LPE-DEPOSITION OF CRYSTALLINE SILICON LAYERS ON RECRYSTALLISED SILICON-BASED CERAMICS

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ABSTRACT:
Recrystallisation of (thick) silicon layers can be accomplished without a capping layer. However, a substantial part of the recrystallised layer is highly defected, and has to be removed before a closed layer can be deposited on it by LPE. By tuning the cooling trajectory, the in LPE well known “grain boundary effect” can be reduced, although we did not yet succeed in completely prohibiting the groove formation. Also, the use of metallurgical grade silicon in the nucleation layer resulted in pinholes in the LPE grown active layer.
Keywords: Si-Films -1: Recrystallization -2: LPE -3

1. INTRODUCTION

Thin film crystalline silicon solar cells present a possible way to lower the price of PV. The thin-film Si approaches can be divided in three area’s, depending on the highest temperature involved in the formation of the active layer: low temperature (below 800°C), high temperature (800 - 1200°C) CVD and liquid recrystallisation of a nucleation layer followed by high temperature CVD or LPE (900 - 1000°C). Generally, the higher the deposition temperature, the larger the crystal size of the layer and the higher the obtainable efficiency [1-5]].

World-wide much more research effort is put into CVD deposition of f-Si compared to LPE deposition. LPE deposition is performed close to thermodynamic equilibrium. This has the disadvantage of poor nucleation on non-silicon substrates, but epitaxial layers deposited by LPE can have superior crystallographic and electronic properties over epitaxial layers deposited by (high temperature) CVD [6]. Due to the poor nucleation properties of LPE on non-silicon substrates, in this work focus is on the formation of low-cost silicon substrates by atmospheric plasma spraying and zone melting recrystallisation (ZMR).

2. METHOD

2.1. Atmospheric Plasma Spraying (APS)

As substrates plasma sprayed coatings of metallurgical grade silicon are used. In atmospheric plasma spraying, the powder is melted in a plasma torch and sprayed on a substrate in ambient atmosphere.

If a suitable substrate is available, plasma sprayed silicon can be applied as a (thin) coating be used after recrystallisation as a nucleation layer for both CVD and LPE. It can, however, also be made as a free standing body without the need of an additional substrate. Then no optical separation of the substrate and the active layer can be used, but no additional substrate is needed. Because the state-of-the-art method to produce free standing silicon bodies resulted in banded samples, in this investigation 400 µm thick coatings on multi crystalline silicon wafer were used.

Because no electronic grade powder suitable for plasma spraying was available, commercial plasma spray Si powder (purity 99.5%) has been used.

2.2. Zone Melting Recrystallisation (ZMR)

Recrystallisation of the APS-Si coatings is done using a lamp heated system. In this system, a focused line of light scans over the substrate. To minimise thermal stresses additional lamps are used to heat the substrate from the rear. In the focussing mirror a CCD camera is fitted to monitor the recrystallisation process. The sample is on a quartz plate in a quartz tube (not shown in the figure) which is flushed with Ar/O_2 (15 ltrs/min) to minimise contamination of the quartz tube. Due to the roughness of the APS-Si coating, no SiO_2 capping layer could be used.

Cross sections are etched using a Sirtle etch to reveal the microstructure.

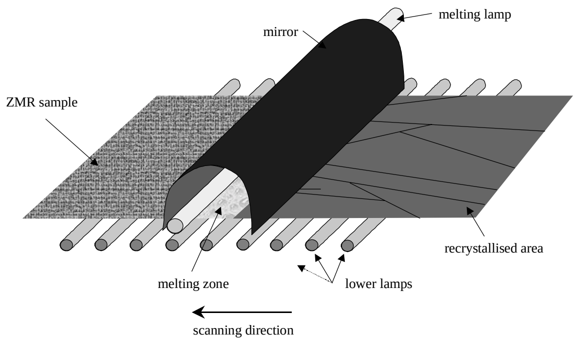

Figure 1: schematic drawing ZMR system

2.3. Liquid Phase Epitaxy (LPE)

Deposition of the active layer has been done with the LPE technique using a tipping boat system described before [7]. Layers are deposited from an indium melt under a high purity H_2 atmosphere (purified using a Pd diffuser).

Before growth the ZMR-APS-Si samples were etched with $HF:HNO_3:CH_3COOH$ (1:7:2) to remove the highly defected surface and cleaned using RCA 1+2, followed by a short HF dip.

3. RESULTS

3.1. ZMR

The depth of the molten zone is controlled by adjusting the power of the upper melting lamp. Using medium power, only part of the APS-Si coating is recrystallised as shown in figure 2a. The lower 100 µm of the coating is highly defective, indicating that it is not recrystallised. The middle 200 µm is recrystallised well, it consists of large (up to 200 µm) crystals, but surprisingly, the upper 100 µm is also highly defective. This is even more pronounced if the whole coating is recrystallised. In figure 2b, the lower part of the coating has crystallised epitaxially on the multi crystalline wafer (indicated by the twinning lines). At about 2/3 of the coating a sharp undulated transition from an epitaxial to a highly defected structure occurs, but the grains in the highly defective part are larger compared to the partly recrystallised coating (fig. 2a).

Two possible reasons can be given for this effect. First, due to the absence of a capping layer and the use of a high Ar/O_2 flow, the surface of the sample looses heat. This results in either limited melting of the upper surface, or in homogeneous nucleation at the free surface. Second, impurities can be swept to the surface during crystallisation, and the impurities can disturb the epitaxial growth process once they reach a certain threshold value.

Figure 2a: partly recrystallised PS-Si coating on mc-Si.

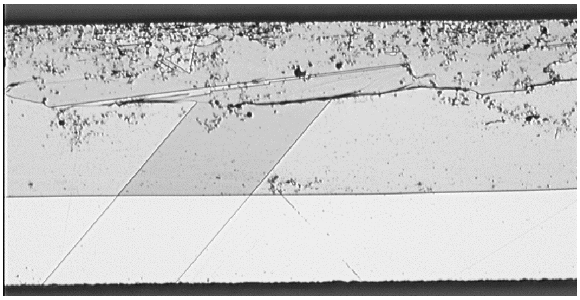
Figure 2b: fully recrystallised PS-Si coating on mc-Si.

3.2. LPE

A well known problem in LPE growth on poly-crystalline silicon wafers is the groove formation at the grain boundaries. By using an intermittent fast heating step with an otherwise constant cooling rate, this effect can be minimised [8]. The use of a constant cooling rate results in a decrease of the deposition rate at lower temperatures, because less silicon will become available per unit time. Better results are obtained if the deposition rate is kept constant by increasing the cooling rate at lower temperatures. Also, the intervals between the heating steps are such that identical amounts of silicon become available for depositions in between. In figure 3 the cooling profiles are shown.

Not only does a constant growth rate results in a better overgrowth of the grain boundary (figure 4), also the growth rate is somewhat higher compared to the constant cooling rate.

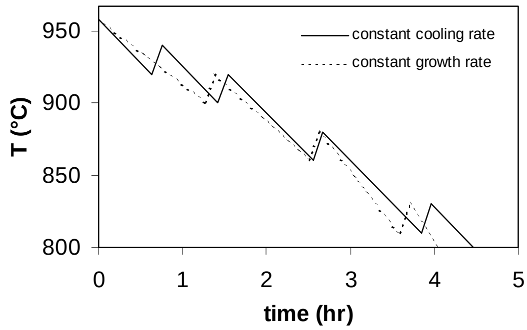

Figure 3: temperature profiles used in LPE deposition.

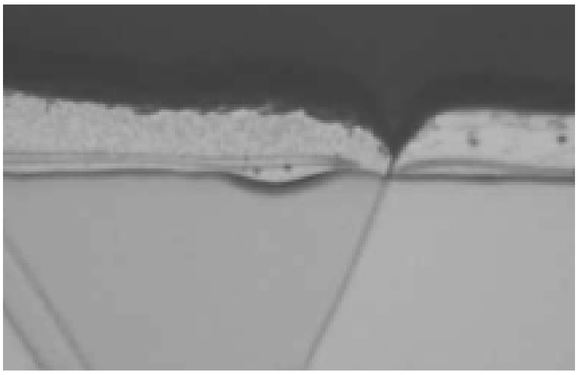
Figure 4a: deposition using constant cooling rate

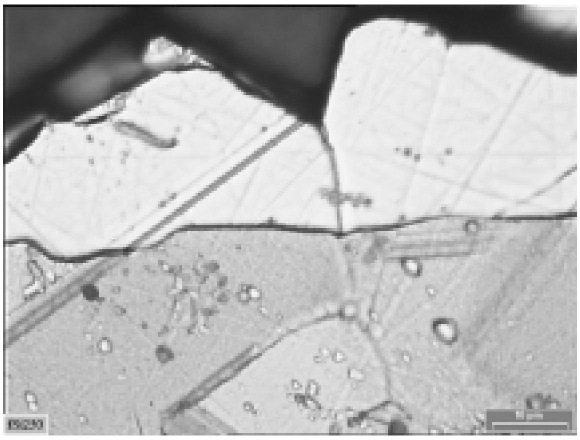
Figure 4b: deposition using constant deposition rate

Although most of the recrystallised samples were given a thorough CP etch to completely remove the top layer, some samples were only shortly etched. Growing on these samples resulted in poor nucleation (see figure 5a). Growth on non-recrystallised PS-Si results in even better layers [7], indicating that slag is (partly) responsible for the poor recrystallisation.

If the upper part of the recrystallised coating is completely removed, a closed epitaxial layer can be grown on the PS-Si (see figure 5b) . Due to the presence of Al and Fe impurities in the Si powder used in plasma spraying, most layers contained pinholes initiated by the impurities (not shown in the figure). Due to these pinholes, solar cells processed from these layers were severely shunted.

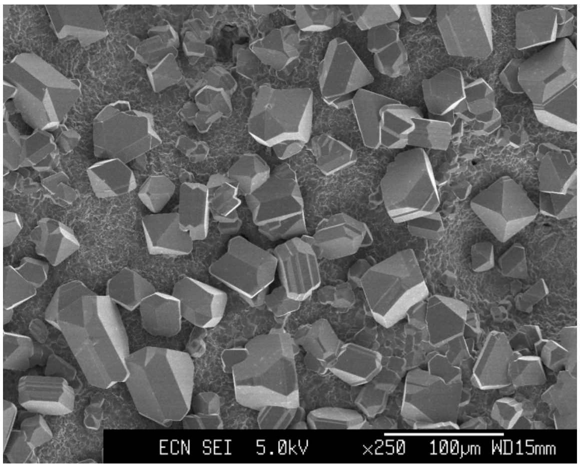

Figure 5a: LPE on partly removed upper layer.

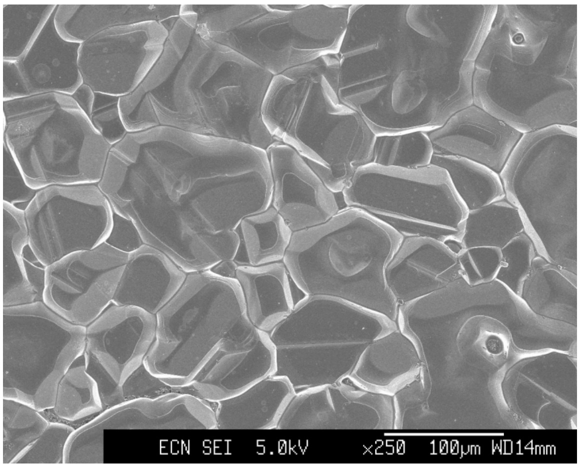

Figure 5b: LPE on fully removed upper layer.

4. CONCLUSION

This investigation shows that recrystallisation of plasma sprayed silicon coatings can be used as substrates for thin film crystalline silicon. Recrystallisation of thick plasma sprayed Si coatings can be done reproducibly.

Despite the relatively high growth speed, crystallisation of the molten zone seems to be epitaxially on the mutli crystalline Si wafer. However, a substantial part of the coating has to be removed to obtain a crystallographic good surface for LPE growth.

Because no barrier layer is used, electronic grade silicon is preferred for the nucleation layer to minimise pinhole formation and impurity diffusion. Also, because no optical separation between the nucleation layer and the active layer is possible, the nucleation layer has to be very thin to minimise current losses.

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