CRYSTALLINE SILICON GROWTH ON SILICON NITRIDE AND OXYNITRIDE SUBSTRATES FOR THIN FILM SOLAR CELLS

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ABSTRACT: Si infiltrated SiAlON substrates were tape-casted and sintered from a SiAlON slurry with additional crystalline Si. The crystalline Si in the matrix of the substrate acts as seeds for epitaxial growth. Silicon layers were deposited by liquid phase epitaxy on these substrates. A closed layer could be grown from a saturated Ga/Al solution on Si infiltrated SiAlON with 42% Si. The crystals forming the layer are faceted and reach sizes of more than 100 µm in diameter. This layer is highly p doped because of the incorporation of Ga and Al.
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1. INTRODUCTION

Thin crystalline silicon layers on inexpensive substrates are of great interest for the fabrication of cost-effective solar cells. Good crystalline quality and favourable electrical properties of the Si layer are the main requirements for high cell efficiencies. Different techniques for depositing silicon thin films on glass or ceramics have been reported. The development of a large number of small grains with dislocations can often not be prevented during deposition processes occurring far from thermodynamic equilibrium. Polycrystalline layers grown under near-equilibrium conditions by LPE show good electrical properties and a very low density of structural defects [1].

The growth of silicon directly on a dissimilar substrate by solution growth techniques is difficult because of the low supersaturation during the process. The Temperature Difference Method TDM and a growth temperature higher than 1000°C made it possible to deposit a Si layer on graphite [2]. A common way for deposition in a lower temperature range is first to deposit a silicon seed layer on the substrate and subsequently grow a high-quality LPE Si layer on this seed layer [1,3-5]. Also plasma sprayed Si layers were successfully used as seedlayers [6].

To eliminate the seedlayer deposition step, a substrate that already contains crystalline Si in sufficient amount and distribution, with a temperature expansion coefficient similar to Si, had to be developed. The Si infiltrated oxynitride SiAlON is a material with such a potential. First growth experiments on Si infiltrated SiAlON showed that there are problems with the distribution of crystalline Si in the matrix of the ceramic and the wetting capacity of the metallic solution [6,7]. On the basis of these results further investigations were done. The content of Si in the Si infiltrated SiAlON substrate was varied and different metallic solutions with a known higher solubility for Si and better wettability were used. Additional growth experiments on Si substrates with a locally opened Si-nitride coating were carried out to obtain information about lateral growth and coalescence of Si crystals.

2. EXPERIMENTAL PROCEDURE

2.1 Substrates

The substrates used for these experiments are oxynitride substrates (Si-SiAlON) and mono Si substrates covered with a silicon nitride coating.

The SiN_x covered substrates were prepared by lasering grooves in the coating for the study of epitaxial growth, lateral overgrowth and coalescence. The laser removed the coating and destroyed the perfect monocrystalline structure of the Si substrate in this area. The grooves are about 50µm wide and arranged in distances from 80 to 150µm.

The Si infiltrated SiAlON substrates were tape-casted from SiAlON powder with an additional amount of Si in the slurry. The tapes were sintered at 1550°C, well above the melting point of Si.

Before the start of the growth experiments the substrates were cleaned with a standard RCA clean and HF-dip.

2.2 Liquid phase epitaxy

The growth experiments were performed in a conventional graphite tipping boat system in purified H_2-atmosphere. LPE was carried out with the super-cooling technique. Indium, gallium and gallium / aluminium were used as metallic solvents. The solvents were saturated with silicon at 950°C and 960°C for 3 hours. During the growth process constant cooling rates of 20 K/h and 100 K/h were used.

After the growth experiment, residual solution on the substrate was removed with hydrochloric and / or nitric acid. The surface morphology of the layers was studied under optical microscope and SEM.

3. RESULTS AND DISCUSSION

3.1 Growth on silicon nitride substrates

Silicon nitride was chosen as a model for a ceramic surface without crystalline Si seeds for epitaxial growth. The experimental conditions were not suited for deposition of a Si layer from an indium solution directly onto the SiN_x coating. The Si crystals started to grow epitaxially on the free Si surface in the openings in the nitride coating. In lateral direction the crystals grew up to 15µm over the film. A relationship between the height of the epitaxially grown crystals, the length of the lateral overgrowth and the distances between the openenings in the coating was found; with increasing distance, the crystals grew larger in vertical and lateral direction. This is the consequence of the relation between supply of Si and suitable local surface area for epitaxial growth.

Coalescence between the crystals grown from neighbouring openings could not be achieved. The amount of Si, supplied from the In solution, was too little to grow crystals large enough for coalescence.

3.2 Oxynitride substrates

The added silicon powder melts during the sinter process and forms crystalline grains in the matrix of the SiAlON-ceramic. On the surface these grains have the shape of spheres with first signs of facets. The amount of Si was increased from 42 to 60% to get a denser distribution of these grains. This attempt failed because of the surface tension of the molten Si. Some larger grains developed in stead of more small grains. The variation in grain size also increased. On the 42% Si substrate the largest grains were 500 µm and on the 60% the maximum size was 1mm.

The crystallographic orientation of the grains related to the substrate surface is random.

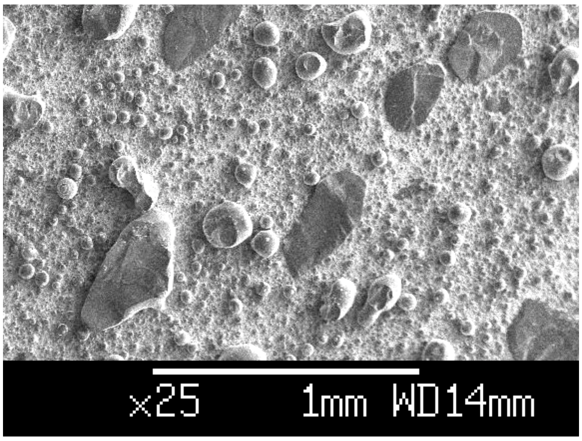

Figure 1: Si infiltrated SiAlON with 42% crystalline Si. The maximum size of the Si grains is 500 µm.

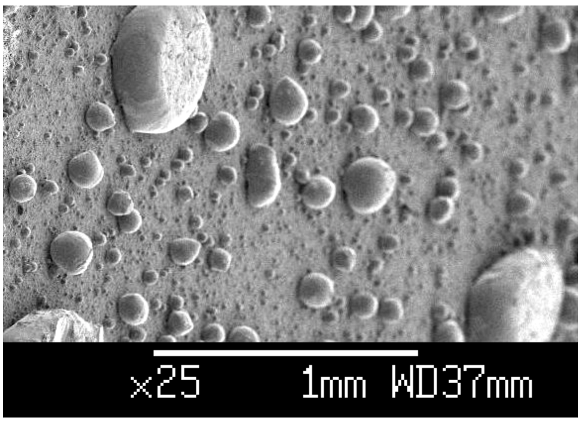

Figure 2: Si infiltrated SiAlON with 60% Si. The crystalline Si grains reach sizes up to 1 mm. The distance between grains has not decreased.

The sintered substrates are conductive and can be used for a cell structure with two-sided contacts.

3.3 Polycrystalline Si layers grown from different metallic solutions

Of all possible metallic solutions for Si growth, indium is the first choice from point of view of electrical quality of grown silicon solar cell [8]. The deposition on the Si infiltrated SiAlON substrates from indium solution results in the growth of the Si grains to greater faceted crystals. Only grains greater than 50 µm seem to act as seeds.

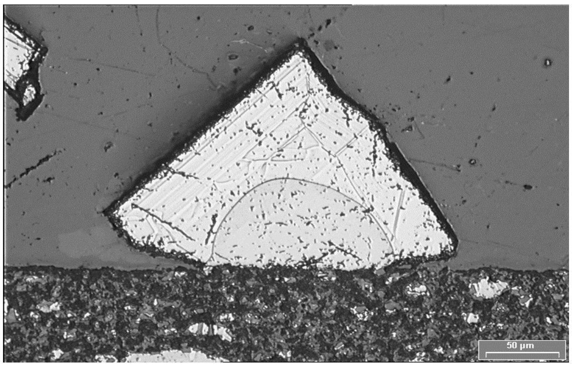

Figure 3: Semicircular Si grain from the substrate is epitaxially overgrown with Si during the LPE process. Etched cross-section.

The crystallographic orientation of the crystals depends on the orientation of the crystalline Si grains on the substrate surface. In figure 3, a cross-section image from an overgrown Si seed grain, can be seen that the epitaxial growth proceeded like the growth of a single crystal. The shape of the crystals was determined by the formation of low-energy {111} faces.

The distance between the epitaxially grown crystals was too large for coalescence. The variation of temperature, growth interval and cooling rate had only little effect on the amount of deposited Si.

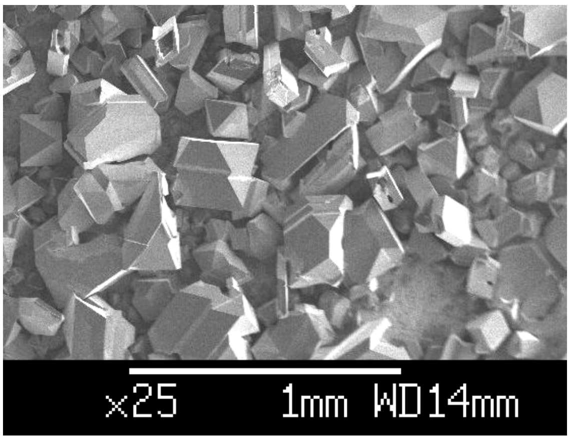

Figure 4: Si layer grown from Ga solution on a Si infiltrated SiAlON substrate. At some places the substrate is still uncovered.

The solubility of Si at temperatures about 920°C in gallium is eight times higher than in indium. The crystals deposited on the Si infiltrated SiAlON substrate from Ga grew larger and closer together. In the top view in figure 4 it can be seen that many crystals coalesced with each other.

Cross-sectional images show that the crystals avoid growing laterally over the substrate as in figure 2 for In. In this region, growth is limited by the limited supply of Si from the solution. Furthermore there are still areas where no growth has taken place. This indicates that the wetting of the substrate surface is insufficient.

The surface tension of liquid gallium decreases with increasing temperature [9]. From silica and quartz surfaces is known that the introduction of Al to a Ga solution improves the wetting of the substrate [10]. Furthermore the solubility of Si in an Al solution is very high.

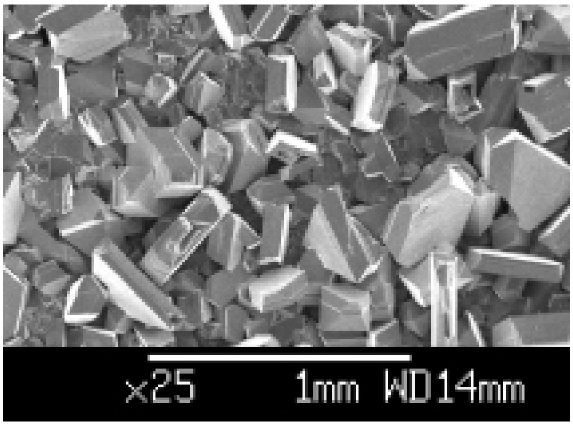

Figure 5: Si layer grown from Ga/Al solution on a Si infiltrated SiAlON substrate.

Figure 5 shows the surface of a layer grown from a Ga solution with 20% Al. Close to the substrate surface a dense layer of small crystals has grown. Larger crystals have formed in and on top of this layer.

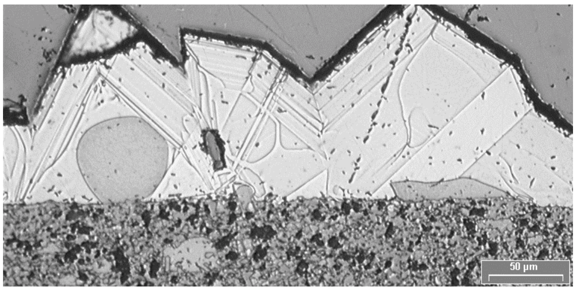

Figure 6: Etched cross-section of a Si layer grown from a Ga/Al solution on a Si infiltrated SiAlON substrate. Grey areas coming out of the substrate surface are the Si seed grains.

The image of an etched cross-section shows that the Si crystals grow directly over the substrate surface and form a laterally closed layer (figure 6). The improved wetting of the substrate surface makes the epitaxial growth of the small grains in pores of the surface possible.

3.4 Application in a thin film cell

A sketch of a possible cell structure based on a Si infiltrated SiAlON substrate and LPE grown Si layers is shown in figure 7. The Si infiltrated SiAlON is conductive so that the cell can be also contacted at the rear side. The Si layer grown from the Ga/Al solution is highly doped with Ga and Al. This layer can act as a barrier layer that avoids diffusion of impurities out of the ceramic substrate into the active layer. It may also serve as a back surface field. An additional silicon layer to form the active solar cell has to be deposited. This can be done by LPE from an In solution. The emitter can be made by P-diffusion.

The rough surface of the Si layers has the advantage of in situ grown light traps, which increase the apparent optical thickness of the cell.

On this rough surface buried contacts can be used as contact fingers.

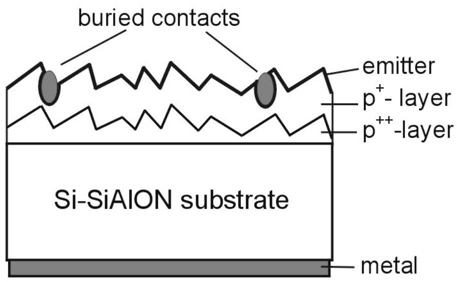

Figure 7: Schematic drawing of a thin film cell with Si infiltrated SiAlON substrate and LPE grown Si layers.

4. CONCLUSION

The low supersaturation of the solvent that is reached with the used conventional LPE technique is not sufficient for seed forming on a non-silicon substrate. At least some crystalline Si grains at the surface of a substrate are required for the epitaxial growth. Such grains could be formed in situ on a Si infiltrated SiAlON substrate. It proved to be difficult to control the distribution of the Si in the matrix.

From the applied metallic solutions only with the Ga/Al solution a sufficient wetting of the substrate surface could be reached and a laterally closed Si layer could be grown with LPE on Si infiltrated SiAlON.

However, the incorporation coefficient and the solubility of these metals into solid Si are high. This results in a highly p-type doped layer.

Next step must be to find a solvent metal system with a comparable high solubility for Si and good wetting properties that will not decrease the electrical performance of the grown layer. A possible system is Si/Cu/Al that was already studied by Wang [11].
Another possibility is to use the highly doped layer as BSF and barrier layer and grow a second layer from an In solution as the active layer on top of it.

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