EPITAXIAL GROWTH OF SILICON THIN FILMS FOR SOLAR CELLS

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ABSTRACT: Crystalline silicon thin film solar cells on glass substrates are a low cost alternative to silicon wafer cells. As an alternative to a simple furnace annealing step in which a-Si is converted to c-Si with 1 µm grains, an epitaxial crystal growth process is presented here. First a seed layer is prepared on glass by diode laser crystallization of an a-Si layer on glass to result in 100 µm grains. Then a-Si is deposited on top of the seed which is converted to c-Si by epitaxial growth. A 1.1 µm thick c-Si layer with 100 µm grains was produced in this way. The paper presents details of the epitaxial growth process.
Keywords: Si-Films, Epitaxy, Multicrystalline Silicon

1 INTRODUCTION

Crystalline silicon thin film solar cells on glass substrates are a low cost alternative to silicon wafer cells. The challenge is to produce a suitable crystalline silicon thin film at temperatures up to 650°C endured by the glass. One way is employed by the company CSG (Thalheim, Germany) [1]. In the CSG-process first an amorphous silicon (a-Si) film with the desired doping profile is deposited by PECVD, which within 18 hours is crystallized by solid phase crystallization (SPC) in a furnace. SPC results in crystal grains in the 1 µm range. Solar cell efficiencies of up to 10.4% were achieved.

Solar cells on glass with grains two orders of magnitude larger can be produced by Layered Laser Crystallization (LLC) [2]. In this process one starts from a diode laser crystallized a-Si layer. The resulting multicrystalline layer has a grain size of about 100 µm and is used as a seed layer for the following epitaxial thickening process. This is done by continuously depositing a-Si on top of the seed and repeatedly applying excimer laser pulses during the deposition. The laser pulses melt the newly deposited a-Si for about 100 ns resulting in epitaxial growth on top of the crystalline layer below. 2 µm thick cells showed an open circuit voltage of 514 mV and 20 mA/cm² short circuit current even without light trapping [3]. The LLC technology gives layers with the worldwide largest crystalline silicon grains on low temperature substrates. However, the repeated excimer laser irradiation of the growing layer is a technological challenge for industrial production.

By combining both the mentioned methods, that is seed layer preparation by diode laser crystallization followed by a furnace annealing step for epitaxial growth of an a-Si layer system 100 µm large crystallites for a multicrystalline silicon thin film cell can be prepared as well. The advantage of this epitaxial solid phase crystallization (ESPC) is the, compared to the LLC process, rather simple technology, which easily may be used in large scale production, and which gives crystal sizes two orders of magnitude larger than the CSG-SPC-process. Moreover, the required crystallization time is even lower.

The temperature dependent nucleation and growth rates of c-Si in an a-Si matrix are described in [4,5]. For the ESPC process the problem is the competition of epitaxial growth from the seed with the nucleation of crystallites in the amorphous matrix, which leads to fine grained silicon. Beneficial for the ESPC process is the time lag of nucleation, which is the time needed for the evolution of a distribution of crystalline nuclei in a-Si exceeding the critical size [6]. Only after this time lag the stationary nucleation rate applies. At 600°C the time lag amounts to several hours whereas at 650°C it reduces to about 1 h. This time can be used for undisturbed epitaxial growth starting on the laser crystallized seed layer. A challenge is to find a temperature regime in which epitaxy is fast enough so that no spontaneous nucleation occurs until epitaxy has converted the whole a-Si layer into c-Si. Another challenge is to get a clean enough interface between the seed and the a-Si so that epitaxy may occur.

In the paper the kinetics of the epitaxial growth and the resulting crystal structure are investigated as depending on deposition rate of a-Si. The properties of the films are discussed. The described methods will be used in the European project HIGH-EF to develop multicrystalline silicon thin film solar cells on glass.

2 EXPERIMENTAL

The preparation of the layer system for the multicrystalline silicon thin film solar cell is done in the following way. In a first step onto a borosilicate glass substrate a several 100 nm thick hydrogen free amorphous silicon (a-Si) layer is deposited by electron beam evaporation. This layer is crystallized by scanning the 100 µm wide line focus beam of a diode laser (806 nm wavelength, about 10 kW/cm² power density) at a rate of 5 cm/s [2,7]. This procedure, which is performed in ambient air, generates crystallites in the 100 µm range to act as a seed layer for further processing. After removing an oxide layer on top of the seed layer by etching in 2% HF and an excimer laser cleaning pulse, up to 1.1 µm of a-Si is deposited by electron beam evaporation at rates ranging from 10 to 230 nm/min. This layer is in the final step converted to a multicrystalline structure by epitaxial growth from the seed. The EPSC step is performed by a furnace anneal at 600°C or 650°C under Ar gas flow. For comparison, a-Si was crystallized by SPC without seed layer under the same conditions.

To monitor the crystallization kinetics the transmission of the Si layers was recorded during the annealing. To this end the beam of a low power HeNe

laser (632 nm wavelength) was introduced into the furnace. After passing the sample the transmitted intensity was recorded by a photodiode outside the furnace. The crystal structure after crystallization was investigated by transmission electron microscopy (TEM) and by EBSD (electron back scattering diffraction) which gives orientation maps of the crystal structure in a surface region of the sample.

3 RESULTS

The typical fine grained crystal structure following from furnace SPC of a-Si on glass is shown in Fig. 1. The grain size is below 2 µm with no preferential crystal orientation. Fig. 2 shows the evolution of the transmission during the annealing which reflects the kinetics of the crystallization. As is obvious a remarkable increase of transmission due to an increasing amount of crystalline parts in the film starts after about 6 h. This is a hint for the time lag of nucleation. After the time lag a sigmoidal increase of transmission and of crystal content occurs due to nucleation and growth of crystallites. After about 10 h complete crystallization is achieved.

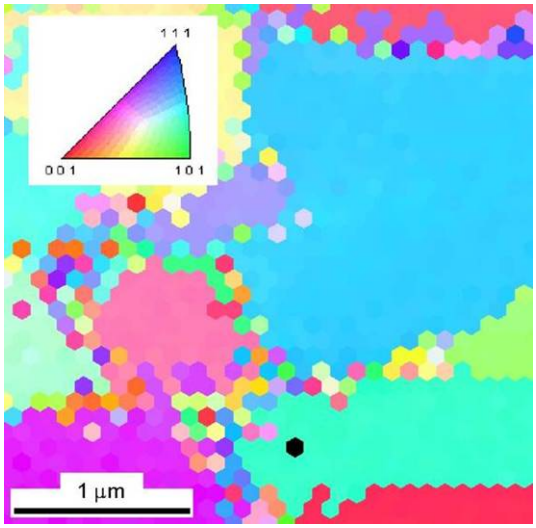

Figure 1: EBSD map of a 1.1 µm thick a-Si layer on glass deposited at 100 nm/min and SPC crystallized by annealing at 600°C for 11 h.

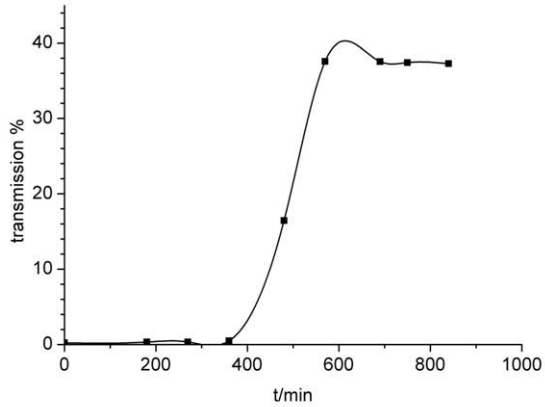

Figure 2: Evolution of transmission of an a-Si layer on glass deposited at 100 nm/min during annealing at 600°C

It turned out that the time lag of nucleation as well as the time needed for complete crystallization of a-Si deposited by electron beam evaporation depends on the deposition rate. This is shown in Fig. 3 for an annealing temperature of 600°C. Of particular interest is the time lag which varies between 6 and 25 h.

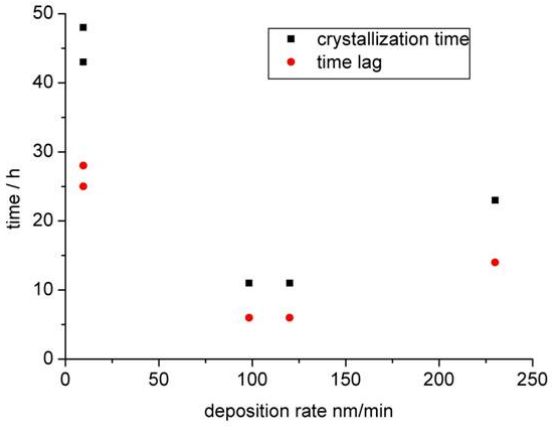

Figure 3: Time lag of nucleation and time for complete crystallization of a 500 nm thick a-Si layer on glass for annealing at 600°C as depending on the deposition rate.

In contrast to SPC the epitaxial growth experiments on top of a laser crystallized seed layer lead to much larger crystallites. Fig 4 shows the EBSD map of a seed layer which demonstrates that it consists of grains in the 100 µm range. There is no preferred crystal orientation.

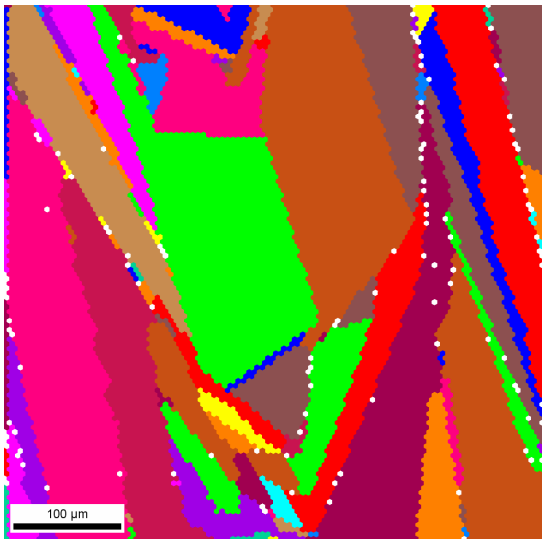

Figure 4: EBSD map of a diode laser crystallized seed layer on glass.

Fig. 5 shows the evolution of the transmission during EPSC of a 500 nm thick a-Si layer at 600°C which was deposited at a rate of 100 nm/min on top of a laser crystallized seed layer on glass. There is no time lag in epitaxial growth. Instead from the beginning a nearly linear increase of transmission and therefore of crystal amount is observed. After 5.5 h the crystallization is complete. This is less than the time lag of nucleation at the same temperature. Therefore one does not expect that

nuclei form in the a-Si matrix during the time needed for epitaxial growth.

The complete transformation to large grains up to the surface is confirmed by the EBSD map of a 500 nm thick layer, which was taken after 5.5 h annealing at 600°C (Fig. 6). This Figure demonstrates that all grain orientations present in the seed grew epitaxially to the surface. Fig. 7 shows a corresponding TEM cross section image of a 550 nm thick ESPC layer on a seed layer demonstrating that perfect epitaxy occurred. For this to occur a perfectly clean surface of the seed prior to a-Si deposition is crucial.

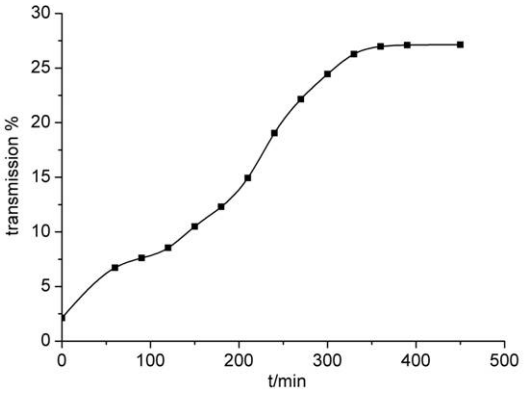

Figure 5: Evolution of transmission of a 500 nm thick a-Si layer deposited at 90 nm/min on a seed layer during annealing at 600°C.

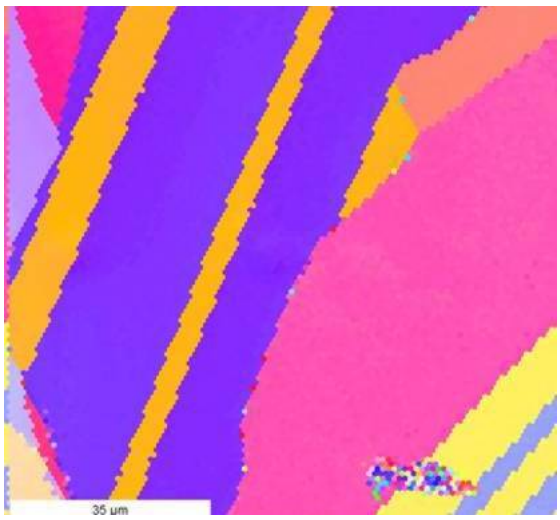

Figure 6: EBSD map of a layer system of a 500 nm thick ESPC layer annealed for 5.5 h at 600°C on top of a laser crystallized seed.

As for SPC also in ESPC the time needed for complete crystallization, i.e. the epitaxial growth speed, depends on the deposition rate of the a-Si (Fig. 8).

Comparing the time needed for ESPC with the time lag (Fig. 3), both as depending on deposition rate, we learn that for 500 nm thick a-Si film at 600°C epitaxial growth is completed within the time lag of nucleation independent of the deposition rate. To completely epitaxially crystallize layers thicker than 500 nm one needs a-Si layers in which the time lag as well as the epitaxial growth speed are as large as possible. This requires a-Si films deposited at rates of about 200 nm/min. In this case the time lag of 14 h is larger than the time needed for epitaxial growth even for a 1µm thick film. Fig. 9 shows the EBSD image of a 1.1 µm thick film crystallized by ESPC at 600°C for 12 h. As for the thinner films large crystals extend up to the surface.

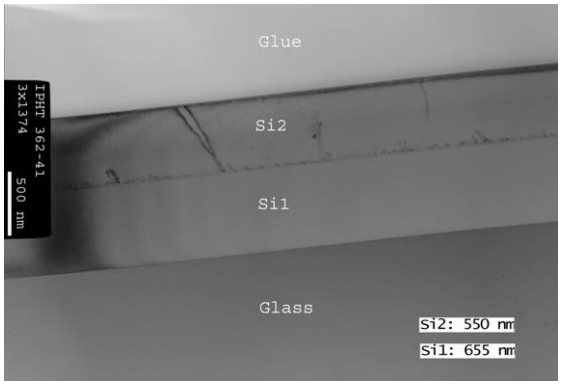

Figure 7: TEM cross section image of a layer system consisting of ESPC layer (Si2) on seed (Si1) after annealing for only 7 h at 600°C.

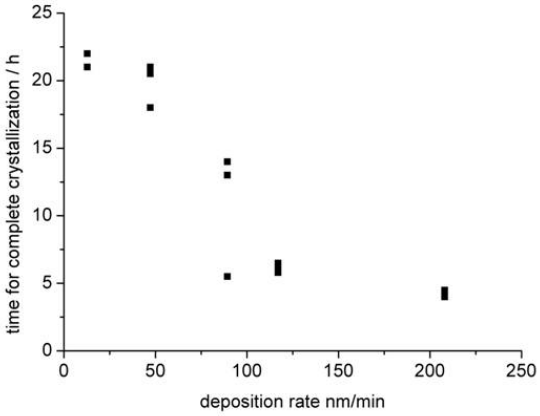

Figure 8: Time needed for complete ESPC of a 500 nm thick a-Si layer on top of a seed at an annealing temperature of 600°C.

An appreciable reduction in the processing time can be achieved by increasing the annealing temperature. Fig. 10 shows the evolution of transmission of a 500 nm thick a-Si layer on a crystalline seed during ESPC at 650°C. The change in transmission immediately starts as is typical for epitaxial growth. After about 1 h the crystallization is complete. The EBSD map of Fig. 11, however, shows that not all grains of the seed continue to the surface. This is confirmed by the TEM cross section image of Fig 12, where on top of the seed (Si1) about 100 nm of the deposited a-Si epitaxially crystallized (Si2) but the remaining a-Si on top was concerted to fine grained material (Si3). Apparently a competing nucleation process took place in a surface near region. As for the annealing process at 600°C the nucleation and growth kinetics depend on the deposition rate of a-Si.

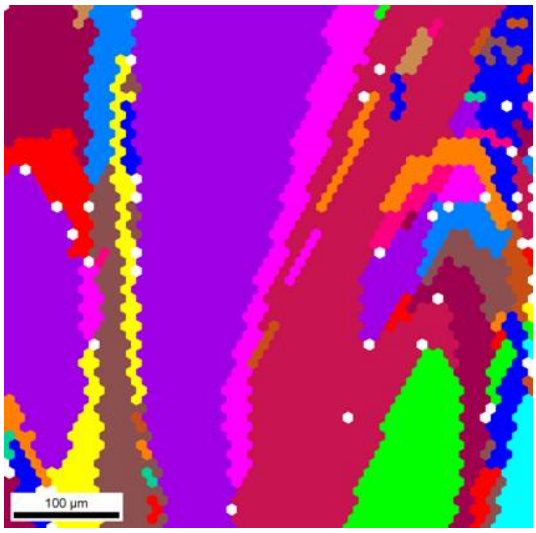

Figure 9: EBSD map of a 1 µm thick ESPC layer deposited at a rate of 180 nm/min and crystallized by annealing at 600°C for 12 h.

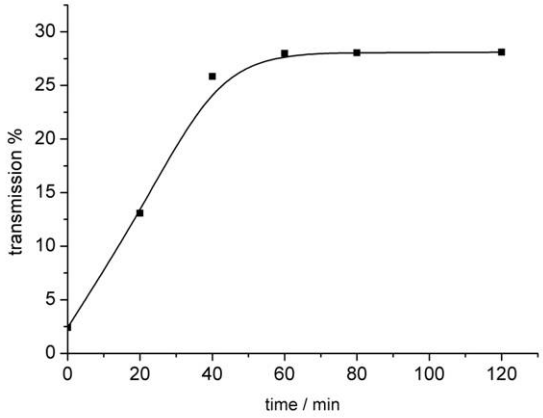

Figure 10: Evolution of transmission of a 500 nm thick a-Si film on crystalline seed during annealing at 650°C.

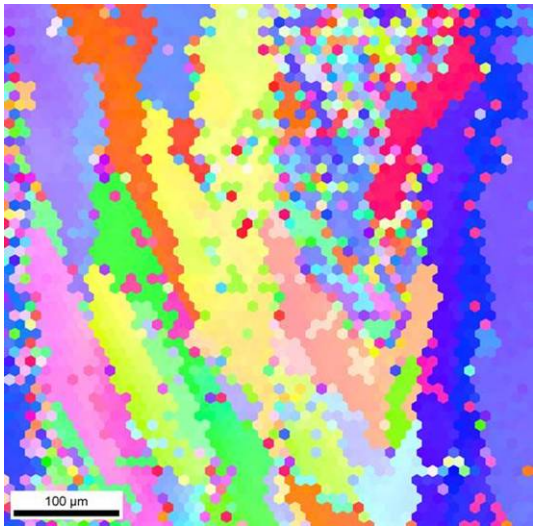

Figure 11: EBSD map of a 500 nm thick ESPC layer deposited at 47 nm/min and annealed at 650°C for 1.5 h.

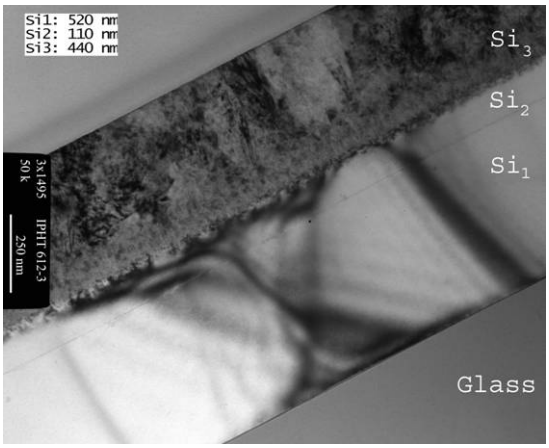

Figure 12: TEM cross section image of an ESPC layer on seed (Si1) annealed at 650°C for 6 h showing an epitaxially crystallized layer (Si2) and a fine grained layer (Si3).

In further work we will investigate if we can deposit a-Si under conditions so that at temperatures between 600°C and 650°C perfect epitaxial growth is possible.

4 SUMMARY

a-Si layers deposited by electron beam evaporation on top of multicrystalline seed layers on glass were crystallized epitaxially at 600°C up to a thickness of 1.1 µm. In this way we succeeded in preparing a layer system as required for multicrystalline silicon thin film solar cells on glass with grains in the 100 µm range. The preparation process is simple and easily can be up-scaled. By optimizing the deposition and growth conditions we work on reducing the required annealing time and to increase the thickness of the epitaxial layers to well above 1 µm. First observations give hints, that doped a-Si grows faster so that thicker films can be crystallized in even shorter time. In the next steps we will prepare complete solar cells in ESPC silicon layers.

5 ACKNOWLEDGEMENT

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