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Wetting, infiltration and sticking phenomena in Si_3N_4 releasing coatings in the growth of photovoltaic silicon

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ABSTRACT

The growth of photovoltaic silicon ingots from the melt is currently performed in silica crucibles covered by a silicon nitride powder coating which prevents from sticking. The purpose of this study is to propose a comprehensive description of interactions in the Si/porous Si_3N_4-coating/SiO_2 system responsible for the non-sticking behaviour. The interpretations are based on wetting experiments performed by the sessile drop technique and on microstructure characterizations carried out by optical and scanning electron microscopies.

We show that the Si_3N_4 porous coating constitutes a barrier to wetting and infiltration due to the presence of a non-wettable SiO_2 layer on nitride particles, and acts as a mechanical fuse due to its weak resistance resulting from its porous microstructure. The consequences of the study findings on the crucible used in solidification of photovoltaic silicon are discussed.

1. Introduction

Currently photovoltaic silicon is produced mainly by liquid route techniques such as ingot growth and ribbon technologies. They involve the use of foreign materials in contact with molten silicon, i.e. crucibles or substrates. It is established from long date that the crucible costs constitute the biggest added value in the solidification of photovoltaic silicon ingots (see for instance [1]). The two main requirements for crucible materials are (i) negligible reactivity to avoid pollution of the silicon and to increase the lifetime of the crucible, and (ii) non-wetting behaviour (i.e. contact angles θ much higher than 90°), which is a favourable condition for obtaining a spontaneous detachment of solidified silicon from the crucible walls under the effect of thermo-mechanical stresses [2,3]. Because of the high affinity of Si for oxygen, nitrogen, carbon and even boron, to our knowledge, no refractory material exists satisfying both these requirements. For instance silica is chemically compatible with silicon but in this system the contact angle is close to 90° resulting in sticking at the Si/SiO_2 interface. Conversely, silicon does not wet boron nitride [4–6] but boron contamination leads to overdoping of Si.

In the absence of a satisfactory dense material crucible, the growth of photovoltaic silicon ingots is currently performed in SiO_2 crucibles coated with a silicon nitride powder which acts as an interface releasing agent between silicon and the crucible. The origin of this process lies in the pioneer work of Saito et al. [7]. The findings of this study have been largely used in the industrial practice [8,9]. However, the mechanism responsible for the spontaneous detachment of the Si ingot from the crucible walls is not known. Particularly, this spontaneous detachment is in contradiction with the fact that Si_3N_4 is well wetted by liquid Si [3,4,10]. The absence of information on the mechanisms of wetting and adhesion in the Si/Si_3N_4-coating/SiO_2 system is prejudicial to researches performed to optimize this coating. The purpose of this work is to propose a comprehensive survey of interaction mechanisms in the Si/porous Si_3N_4-coating/SiO_2 system. These interactions are studied by means of wetting experiments performed by the sessile drop technique and microstructural characterizations carried out by optical and scanning electron microscopies. For demonstration purposes, complementary experiments are performed on coated vitreous carbon and porous graphite instead of coated SiO_2.

2. Experimental procedure

Wetting is studied by the sessile drop method in a metallic chamber furnace. The device is induction heated by coupling on a graphite susceptor. The working zone is surrounded by a graphite thermal insulator. A vacuum unit allows a total pressure of 10^{-4} Pa to be attained at ambient temperature. The presence of graphite inside the furnace allows atmospheres with a very low oxygen partial pressure $P(O_2)$ to be obtained. Experiments were

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carried out in an Ar flow. A sessile drop experiment consists in placing a 100–200 mg piece of silicon on a solid substrate inside the furnace at room temperature. The shape of the silicon piece is chosen so that it promotes advancing contact angles during spreading of the liquid drop. Heating is performed under vacuum at 10°/min up to 1000 °C, then Ar is introduced and the temperature is increased at 5°/min up to the holding temperature of 1430 °C. The furnace is equipped with windows enabling the melting and spreading processes to be filmed with a video camera (25 frames per second). The camera is connected to a computer for automatic image analysis. The drop-base diameter D and drop height H (defined on Fig. 3) are extracted with an accuracy of $\pm 2\%$ and the contact angle θ is determined with an accuracy of $\pm 3°$.

Vitreous silica substrates with an average surface roughness of a few nm are supplied by VS Technologies. Dense Si_3N_4 samples are processed by sintering using Y_2O_3 and Al_2O_3 (both 6 wt%) as sintering aids. The residual porosity is less than 2%. The samples are mechanically polished using diamond paste up to an average roughness R_a=70 nm. Two types of carbon substrates are investigated: vitreous carbon with no open porosity supplied by Carbone Lorraine, and graphite with a porosity of 32% supplied by Poco. Electronic grade silicon (total metallic impurities less than 20 ppb wt) is used as source material.

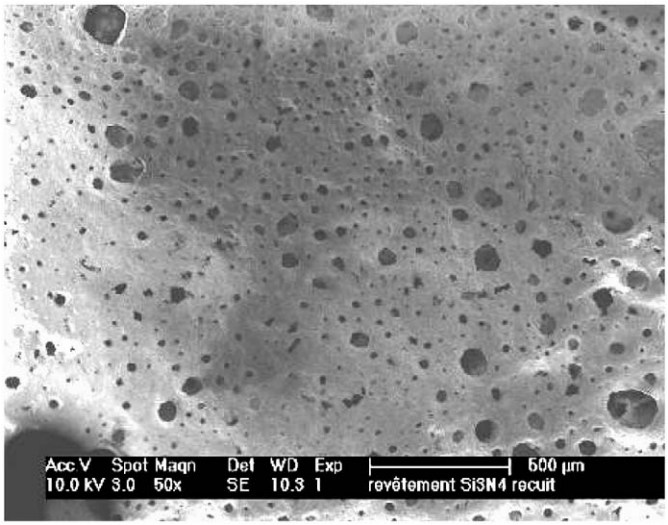

Fig. 1. Top view of a coating after heat treatment at 900 °C in air (SEM). The black zones are large pores produced by bubbles.

As for the substrate-coating procedure, a slurry composed of Si_3N_4 submicronic powder and polyvinyl alcohol dissolved in deionized water as binder is first prepared. The slurry is applied to the surface of the substrate by spraying. The coated substrate is dried to remove the water and then heated in air above 450 °C to burn the binder and to oxidize Si_3N_4 grains. This treatment is performed at 500 °C (for carbon substrates) and 900 °C (for SiO_2 substrates) for two hours or more. The coating thickness ranges from 30 to 150 µm depending on the number of strokes of spraying. The coating exhibits a microscopic porosity between individual Si_3N_4 grains and a macroscopic porosity formed by bubbles of some tens to some hundreds of microns produced by the spraying process (Fig. 1).

3. Results and discussion

Experimental results are given in Table 1. For each experiment, the thickness of the coating, the temperature and duration of the oxidation treatment, the drop mass, the total time at 1430 °C of the sessile drop experiment and the final contact angle θ_F are specified. As it will be indicated below, θ_F is taken at the time when the drop-base diameter becomes constant. Table 1 also gives the behaviour of the solidified droplet at room temperature.

3.1. Wetting on dense SiO_2 and Si_3N_4

In the first experiment #1 performed on non-coated SiO_2, a contact angle of $83 \pm 4°$ has been obtained instantaneously after Si melting. The solidified Si drop adheres strongly on SiO_2 on cooling down to room temperature. Before studying wetting of the complex microstructure porous Si_3N_4 coating, the experiment #6 has been made on dense Si_3N_4. Prior to sessile drop experiment, this substrate was heated in air at 900 °C for two hours in a similar way as for the porous coating. This treatment is expected to lead to the formation of a SiO_2 surface layer with a thickness of several nm [11]. Fig. 2 shows the wetting curves (contact angle θ and drop-base diameter D) for molten Si on dense Si_3N_4. The time t=0 corresponds to complete melting of Si. The detailed interpretation of these results is given in [4]. Briefly, the initial contact angle, equal to $\theta_0=92 \pm 3°$, corresponds to oxidized Si_3N_4. The final value of the contact angle $\theta_F=45 \pm 3°$, attained after a "spreading time" of $t_s \approx 500$ s (t_s is the time needed for the

Table 1
Results of sessile drop experiments performed at 1430 °C in argon with coated and uncoated substrates.

Experiment reference	Substrate	Coating thickness	Temperature and duration of oxidation	Drop mass	Total time at 1430 °C	θ_F	Adhesion	Observations
#1	SiO_2	–	–	92 mg	10 min	$83 \pm 4°$	Sticking	
#6	Si_3N_4	–	900 °C, 2 h	97 mg	18 min	$45 \pm 3°$	Sticking	
#21	Si_3N_4-coated SiO_2	150 µm	900 °C, 2 h	112 mg	65 min	$42 \pm 3°$	No sticking	V_{av}(film)=60 µm/min
#18	Si_3N_4-coated SiO_2	150 µm	500 °C, 3 h	106 mg	17 min	$48 \pm 3°$	No sticking	V_{av}(film)=140 µm/min
#22	Si_3N_4-coated vitreous carbon	150 µm	500 °C, 3 h	83 mg	20 min	$49 \pm 3°$	Sticking	V_{av}(film)=270 µm/min
#9	Si_3N_4-coated graphite	30 µm	500 °C, 5 h	212 mg	6 min	–	–	V_{av}(film)=2100 µm/min total infiltration of Si in graphite in 6 min
#11	Si_3N_4-coated graphite	150 µm	500 °C, 3 h	150 mg	90 min	–	–	total infiltration of Si in graphite in 16 min