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Orientation relationship between β-Si_3N_4 and Si in multicrystalline silicon ingots for PV applications

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ABSTRACT

β-Si_3N_4 particles are thought to be nucleation sites for silicon in multicrystalline silicon (mc-Si) ingots for PV applications. The orientation relationship (OR) between Si and β-Si_3N_4 has been investigated by transmission electron microscopy (TEM). The following OR was found by analyzing diffraction patterns from a site specific sample prepared by focused ion beam (FIB)

$$[0001]_{\beta-Si_3N_4} \| \left[1\,\bar{1}\,1\right]_{Si}$$

$$\left(\bar{4}\,5\,\bar{1}\,0\right)_{\beta-Si_3N_4} \| (011)_{Si}$$

The β-Si_3N_4 particle was identified as a likely nucleation site based on the grain boundaries (GB) extending from it. It was shown that these GBs were $\Sigma 3$ boundaries. The nucleation process was discussed as a source for formation of twins in mc-Si.

1. Introduction

The industry standard for producing mc-Si ingots for PV applications is to cast the material directly in silicon nitride (Si_3N_4) coated quartz crucibles by directional solidification. The role of the nitride coating is to prevent sticking between Si and the quartz crucible. The nitride coating commonly used by mc-Si producers is composed of mainly α-Si_3N_4 (>95%) and small amounts of β-Si_3N_4 particles. The particles in this coating are small, with a size below 1 µm [1].

In the solidification step of the mc-Si solar cell value chain, improvements in final efficiency can be made by decreasing impurities and by controlling the structure of the ingot. For ingots made by non-seeding techniques, understanding the nucleation process is important for structure control, as the grain population is mostly established during this step [2]. Currently, seeding techniques produce the highest quality ingots, but more knowledge of the solidification process for ingots made through nucleation could lead to comparable or better quality ingots. This could give a significant cost reduction, as the seeded ingots require high quality seeds and has a lower yield as more material must be removed from the final ingot.

Previous work by our group has shown that during solidification the α-phase undergoes a phase transformation to the β-phase. This causes the existing β-particles, as well as new particles, to grow. The β-phase particles grow to much larger sizes than the α-phase particles in the original coating, e.g. the α-particles are smaller than 1 µm while the β-particles are on the order of 10–20 µm [3]. Our work shows that the larger β-particles are more favorable nucleation sites than the α-Si_3N_4 particles [1,3].

The crystal structure of β-Si_3N_4 is hexagonal with a space group $P6_3/m$ and lattice parameters equal to a = 7.61 Å and c = 2.91 Å [4,5]. The α-phase has a trigonal structure, with space group P31c and lattice parameters a = 7.75 Å and c = 5.62 Å [6,7].

β-particles grown from a silicon melt form hexagonal needles along the c-direction ([0001]) [8,9]. Epitaxial growth of β-Si_3N_4 on silicon has been studied both experimentally and theoretically [10–12]. Experimentally a Si/β-Si_3N_4 structure is created by nitridation of a silicon wafer, which gives a thin nitride layer [11,12]. Both experimental and theoretical work focuses on the Si (1 1 1) and β-Si_3N_4 (0 0 0 1) interface. These interface planes give a low lattice mismatch (1%), where one unit cell of Si_3N_4 almost matches two unit cells of Si [10].

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The β-particles found in mc-Si ingots do not show the (0 0 0 1) facet, but show a more complex combination of facets [3]. The clearest facets that appear consistently for all particles are the side facets, and it is on these the nucleation of Si is believed to occur. These facets are the $(1 0 \bar{1} 0)$, (1 1 0 0), and $(0 1 \bar{1} 0)$ planes and provide likely nucleation sites as the undercooling necessary for growth is dependent on the facet size, as suggested by athermal nucleation theory [13,14].

Where Si nucleates on the β-phase particles there should be a preferred OR between the two phases. In this work the OR between Si and β-Si_3N_4 particles has been studied in detail using TEM.

2. Experimental

The TEM samples were prepared from bottom cuts of an industrial mc-Si ingot. In order to identify possible areas of interest for TEM sample preparation the bottom cuts had to be polished and etched. As reported by Ekstrøm et al. the bottom of mc-Si ingots is covered in a layer of α-Si_3N_4 particles [3]. This layer is followed by a layer of β-Si_3N_4 particles which are in contact with the silicon. This layer is a direct result of the phase transformation of the α- to β-phase. Fig. 1(b) shows these two layers and the underlying Si for an etched mc-Si sample from the study by Ekstrøm et al. [3]. In order to remove most of the α-Si_3N_4 layer, the samples were polished carefully, to avoid removing too much of the underlying silicon. After the polishing, the sample consisted of silicon "islands" surrounded by remnants of coating particles. The polishing process removed less material than the roughness of the sample, creating Si islands, as shown in Fig. 1. These islands are surrounded by β-Si_3N_4 particles on the outside border, and in some cases β-particles are found covering the islands, as seen in Fig. 1(c). The β-particles are identified based on size and shape.

After polishing the samples were etched in Sopori etchant for 15 s to reveal the GBs. Areas for possible TEM sample lift-outs were identified by finding GBs extending from single β-Si_3N_4 particles. This is a sign that nucleation occurred on this particle and this is discussed in further detail in the next section. Cross-section TEM samples were prepared in a FEI Helios NanoLab DualBeam FIB equipped with an omniprobe lift out needle using the "lift-out" technique, shown in Fig. 2. In this technique a carbon pad is first deposited on top of the area of interest to protect the sample area from damage during milling (Fig. 2(a)). The material around the sample is then milled away on three sides, as seen in Fig. 2(b), as well as under the sample. The omniprobe W needle is welded to the sample by platinum deposition and the final side milled away. The sample is then removed, shown in Fig. 2(c), and transferred to a 3-post omniprobe copper grid, where a slot the size of the samples has been milled out (Fig. 2(d)). Here the sample is welded by deposited Pt and the sample is milled on both sides until it is electron transparent.

A JEOL 2100 TEM, operated at 200 kV, was used to study the TEM samples. A Zeiss Ultra scanning electron microscope (SEM), operated at 2–5 kV, was used to identify areas of interest after polishing and etching.

3. Results and discussion

3.1. Areas of interest

Polishing and etching of the bottom cuts revealed several interesting areas for TEM sample preparation, shown in Fig. 3. An assumption was made when looking for possible areas to study; that a particle could nucleate silicon on at least two facets of the same particle. For particles where Si nucleated twice, two GBs could be traced back to the particle, as can be seen in the examples shown in Fig. 3(a)–(c). For particles where Si only nucleated on one facet, it would be impossible to determine on which of the facets the nucleation started or even if Si nucleated on the particle at all. For nucleation on two or more facets, this could be decided with a much higher degree of certainty, e.g. in Fig. 3(a) and (c) GBs are seen to extend from the edges of one facet and thus it is highly likely that nucleation started on the facet bounded by the GBs.

In this study only one successful sample, i.e. a TEM sample that was good enough to be investigated and that also showed an OR, was made. This sample was made from the particle shown in Fig. 3(a). The area where the TEM sample was made is shown in Fig. 4(a) with the areas of interest marked, the β-Si_3N_4 – Si boundary is shown by a red square and the Si-Si GB by a blue square. A bright field (BF) micrograph of the finished TEM sample is shown

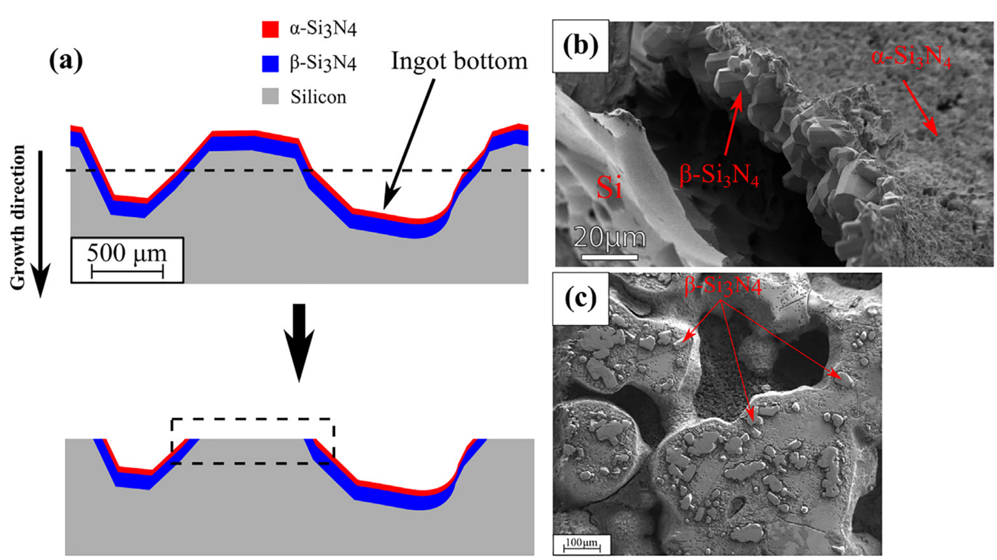

Fig. 1. (a) Schematic of a bottom cut from a mc-Si ingot viewed from the side. The layers consist of α- and β-Si_3N_4 particles. The top image represents the sample before polishing, with the dotted line indicating the material removed during polishing. The bottom image is a schematic of the sample after polishing. The dotted area represents a so called Si "island". (b) A real case example of the layers shown in (a). The micrograph is of an etched mc-Si sample from [3] (c) Example of the Si islands of a sample after polishing and etching. Also indicated are some of the β-particles.