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Wetting and infiltration of nitride bonded silicon nitride by liquid silicon

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ABSTRACT

Nitride bonded silicon nitride (NBSN) is a promising crucible material for the repeated use in the directional solidification of multicrystalline (mc) silicon ingots for photovoltaic applications. Due to wetting and infiltration, however, silicon nitride in its initial state does not offer the desired reusability. In this work the sessile drop method is used to systematically study the wetting and infiltration behavior of NBSN after applying different oxidation procedures. It is found that the wetting of the NBSN crucible by liquid silicon can be prevented by the oxidation of the geometrical surface. The infiltration of liquid silicon into the porous crucible can be suppressed by oxygen enrichment within the volume of the NBSN, i.e. at the pore walls of the crucibles. The realized reusability of the NBSN is demonstrated by reusing a NBSN crucible six times for the directional solidification of undoped multicrystalline silicon ingots.
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1. Introduction

Currently about 50% of the solar cells are fabricated by multicrystalline (mc) silicon which is mainly grown by the directional solidification process using fused silica (SiO_2) crucibles which are coated on the inner surface with silicon nitride (Si_3N_4). The fused silica crucible offers a relatively high purity at moderate production costs [1]. Due to a destructive phase transformation, however, fused silica crucibles are confined to a *single use*. Above 1450 °C, i.e. during the silicon melting process, the initially amorphous silica converts partly into beta-cristobalite which is the high temperature modification of SiO_2. At around 275 °C, i.e. subsequent to the silicon ingot growth, the beta-cristobalite transforms into the alpha phase. Because of a volume change of several percent this second phase transformation is destructive and finally results in a breakage of the crucible [1]. For this reason a new fused silica crucible has to be used for each growth run. Since 16% of the module costs are attributable to the production of the mc silicon wafers [2] the cost reduction in terms of consumables is still a major task [2]. Consequently there is a great interest in the availability of a “reusable” crucible which can be used for several growth runs.

Because of its mechanical stability silicon nitride (Si_3N_4) is considered to be a promising material to overcome the single use constraint of fused silica crucibles. Next to an adequate mechanical stability a long lifetime of the crucible, a small pollution of the silicon and a non-wetting behavior in contact with liquid silicon are among the main requirements for reusable crucibles [3]. The first and the second of these requirements, i.e. the lifetime of silicon nitride crucibles for the directional solidification of silicon as well as the silicon ingot contamination by the reusable silicon nitride crucible, have recently been studied [4]. Studies concerning the third requirement, i.e. the non-wetting behavior in contact with liquid silicon, however were limited to Si_3N_4 coatings so far.

Brynjulfsen et al. [5] for example who analyzed the wettability of silicon nitride coatings by liquid silicon as a function of the oxidation and of the superheat described the important role of the oxygen content of the coating. Eustathopoulos et al. [6] reported on wetting curves of silicon on Si_3N_4-coated SiO_2 crucibles and on the infiltration of silicon into the porous silicon nitride coating. They found that wetting as well as infiltration is governed by the reactions occurring at the solid/liquid/vapor triple line and that the removal of the gaseous species is of special importance. Drevet et al. [7] published results about the interactions in the silicon/porous Si_3N_4-coating/SiO_2 system and attribute the barrier to wetting to the presence of a poorly wettable SiO_2 layer on the surface of the Si_3N_4 particles. Finally, the group around Martin [8] studied the wetting behavior of silicon nitride coatings doped with

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oxygen. Their results indicate the necessity of a minimum oxygen content to prevent the wetting of the silicon nitride coating.

Up to now silicon nitride crucibles did not yet reach the status of a large scale industrial application. This situation could originate from the inappropriate wetting behavior of the silicon nitride crucibles in contact with molten silicon (contact angle of Si on pure Si_3N_4 near to 43° [6]). Therefore, the goal of the present work is the development of an oxidation procedure which protects the silicon nitride crucible from wetting and infiltration and which consequently allows the reusability of the silicon nitride crucible for several growth runs in the directional solidification process of mc silicon. For this purpose the wetting and infiltration of nitride bonded silicon nitride (NBSN) crucibles are studied systematically in dependence of the applied oxidation conditions. The suitability of the oxidation procedure will be demonstrated by the repeated use of an oxidized NBSN crucible in the directional solidification of mc silicon.

2. Sample preparation and sessile drop experiments

2.1. Description of sample material

Two nitride bonded silicon nitride (NBSN) crucibles (crucible A and crucible B) were fabricated by H.C. Starck Ceramics by mixing 30% silicon powder with 70% silicon nitride powder and by nitriding the molds at temperatures exceeding 1450 °C. For the fabrication of crucible A, which is described in detail in [4], a small amount of a binding agent was additionally used. For crucible B no binding agent was added.

For the sessile drop experiments NBSN samples with a dimension of 12 mm × 12 mm × 4 mm were produced from these crucibles. These NBSN samples were analyzed with respect to its silicon nitride phase compositions by X-ray diffraction (XRD) revealing 83% alpha and 17% beta phase of Si_3N_4 for crucible A and 92% alpha and 8% beta phase for crucible B (see also Table 1).

To detect the initial oxygen concentration of the samples the carbon monoxide was thermally extracted with a carrier gas and analyzed by infrared spectrometric detection. The initial oxygen concentration of crucible B (2 wt%) exceeds the oxygen concentration of crucible A (1 wt%) for a factor of two, as illustrated in Table 1.

The initial porosity of the NBSN crucibles was determined by mercury porosimetry resulting in values of 37 vol% for crucible A and 38 vol% for crucible B (see Table 1).

2.2. Sample preparation

Prior to the sessile drop experiments which were used to study the wetting and infiltration the silicon nitride samples of the crucibles A and B have been subjected to several oxidation procedures.

The duration of the oxidation process has been chosen to be 6 h in all cases, whereas the oxidation temperature (1050 °C, 1200 °C) as well as the oxygen content in the atmosphere (6.7 vol%, 20.9 vol%) used for the oxidation have been varied. An overview of the oxidation procedures for the samples A and B is given in Table 2.

The mass change for sample A reaches values of 0.5 wt% for an oxidation at 1050 °C under 6.7 vol% O_2, of 1.3 wt% for an oxidation at 1050 °C under 20.9 vol% O_2 and of 9.7 wt% for an oxidation at 1200 °C under 20.9 vol% O_2. For sample B the oxidation at 1050 °C under 20.9 vol% O_2 results in a mass change of 2.0 wt% (see Table 2).

In some cases the resulting oxygen contents as well as the porosities have been measured after the oxidation procedures. The oxidation at 1050 °C under 20.9 vol% O_2 increases the oxygen content of the samples A and B to values of 4 wt% and 6 wt% and decreases the porosity to values of 34 vol% and 35 vol%. These results are summarized in Table 2.

2.3. Sessile drop experiments

2.3.1. Contact angle

The contact angles for the samples summarized in Table 2 are measured by the sessile drop method in a furnace which has been developed in the SolarWinS project (support code 0325270G) funded by the Federal Ministry for Economic Affairs and Energy [9]. A schematic drawing of the sessile drop furnace is given in Fig. 1. Around 1 g of solar grade silicon (Wacker Chemie AG) was

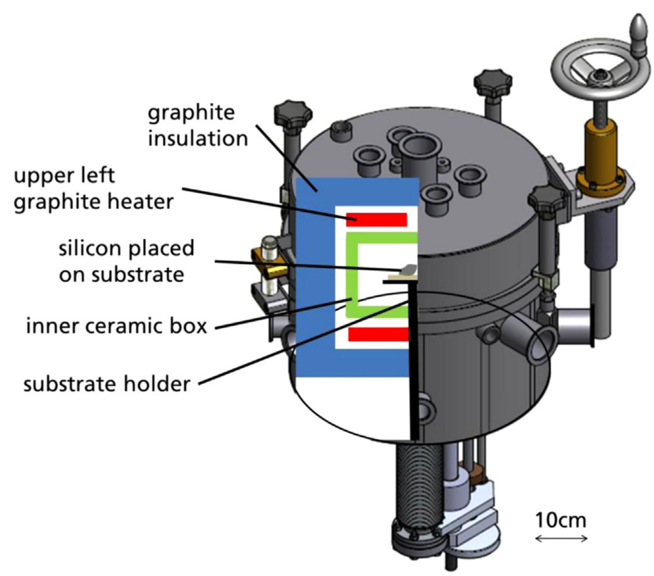

Fig. 1. Schematic drawing of the sessile drop furnace.

Table 1
Initial values for phase composition, oxygen content, porosity and pore diameter of the nitride bonded silicon nitride (NBSN) crucible materials A and B used in this study. The silicon nitride phase compositions were detected by X-ray diffraction. The oxygen contents and the porosities respectively pore diameters were analyzed by infrared spectrometric detection and mercury porosimetry.

Crucible	α-Si_3N_4 [%]	β-Si_3N_4 [%]	O [wt%]	Porosity [vol%]	Pore diameter [μm]
A	83	17	1	37	0.16
B	92	8	2	38	0.08

Table 2
Overview of the temperatures and the oxygen contents of the atmospheres which were used for the oxidation of the nitride bonded silicon nitride (NBSN) samples A and B. The resulting weight changes as well as the oxygen contents and the porosities of the silicon nitride samples after the oxidation procedures are summarized in the columns 4, 5 and 6.

Crucible	Oxidation temperature [deg]	O_2 content in atmosphere [vol%]	Weight change [wt%]	O [wt%]	Porosity [vol%]
A	No oxidation	No oxidation	No oxidation	1	37
A	1050	6.7	0.5	Not measured	Not measured
A	1050	20.9	1.3	4	34
A	1200	20.9	9.7	Not measured	Not measured
B	No oxidation	No oxidation	No oxidation	2	38
B	1050	20.9	2.0	6	35

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