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Study of the effect of boron doping on the solid phase crystallisation of hydrogenated amorphous silicon films

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ABSTRACT

Thin-film polycrystalline silicon on glass obtained by crystallization of hydrogenated amorphous silicon (a-Si:H) films is an interesting alternative for thin-film silicon solar cells. Although the solar-cell efficiencies are still limited, this technique offers excellent opportunity to study the influence of B-doping on the crystallisation process of a-Si:H. Our approach is to slowly crystallize B-doped a-Si:H films by solid phase crystallization in the temperature range 580–600°C. We use plasma-enhanced chemical vapour deposition (PECVD) and expanding thermal plasma chemical vapour deposition (ETPCVD) for the B-doped a-Si:H deposition. In this work we show the first in-situ study of the crystallization process of B-doped a-Si:H films produced by ETPCVD and make a comparison to the crystallization of intrinsic ETPCVD deposited a-Si:H as well as intrinsic and B-doped a-Si:H films deposited by PECVD. The crystallization process is investigated by in-situ x-ray diffraction, using a high temperature chamber for the annealing procedure. The study shows a strong decrease in the time required for full crystallisation for B-doped a-Si:H films compared to the intrinsic films. The time before the onset of crystallisation is reduced by the incorporation of B as is the grain growth velocity. The time to full crystallisation can be manipulated by the B_2H_6-to-SiH_4 ratio used during the deposition and by the microstructure of the as-deposited a-Si:H films.

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1. Introduction

Photovoltaic solar cells based on thin silicon films have gained wide interest because of the low material consumption, and light-weight and/or flexible applications. These thin-film silicon solar cells are mostly based on hydrogenated amorphous silicon (a-Si:H), deposited using plasma enhanced chemical vapour deposition (PECVD). This material has a high absorption coefficient due to the disorder, allowing almost full absorption of the visible part of AM 1.5 spectrum for a layer thickness of 1 μm [1]. The performance of these thin-film silicon solar cells decreases after prolonged AM 1.5 illumination as a result of the Staebler–Wronski effect [2]. So far the highest reported stabilized efficiency is 10.1% for a single junction a-Si:H cell [2–5]. For this reason researchers have investigated the manufacturing of solar cells based on thin layers of crystalline silicon (c-Si) [6,7]. This material has a much lower defect density and therefore a reduced recombination rate. Although the absorption coefficient of c-Si is much lower than of a-Si:H, 10 μm film thickness would suffice to absorb the sun radiation with an energy above 1.1 eV [8,9].

Thin layers of c-Si have been obtained using several methods. The most direct way of making thin c-Si layers is by cleaving or sawing casted crystalline silicon from ingots [7]. Alternatively, other methods use the crystallization of amorphous silicon (a-Si) or a-Si:H, in particular laser-induced crystallization (LIC) [10] and solid-phase crystallization (SPC) [10,11] resulting in polycrystalline silicon (poly-Si). Using LIC Dore et al. [12] made c-Si grains with a size of 1 mm wide and 10 mm long for 10 μm thick films, and solar cells were made having a conversion efficiency of 8.4% [12]. Problems using LIC are associated with the control of the heat transfer of the laser light to the silicon layer, in particular for films with thickness of more than 300 nm [13]. Another method for the production of thin-film poly-Si is SPC of a-Si(:H) films. In this method a thin layer of a-Si(:H) is annealed at temperatures in excess of 560 °C [14], leading to the formation of c-Si regions. The annealing temperature can be reduced when the crystallization process is catalysed using a metal, most notably Al. This Al-induced crystallization of a-Si(:H) leads to layers having grain sizes of up to 18 μm [15] and as Al is a dopant in Si, the material is always p-type doped. Gall et al. [15] demonstrated this method making solar cells with an efficiency of 2.7%, but higher efficiencies have been reached for other SPC solar cells. A major drawback of the SPC methods is the low open-circuit voltage, V_{oc}, resulting from a high intragrain defect densities [16].

The defect densities in cast c-Si are often associated with the B-content. However, studies on the crystallization process by SPC have mostly been carried out on intrinsic a-Si(:H) layers or on complete solar-cell stacks. Sharma et al. [17] showed that the crystallization kinetics of intrinsic a-Si:H depends strongly on the hydrogen

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concentration and the microstructure of the material, expressed in the microstructure parameter, R^*, obtained from the stretching modes in the infrared absorption spectra of as-deposited films. Faster crystallisation was observed for lower values of R^*. The largest average grain size was obtained for material having an R^* value of about 0.3. The faster crystallisation was induced by a faster onset of crystallisation, the onset changes in two ways: (i) the crystallisation onset time increases with decreasing the medium range order (MRO) for low R^* values; (ii) for layers with increased disorder (i.e., $R^* > 0.3$) the onset decreases with a further decrease in the MRO of the a-Si:H. This could be induced by nanosized voids collapsing upon hydrogen out-diffusion, leading to a more compact structure during SPC.

Technologies based on CVD allow for doping of a-Si:H films during the deposition process. The great benefit of doping during the deposition is that (depending on the cell design) post crystallization doping is no longer necessary. Olson and Roth [18] described the crystallization process of doped a-Si(:H) and found that both B and P doping increase the crystallization velocity in epitaxial growth experiments [18,19]. For amorphized compensated intrinsic a-Si Suni [20,21] showed that the crystallization velocity is dependent on the doping level and not on the dopant atom. Additionally, B doping greatly enhances the diffusion of hydrogen in a-Si:H [22]. Therefore it is expected that the SPC of a-Si:H is influenced by the B doping. The solubility of H in c-Si is in the order of 10^{16} cm^{-3} [23] while up to 25% H can be present in a-Si:H and therefore full crystallisation requires effusion of H. The H effusion characteristics of a-Si:H are very dependent on the microstructure of the material. In this article we show SPC of B-doped a-Si:H, deposited using PE- or expanding thermal plasma (ETP-) CVD. By varying the deposition conditions we have changed the B doping level and the microstructure of the material. We will show that the microstructure of the as-deposited material is hardly affected by incorporating B in the material, whereas the SPC kinetics become much faster.

This article is organized as follows. In the next section we will discuss the experimental procedures for making the a-Si:H layers and the x-ray diffraction (XRD) characterization. We will also show how we obtain the microstructure parameter, R^*, of a-Si:H that has been deposited on glass. In Section 3 we present the results of in-situ XRD on doped a-Si:H layers having varying dopant concentration and microstructure. This section is followed by the discussion section in which we discuss the results using the Avrami–Johnson–Mehl (AJM) model for phase transition [24–26].

2. Experimental details

Samples have been deposited using two different techniques: Radio-Frequency PECVD at 13.56 MHz and ETPCVD. The PECVD setup has a conventional parallel plate configuration with an electrode distance of 10 mm for the intrinsic deposition chamber and 11 mm for the B-doped deposition chamber. The precursor gases were SiH_4 and H_2. For B-doped a-Si:H, B_2H_6 (2% in H_2) was added to the gas mixture. The layers were deposited using an RF power of 28 mW/cm^2 and a deposition pressure of 70 Pa. The deposition temperature of the PECVD samples was 180 °C and the layers were deposited at a rate of approximately 0.15 nm/s.

For ETPCVD of a-Si:H, a DC Ar–H_2 plasma is created in a narrow channel of a cascaded arc at a pressure of approximately 45×10^3 Pa. The current in the arc is 40 A. The plasma expands through a nozzle into the deposition chamber and at this point H_2 is injected. B-doped films are made by adding B_2H_6 to the H_2 injected at the end of the nozzle. In the deposition chamber, about 8 cm below the nozzle, SiH_4 is injected into the plasma beam and the a-Si:H film is deposited on a temperature controlled glass substrate approximately 40 cm downstream. The pressure in the deposition chamber is about 20 Pa. The deposition temperature is 350 °C and deposition rates used for these samples are between 0.35 and 0.5 nm/s. The films have a thickness of approximately 300 nm. The temperature difference between the PECVD and the ETPCVD deposition was chosen to correspond to the solar grade material from both techniques.

The as-deposited (doped) a-Si:H layers were examined by Raman spectroscopy using a Renishaw InVia Raman spectrometer with a resolution of 2 cm^{-1}. More specifically attention was paid to the Raman active stretching modes of Si – H vibrations at about 2000 to 2100 cm^{-1} [27]; see Fig. 1. By determining the relative contributions of the low and high stretching mode, the microstructure parameter, R^*_R, is obtained. This parameter is defined as:

$$R^*_R = \frac{I_{\mathrm{HSM}}}{I_{\mathrm{HSM}} + I_{\mathrm{LSM}}}, \tag{1}$$

where $I_{\mathrm{LSM,HSM}}$ is the integrated intensity of the LSM (HSM) mode. It has been shown that the HSM contribution is associated to Si – H_x bonding configurations indicative of void-rich material, whereas the LSM contribution is linked to Si – H bonds in divacancies [28].

The a-Si:H films were monitored during the crystallization process by in-situ XRD in two sets of experiments. Earlier we demonstrated that the ex-situ XRD patterns of SPC of intrinsic a-Si:H matched those of a polycrystalline silicon reference [29]. We found that the XRD patterns of both B-doped and intrinsic annealed Si films are similar to the pattern of the reference powder, implying that the grains in the films are randomly oriented. The first experiment consisted of annealing at two temperatures: 580 and 600 °C, in an Anton Paar high temperature chamber HTK 1200 under Ar atmosphere. The samples used in this experiment were intrinsic (PE i and ETP i) or deposited using B_2H_6-to-SiH_4 ratios of 2×10^{-4} (PE B and ETP B).

The second experiment was carried out at 580 °C and 590 °C, in a similar Anton Paar HTK setup. In this second experiment the high-temperature chamber was pumped down to 2×10^{-1} Pa, thereby creating a more controlled atmosphere. The B concentration in a-Si:H films influences the H-effusion. For this reason the films with varying doping levels are annealed in vacuum. In earlier experiments (not reported here) we have found no indication of oxygen incorporation in the films during annealing. In this experiment two B-doped PECVD films were annealed at 580 °C and two B-doped ETPCVD films were annealed at 590 °C. The B_2H_6-to-SiH_4 ratios of the PECVD samples were 2×10^{-4} and 7×10^{-4} for PECVD 2B and PECVD 7B, respectively. The ETPCVD films for the second experiment were made with B_2H_6-to-SiH_4 ratios 1.7×10^{-4} and 7.3×10^{-4} (ETP 1.7B and ETP 7.3B, respectively). We assume that the boron concentration in the as-deposited a-Si:H films varies with the B_2H_6-to-SiH_4 ratio [30]. We note that the B incorporation efficiency is possibly different for the two deposition methods.

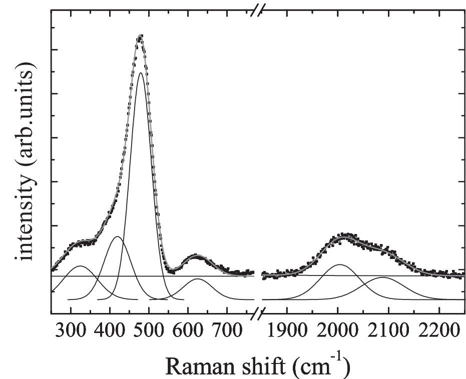

Fig. 1. Two parts of a typical Raman spectrum of a-Si:H are shown. The 250 to 850 cm^{-1} range shows the phonon modes related to the Si – Si bonds of a-Si:H, the 2000–2100 cm^{-1} region shows the Si – $H_{(x)}$ related low and high stretching modes.

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