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CW laser induced crystallization of thin amorphous silicon films deposited by EBE and PECVD

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ABSTRACT

This work presents the Continuous Wave (CW) laser crystallization of thin amorphous silicon (a-Si) films deposited by Plasma Enhanced Chemical Vapor Deposition (PECVD) and by Electron Beam Evaporation (EBE) on low cost glass substrate. The films are characterized by Elastic Recoil Detection Analysis (ERDA) and by Fourier-Transform Infrared (FTIR) spectroscopy to evaluate the hydrogen content. Analysis shows that the PECVD films contain a high hydrogen concentration (∼10 at.%) while the EBE films are almost hydrogen-free. It is found that the hydrogen is in a bonding configuration with the a-Si network and in a free form, requiring a long thermal annealing for exodiffusion before the laser treatment to avoid explosive effusion. The CW laser crystallization process of the amorphous silicon films was operated in liquid phase regime. We show by Electron Backscatter Diffraction (EBSD) that polysilicon films with large grains can be obtained with EBE as well as for the PECVD amorphous silicon provided that for the latest the hydrogen content is lower than 2 at.%.

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1. Introduction

Crystallization of thin amorphous silicon (a-Si) film on low cost glass substrate and the resulting grains size are of technological interest for semiconductor materials applications such as thin film transistors and photovoltaic solar cells. For both fields, the desired result is polycrystalline silicon film with the largest defects free grains, produced at low thermal budget [1,2]. Small grains generate a high density of grain boundaries that causes the reduction of the charge carriers density, resulting in low photovoltaic performances of the solar cell [3]. Additionally intra-grains defects (i.e. stacking faults, dislocations and twin boundaries Σ9 and Σ27) are also traps for charge carriers [4,5]. On the other hand, the crystalline structure as well as the grain size depends strongly on the deposition process of the a-Si film and the thermal process used for the crystallization. This latter can be achieved either in solid phase by thermal annealing at temperature below the softening point of glass substrates and for long durations [1,6] or in liquid phase by laser annealing [7–9]. In solid phase crystallization, the grain size is limited to few microns [1,6].

Crystallization of a-Si induced by a moving Continuous Wave (CW) laser irradiation in liquid phase considering the melting of the a-Si layer was recently shown to produce polycrystalline silicon films with large grains [8–10]. The low thermal budget and the short processing time allow the use of low cost glass substrate. In the CW laser crystallization approach, the grain size is limited by the hydrogen and impurity content in the film on one hand and by the structural quality of the film on the other hand. Few works were dedicated to these effects. Thus, Kim et al. [11] have shown that the crystallization induced by excimer laser annealing of a-Si film containing Argon leads to dewetting of the molten silicon during the argon effusion, causing the agglomeration of the crystallized layer. Toet et al. [12] and Suzuki et al. [13] have studied the laser crystallization of a-Si:H with high hydrogen content. They reported bubbles and blistering due to molecular hydrogen explosion in the layer during the laser annealing at high temperature. The first authors found a critical hydrogen concentration of 5 at.% to avoid damages while the second claim a threshold value less than 1 at.%. As for the CW laser, Andrä et al. [8] have reported that Nd:YAG (λ = 532 nm) laser crystallization of PECVD a-Si:H films containing 3 at.% hydrogen results in polycrystalline films with grains longer than 100 μm.

The aim of this work is to study the effect of the structural quality of the a-Si:H layer on the crystallization process by means of a CW laser emitting at 808 nm. The amorphous silicon layers were obtained by EBE and PECVD deposition methods. The PECVD a-Si:H

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layer carried different thermal annealing conditions for hydrogen effusion before laser processing. ERDA measurement and FTIR spectroscopy were employed to evaluate the hydrogen content and the bonding configurations of hydrogen in the a-Si network. We have found the critical hydrogen content for the best crystallization at 2 at.%. Silicon grains as large as tens microns and hundreds microns long were observed after CW laser crystallization of the amorphous silicon films containing a low amount of hydrogen atoms.

2. Experiment

Thin amorphous silicon (a-Si:H) films with different hydrogen content are considered in this study. The depositions were performed on single crystalline silicon or on Borofloat 33 glass. Two kinds of deposition techniques were used:

(i) The Plasma Enhanced Chemical Vapor Deposition (PECVD) using a Micro-Wave (MW) with a frequency of 2.45 GHz. The deposition conditions were a MW power of 650 W, a substrate temperature of 450 °C, a pressure of 10^{-1} mbar, and gas flows of SiH_4:H_2 = 40:50. With these conditions, the deposition rate is about 9.4 Å/s. The thickness of the deposited layers was 360 nm as measured by a Talystep profilometer. Some PECVD a-Si:H layers were thermally annealed for the effusion of hydrogen at 450 °C/3 h (sample B), 550 °C/3 h (sample C), 450 °C/3 h followed by 550 °C/3 h (sample D) under nitrogen flux. Sample E was annealed at 450 °C/3 h followed by 550 °C/3 h but in vacuum.

(ii) The Electron Beam Evaporation (EBE) tool in high quality vacuum (2×10^{-6} mbar) from a single crystalline silicon target. During the deposition, the substrate temperature was kept at 250 °C and the deposition rate was about 15 Å/s. 200 nm thick films were then prepared. The EBE films with a purity of 5 N (99.999%) were not annealed since they are hydrogen-free as it will be shown below. These samples are denoted sample F.

The as-deposited PECVD and EBE and thermal annealed silicon layers were analyzed using the Elastic Recoil Detection Analysis (ERDA) technique and the Fourier-Transform Infrared (FTIR) spectroscopy in order to respectively evaluate the hydrogen content and the hydrogen bonding configuration prior to laser treatment. For this purpose, the same a-Si:H layers were deposited on silicon substrate. The FTIR spectra were obtained using the Brucker Equinox 55 spectrometer. The ERDA measurements were carried out on a Van de Graaff accelerator using a ^{4}He beam in quasi-normal incidence (10°) with a 2.8 MeV energy. All amorphous silicon films were irradiated by a high power CW laser diode emitting at λ = 808 nm with a maximal output power of 150 W. The spatial energy distribution of the laser beam was near Gaussian profile in both scanning and transversal directions with 400 μm width at 1/e^2 of the laser intensity. The substrates were mounted on a 2D translation stage with speed up to 10 cm/s. The surface morphology and grain size were determined by Optical Microscopy (OM), Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM). The crystallinity of the laser treated samples was investigated by Electron Backscatter Diffraction (EBSD) and Raman spectroscopy. The EBSD maps have been acquired on a Field Emission Gun Scanning Electron Microscope (FEG-SEM) LEO 1530 equipped with a Oxford/HKL Channel5 EBSD system.

The laser power and scan speed were varied to achieve the desired structural change observed under optical microscope.

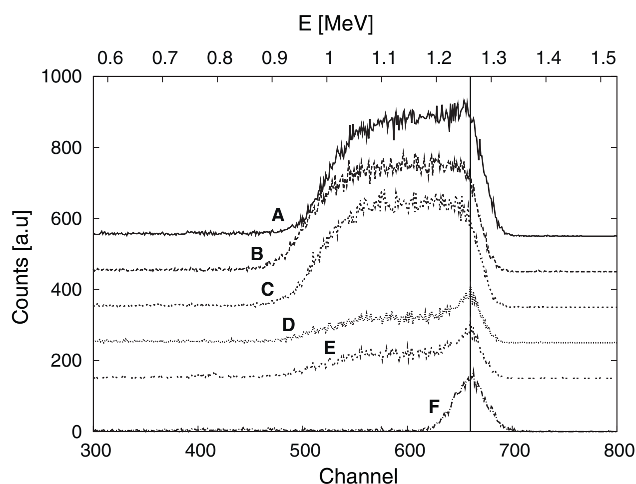

Fig. 1. ERDA spectra for samples A–F (see text) on c-Si. The vertical line shows the surface of the a-Si film.

3. Results and discussion

3.1. Impurity content in the a-Si:H layers

Fig. 1 shows the ERDA spectra of the as-deposited PECVD a-Si:H layers (sample A) and the thermally annealed ones under different conditions (samples B to E). The surface of the a-Si film is located at 1.27 MeV (indicated by a vertical line in the figure). The hydrogen profiles look quite comparable and of similar shape for samples A, B and C but very different for sample D and E which were double annealed at 450 °C/3 h and then at 550 °C/3 h in nitrogen ambient and in vacuum, respectively. A strong effusion of hydrogen from the layer is expected for these latter. The ERDA spectrum of the 400 nm thick a-Si deposited by EBE is also plotted (sample F) for comparison. The analysis reveals the presence of a hydrogen peak only near the surface that can be explained by the adsorption process. No hydrogen trace is detected in the volume for this sample. The corresponding RBS spectrum (Fig. 2), achieved with a ^{4}He beam energy of 3 MeV, shows a peak of oxygen at the surface of the a-Si film which corresponds to the native oxide.

The FTIR absorption spectra of the as-deposited and thermal annealed PECVD a-Si:H layers are shown in Fig. 3. The FTIR spectrum of the as-deposited a-Si:H layer (sample A) exhibits peaks

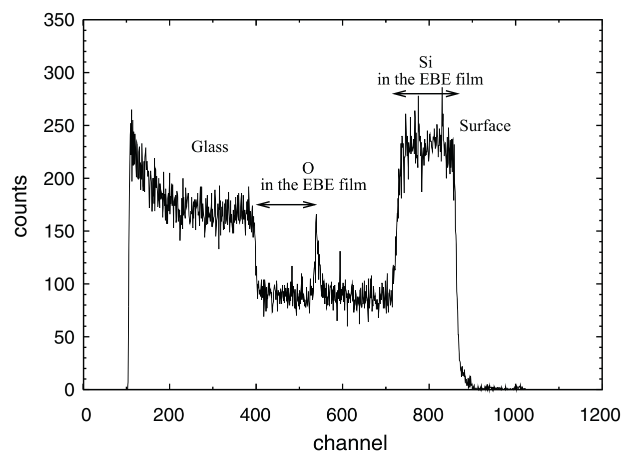

Fig. 2. RBS spectrum for a-Si deposited by EBE (sample F) on glass. Oxygen content is detected only on the surface of the layer.

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