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Polycrystalline silicon films obtained by crystallization of amorphous silicon on aluminium based substrates for photovoltaic applications

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ABSTRACT

The fabrication of crystalline silicon thin films on foreign substrates is an attractive and alternative approach to the ingot casting aiming to the reduction of the total costs of photovoltaic cells and modules. The purpose of this work is to describe the CRYSTALSI process which aims at forming polycrystalline silicon films thanks to the thermal crystallization of amorphous silicon layer deposited on aluminium based substrates. The latest are used as a catalyzer for silicon crystallization but also as a back metal contact and reflector for photovoltaic solar cells. Two types of aluminium substrates were applied in these studies: a pure aluminium substrate (99.7% purity) and a silicon rich aluminium substrate containing about 12% of silicon. Silicon thicknesses between 1 and 10 μm were deposited and then annealed at temperatures of 490 °C, 520 °C and 550 °C and for duration times from 5 min to 12 h. The crystallized silicon films were then characterized by Raman spectroscopy, by scanning electron microscopy and by electron backscatter diffraction. The analyses show that the resulting annealed film is composed of two distinct layers: a thin polycrystalline silicon film located just above the substrate and a thicker layer made of a mixture of silicon and aluminium. Contrary to the case of the pure aluminium substrate, the silicon rich aluminium substrate allow to obtain thick and continuous polycrystalline silicon layers due to a controlled diffusion of the silicon within the substrate. As a result, the crystallization at 550 °C of 5 μm thick amorphous silicon on silicon rich aluminium substrate led to the formation of a thick polycrystalline silicon layer composed of grains of few micrometers in size. A low activation energy of about 2 eV is extracted suggesting that the silicon rich aluminium substrate is a catalyzer for the crystallization of amorphous silicon. As for the AIC process, it can be noticed that the limiting step of the CRYSTALSI process is the diffusion of the silicon in the aluminium. A chemical etching using a HNO_3, HF, H_2O (72.5 ml/1.5 ml/28 ml) solution is found to be appropriate to remove the residual top layer, in order to have access to the polycrystalline silicon layer. This work demonstrates that the CRYSTALSI process can lead to the formation of polysilicon films that can serve as a seed layer for the growth of a thicker absorbing silicon film for photovoltaic applications.

1. Introduction

During the last decades, silicon deposition has generated a lot of interest for the photovoltaic applications [1]. In 1970s–1980s, works already showed that amorphous silicon can be deposited at low temperatures (about 200 °C), on large areas and using high deposition rates [2,3]. Nevertheless, the conversion efficiencies remain low after solar cell fabrication and a degradation of the electrical performances is noted under illumination [4]. To overcome this limitation, polycrystalline silicon (Poly-Si) films have been elaborated from different techniques such as Solid Phase Crystallization (SPC), Laser Induced Crystallization (LIC) and Metal Induced Crystallization (MIC). The SPC technique allows the crystallization of amorphous silicon at a low temperature around 600 °C during approximately 10 h. A grain size of around 1 μm can be obtained and the structural defects appear with the formation of grain boundaries caused by a non-perfect match up [5–7]. A conversion efficiency of 10% has been reported by the CSG solar company from the solid phase crystallization of 2 μm of amorphous silicon deposited on quartz [8]. The LIC process can be realized using pulsed lasers (excimer laser, 308 nm) or continuous lasers (CW Nd-doubled-YAG, 532 nm). Circular silicon grains around 1 μm were obtained using excimer lasers. The grain size is limited by a high density of nucleation sites caused by the fast cooling [9].The crystallization by Nd-doubled-YAG CW laser provides elongated silicon grains of several tens

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of micrometers, which are created from the silicon melting and the nucleation sites which appear at the edge of the melting zone [10,11]. The MIC technique has been investigated in order to decrease the thermal budget of the amorphous silicon crystallization. Indeed, the amorphous silicon in presence of some metals such as silver, aluminium or nickel can crystallize faster at low temperature. Two different cases have been observed: the nucleation occurs at the metal/deposited amorphous silicon interface (for example, the silver/silicon case) [12] or the silicon diffuses and crystallizes inside the metal (case of Al/Si) [13]. As a particular example of MIC, the AIC (Aluminium Induced Crystallization) process results in the formation of a polycrystalline silicon layer heavily doped with aluminium. In this case, an aluminium layer of 320 nm is deposited on a quartz substrate followed by a deposition of 500 nm thick intrinsic amorphous silicon. During the annealing step, silicon diffuses; it reaches the limit of solid solubility and it crystallizes within the aluminium layer. At the same time, the excess of aluminium, which did not react with silicon, is expelled by the silicon grain during its formation. As a final result, a polycrystalline silicon layer is formed on the glass substrate in addition to a top surface layer composed of a mixture of aluminium and silicon. The top layer is then etched chemically to have access to the polycrystalline film. The later can be used as back surface field of the solar cell as it is heavily doped by aluminium.

The present work reports on the thermal crystallization of amorphous silicon films on silicon rich aluminium substrates (SRAS). This SRAS substrate is acting as a catalyzer for the nucleation of silicon. If applied to solar cells, the substrate can serve as a back contact as well as a rear reflector for the major part of solar radiation going through the silicon film. We labeled this novel process CRYSTALSI. The difference between CRYSTALSI and the conventional AIC, has to do with the thickness layer and the amount of aluminium atoms available for the exchange with the silicon. For the AIC, the process is limited by the thickness of the aluminium layer (100–200 nm) while thick SRAS substrate (0.5–2 mm) is an infinite source of aluminium atoms.

In the first part, we will compare the results of formation of polycrystalline silicon films using pure aluminium (PAS) and silicon rich Al substrates. Then, we will investigate in deeper detail the dimensional, structural and chemical properties of the crystallized silicon films on SRAS substrates versus the annealing temperature, annealing time and thickness of the initial amorphous silicon. The main aim is to form a thick and continuous polycrystalline silicon layer on the top of the conducting SRAS substrates for photovoltaic applications.

2. Experimental details

The crystallization process for the fabrication of polycrystalline silicon (poly-Si) films is schematically drawn in Fig. 1. Two types of aluminium based substrates were used for this work: an aluminium substrate of 99.7% purity called “PAS” and an aluminium substrate containing a silicon concentration of around 12% which will be labeled below as SRAS. The later was fabricated at SINTEF by introducing silicon lumps with solar grade purity in the molten aluminium. Thereafter, the melt is carefully stirred to dissolve the silicon. The ingot obtained after cooling was cut by a cold-sawing process in small pieces of 1.5×1.5 cm^2 and 2 mm in thickness. The deposition of the intrinsic amorphous silicon (i-aSi) films was performed using an ECR-PECVD reactor (Roth-Rau system). Silicon thicknesses between 1 and 10 μm were deposited with a rate of 90 nm/s using the following deposition conditions: microwave power: 650 W, substrate temperature: 250 °C, silane flow rate: 30 sccm, argon flow rate: 35 sccm and pressure: 5.33 Pa. The thermal annealing was performed in an open tube furnace with a controlled flow of nitrogen at a temperature of 490 °C, 520 °C or 550 °C for different duration times ranging from 5 min to 12 h. After annealing, some samples were polished mechanically on the cross section, and the annealed stack was investigated by the Scanning Electron Microscopy (SEM), Electron Backscatter Diffraction (EBSD), the Energy-Dispersive X-Ray Spectroscopy (EDS) and the micro-Raman spectroscopy techniques to determine the microstructure of the different layers formed after the exchange process. The EDS analysis allows getting an insight on the chemical composition and particularly the concentrations of oxygen, aluminium and silicon within the layers. To get access to the polycrystalline silicon film, samples were etched by a solution composed of HNO_3, HF, H_2O (72.5 ml/1.5 ml/28 ml).

2.1. Results and discussion effect of the substrate in the CRYSTALSI process

For this study, the Pure Aluminium Substrate (PAS) and the Silicon Rich Aluminium Substrate (SRAS) were coated with a 10 μm of amorphous silicon films, and then annealed at 550 °C during 12 h. In order to insure that the crystallization process is complete, a high temperature and a long duration time were deliberately chosen. Fig. 2a exhibits cross-section SEM images of the annealed samples. The back-scattering mode of SEM was used in order to reach a better contrast of the different chemical elements present after the annealing process, as well as their concentrations. An EDS local analysis at different positions of the cross section, namely A1, A2 and A3, is shown in Fig. 2b. According to the SEM and EDS analyses, three different regions containing different elements can be easily distinguished from the images of both samples as displayed in Fig. 2b: a first clear zone directly in contact with the substrates is found to be composed mainly of silicon atoms (A1); a darker zone on top of the silicon turns out to contain a large amount of aluminium, oxygen and silicon atoms (A2), and finally, a clearer zone on the top surface seems to be composed of silicon and oxygen with no aluminium present (A3). From these observations, it can be suggested that the crystallization process using aluminium based substrates proceeds through an exchange with silicon layer during the annealing in order to form a polycrystalline silicon layer above the aluminium substrate [14]. Thus, the silicon atoms diffuse and dissolve into the top surface of the aluminium substrate until the silicon concentration reaches the saturation, initiating the silicon grain nucleation. Such phenomenon is quite similar to the AIC mechanism, except that for AIC the limited thickness of aluminium and the substrate, usually quartz or ceramics, stops the diffusion of silicon towards the bulk and favors the lateral growth.

When comparing the SEM cross-sections in Fig. 2, it is obvious that the polycrystalline silicon (poly-Si) layer formed on PAS is strongly discontinuous while it is continuous in the case of a SRAS substrate. A comparison on the use of the two substrates will be described below.

To get more insights on the chemical composition of the poly-Si/SRAS stack, SEM analysis using the compositional mode (Fig. 3a) and EDS mapping analysis of silicon (Si, Fig. 3b), aluminium (Al, Fig. 3c) and oxygen (O, Fig. 3d) were performed on the cross section of the same sample. As expected, EDS analysis shows that the dark zones visualized by SEM contain a strong aluminium concentration and the clear zones are constituted mainly of silicon. A strong oxygen concentration

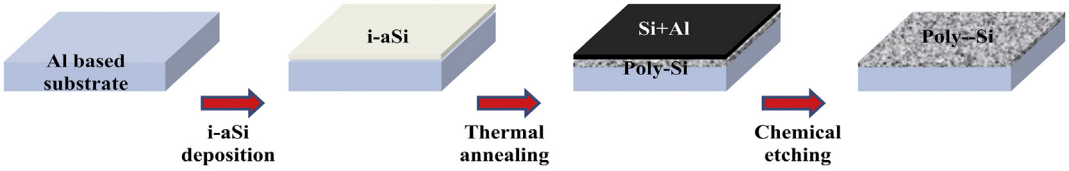

Fig. 1. Schematic of the amorphous Si (aSi) crystallization process on aluminium substrates (figure not to scale).