Si: H was deposited by decomposition of SiH_4 (10% SiH_4+90% Ar; 250sccm) applying an RF power of about 40W. The substrate temperature of 250 °C and the total reaction pressure of 67 Pa were held constant during the depositions on the grounded substrates. The deposition rate was about 1nm/s. Subsequently, the as-deposited multi-layered films were heat-treated (annealed) in a high-temperature vacuum chamber HTK 1200N (Anton Paar) at a temperature of 1100 °C in vacuum (at ~10^{-3}Pa). Due to the heat treatment, the hydrogen is eliminated and the amorphous phase of the silicon is converted into nanocrystalline silicon (nc-Si).

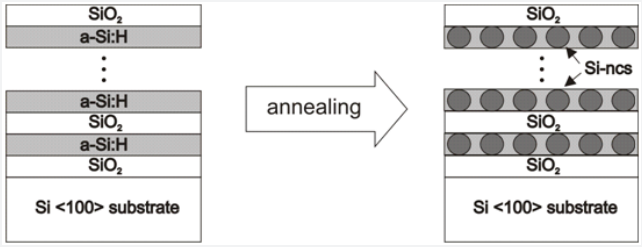

Figure 1: Schematic illustration of the a-Si: H/a-SiO2 and nc-Si/a-SiO2 thin film fabrication.

XTEM specimen preparation

Preliminary steps/procedure

The multi-layer thin film cross-section preparation depends on Ar^+ ions milling machine, in our case the Cryo Ion Slicer from JEOL was used. Samples for milling have to be fit in dimension 3×0.5×0.1mm of rectangular block (Figure 2) with parallel and perfectly polished surfaces. Thinning area will be created parallel with large surface of the block, and the intended layer must be perpendicular to the thin film surface for TEM observation. To accomplish the required conditions, the sample is prepared by diamond cutting and polishing. Initially, thin film is protected by 80µm thick cover glass glued with the sample at ~130 °C for 15min (using the G2 Epoxy Glue with hardener at a ratio of 10:1). The sandwich of substrate/thin film/glue/cover glass was mounted with wax (melted at ~130 °C) on a clean glass plate with the substrate surface facing the glass plate. Further, thin rectangular pieces with dimensions approximately 0.5mm×2.5mm were cut by diamond saw cutter (Buehler-IsoMet). The pieces were arranged on a thick glass plate (cover glass facing down) and glued by white-wax with a piece of reference sample (100µm black twin-blade razor) to the glass plate. Then the glued thick glass was fixed in a centre-axis holder of the JEOL Handy Lap polisher. The base of the Si-substrate (0.7mm) was thinned down to a thickness of 0.5mm using 30µm, 6µm and 1µm diamond sheets, subsequently. Then the sides of the samples were polished with similar procedure to get smooth surfaces. The samples were turned on one side, glued, polished and then turned on the other side, glued again and polished down to a thickness of 100µm which results the required sandwich structure with dimensions of 3mm×500µm×100µm as shown in Figure 2. Then a suitable piece for ion slicing was cleaned with acetone to remove the white wax and dirt.

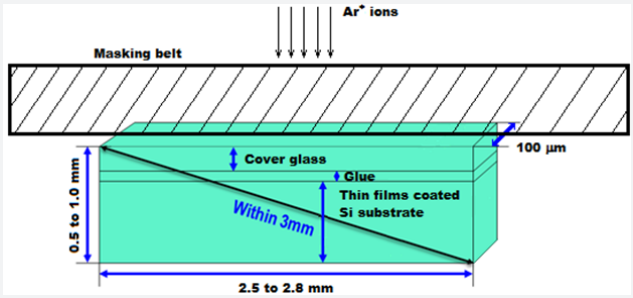

Figure 2: The schematic design of the structure of mechanically prepared sample for ion slicing with the positions of the cover belt and ion beam.

Preparation of TEM cross-section by two-step ion milling

The ion slicing was carried out in a JEOL IB-09060CIS cryo ion slicer with the ion accelerating voltage range of 1-8kV, milling speed of 5µm/min, incident angle of 4.5 °C and cooling temperature of the specimen stage -100 °C or less. The high vacuum conditions (pressure on the order of 10^{-4}Pa) ensure an efficient evacuation of the particles sliced from the sample and thus a good efficiency and precision of the milling process. The ion source (gun on top) has the capacity to tilt ion beam from vertical to ±6 degrees. Before starting the use of the ion milling, it is necessary to complete the initial adjustment of the Ar gas (99.9999%) flow rate to optimized ion beam and position adjustment of the beam. Then, a cleaned specimen was mounted

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carefully on a specimen holder jig using an aligning standard kit. In the reported thin films, two types of slicing methods were used, namely the two-step method and the bulk sample method.

In the two-step method, the sample is fixed in the ion slicer with the cover glass facing up, i.e., facing the ion gun. Then the shielding belt with a thickness of 10μm was introduced just above the specimen to prevent and make a thinner part of the sample. The acceleration voltage of 6.5kV and the tilt angle amplitude of 0 °C were set for the first step. The sample was milled by the ion source from above to create a thinning of the sandwich structure in the specimen (down to the bottom-substrate) with a thickness corresponding to the thickness of the cover belt (10μm). The width of the thinned area corresponds to the width of the ion beam. The sample was turned to the opposite side (with the substrate side facing the ion source) and the shielding belt was removed from the second step. The same acceleration voltage and pressure were maintained, but the beam tilt angle amplitude was set to 4.5º (for each 60s). The tilting of the ion source occurs in the plane perpendicular to the thinned surfaces. After a certain time, a "valley" forming in the cover glass reached the thin film layer. At this moment, a fine milling was introduced to remove the amorphous part and artifacts produced during milling to get a smooth surface of the cross-section. For the fine milling, an acceleration voltage of 2-2.5kV and beam tilt angle amplitude of 4.5 °C (30s) was applied for 10-15min. Finally, a thickness in the range from 10nm to 100nm was achieved in a small region in the area of the thin film (perpendicular to the cross-section of the thin film). A very thin cross-section of ~10nm could be used to obtain high resolution TEM images. The as-prepared specimen is shown in (Figure 3a).

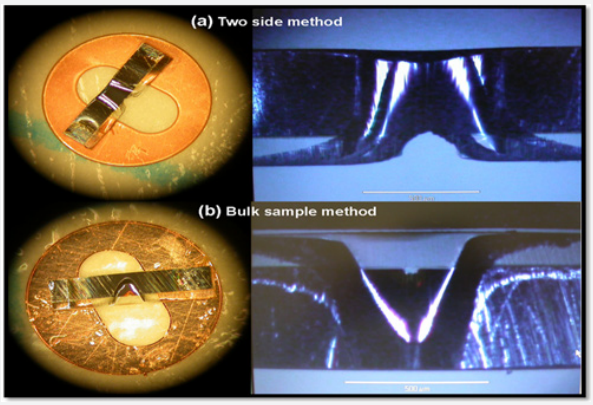

Figure 3: The ion sliced specimens for TEM and HRTEM observation.
a) Two step method, and b) Bulk sample method

Preparation of TEM cross-section by the bulk sample ion milling (one step method)

In the case of the bulk sample method, the initial procedures to fix the sample are the same as the two-step method. The beam tilt angle amplitude was set between 1.5-2º (60s) for the bulk method. The sample was milled to create a thin hole at the interface between the thin film and the cover glass as shown in Figure 3b. Tilting angle is connected to the position of the hole in the sample. The edges of the thin hole have a thickness of about 10-100nm. Once a region with brown colour developed, care had to be taken to prevent the formation of a large hole. At this moment, fine milling was introduced as in the case of the two-step method to get the XTEM specimen.

Characterization by XRD, TEM and HR-TEM

High-resolution transmission electron microscopy (HRTEM) was carried out using the transmission electron microscope JEOL JEM 2200FS operated at 200kV (Schottky auto emission gun, point resolution 0.19nm) with an in-column energy Ω-filter for EELS/EFTEM, a STEM unit and Oxford EDS X-Max detector. Images were recorded by the Gatan CCD camera with resolution of 2048×2048 pixels using the Digital Micrograph software package. The polished and sliced samples were manipulated using the NIKON optical microscope. The ion sliced samples were fixed on the copper O-ring using the G2 Epoxy Glue for the TEM observations. The X-ray diffraction experiments were carried out using an automatic powder X-ray diffracto meter X'Pert Pro (PANalytical) equipped with a point detector in asymmetric omega-2 theta geometry. Copper Kαradiation (λ=0.154nm)

was used as an X-ray source. The ceramic alumina from NIST (National Institute of Standards and Technology) was used as an instrumental standard.

Results and Discussion

The crystalline phase analysis of the as-prepared a-Si: H/a-SiO_2 and heat-treated (annealed) nc-Si/a-SiO_2 thin film structures from X-ray diffraction is presented in Figure 4. The annealed thin film of nc-Si/a-SiO_2 deposited on c-Si substrate shows the diffraction peaks at 28.5 °C, 47.5 °C and 56.3 °C corresponding to nc-Si orientations of (111), (220) and (311) planes, respectively, which are declined from the film surface about 13.75°, 23.25° and 27.65°. But, there was no significant diffraction observed for the as-deposited amorphous a-Si: H/a-SiO_2 thin films. Hence, it confirms that the annealing makes the amorphous Si layer into nanocrystalline Si layer. No significant preferred orientation of crystallites against the film surface was observed. Figure 5 shows the TEM images of the nc-Si/a-SiO_2 multi-layers. The stacked layers are clearly identified by TEM and the periodic structure was still maintained even after thermal annealing at high temperature (1100 °C). In (Figure 5), the 600nm thick nc-Si/a-SiO_2 multi-layers are shown between the glue layer and the Si substrate. The layers were grown alternately in order to increase the light capturing property of the solar cell. The multi-layered, textured structure is responsible for the surface light scattering (bulk scattering) due to the heterogeneity of the deposited thin layers [12,13]. (Figure 5) shows the silicon L map of the nc-Si/a-SiO_2 layers from EFTEM (Energy Filtered TEM), which clearly shows the contrast between crystalline and amorphous regions. The homogeneous amorphous and crystalline sequences of nc-Si

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and a-SiO_2 layers are shown in (Figure 5). The shrinkage in the crystalline layers occurred due to the heat-treatment causing the formation of a denser polycrystalline layer. The a-SiO_2 layers are still amorphous since their conversion to crystalline silica would require a very high temperature.

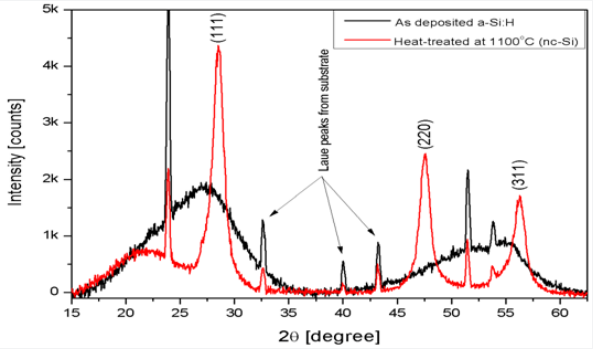

Figure 4: XRD ptterns of the as-deposited (a-Si: H/a-SiO2) and heat-treated (nc-Si/a-SiO2) multi-layered thin films.

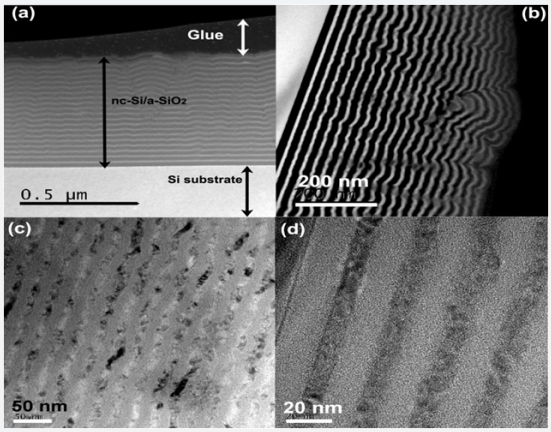

Figure 5: TEM micrographs of the nc-Si/a-SiO2 textured thin film multi-layers of thickness 600nm.

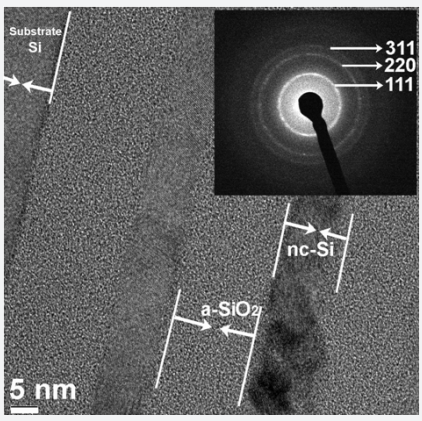

Figure 6: HR-TEM micrographs of the ion sliced (nc-Si/a-SiO2) multi-layered thin film.

The amorphous and crystalline phases of a-SiO_2 and Si are observed clearly from the HRTEM micrographs shown in Figure 6. The thickness of the nc-Si and SiO_2 is about 10nm and 15nm, respectively. The size of the nc-Si was found to be in the range from 8 to 10nm. The SAED spectra in Figure 6 confirmed the diffraction of electrons from the polycrystalline Si planes (111), (220) and (311).

Conclusion

Multilayer nc-Si/a-SiO_2 thin film structures were obtained by heat-treatment at 1100 °C from PECVD grown a-Si: H/a-SiO2 multi-layer thin films. Samples of the nc-Si/a-SiO2 film for cross-sectional TEM (XTEM) were successfully prepared using the Cryo Ar ion slicing by two different procedures. Very thin (up to 10nm) XTEM specimens without any artefacts were successfully prepared by this method. The amorphous and crystalline phases of the Si structures in the as-prepared and annealed thin films were analysed by X-ray diffraction. The lattice planes of the nanocrystalline silicon (nc-Si) structure were indexed for the prominent planes observed from X-ray diffraction. The TEM and HRTEM micrographs of the 600nm thick nc-Si/a-SiO_2 multi-layers were observed clearly. The average thicknesses of the nc-Si and a-SiO_2 layers were 10nm and 15nm, respectively. The nanocrystals in the Si layers extended up to the boundary of a-SiO_2. The size of the nanocrystals was found to be in the range from 8 to 10nm. The XTEM observations of the specimens prepared by Cryo Ar ion slicing exhibit a good resolution of the individual layers in the multi-layer structures.

Acknowledgement

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