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Chemical stability of silicon nitride coatings used in the crystallization of photovoltaic silicon ingots. Part II: Stability under argon flow

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ABSTRACT

Processing of photovoltaic silicon by solidification is currently carried out under argon flow in silica crucibles coated with an oxidized silicon nitride powder. A series of experiments was performed to study the reactions between coating components under argon flow by varying the temperature, the holding time and the oxygen content in the coating. The results are discussed with the help of a simple analytical model taking into account the diffusive transport of gaseous reaction species from the inside of the porous coating to the flowing argon. The conclusions drawn are used to discuss different practical aspects of the photovoltaic silicon crystallization process.

1. Introduction

Photovoltaic silicon is currently mainly produced by directional solidification in silica crucibles. In order to avoid sticking of the solidified silicon to the crucible walls, the crucibles are coated with a silicon nitride powder which acts as an interface releasing agent between the silicon and the crucible. The coating is porous and consists of oxidized silicon nitride particles surrounded by a thin (nm thick) silicon oxide skin. The presence of that skin is interesting because it contributes to the cohesion of the coating [1,2] and also to its resistance to silicon infiltration [3].

It is well established that oxygen present in silicon is detrimental for the future electrical performances of photovoltaic cells. Therefore, great efforts are made in order to reduce the oxygen present in the liquid silicon, by removing it in the vapour phase as much as possible during the melting-solidification cycle. In principle, a high vacuum could ensure a rapid deoxidation of Si. However it leads also to the deoxidation of the coating itself occurring rapidly at temperatures well below the silicon melting point (see the Part I of this study [4]). To avoid coating degradation, silicon deoxidation during the melting-solidification cycle is currently carried out under argon flow.

The aim of this investigation is to study the chemical stability of the coating under argon flow at temperatures up to 1500 °C that can be attained during the melting-crystallization process. Notice that during the last ten years, several studies have been published concerning the wetting [5–8] and infiltration [3,9] of silicon nitride by molten silicon, as well as the effect of the coating on the purity of solidified silicon [10]. In these studies, it has been implicitly admitted that under argon flow the intrinsic chemical and microstructural coating properties do not change during the melting-solidification cycle: if a change in these properties is observed, this should result from the interactions of the coating either with liquid silicon [3] or with the silica substrate [10]. However, in crystallization experiments, it is frequently observed that coating parts lying well above the silicon melt (at tens of cm) are strongly affected during the temperature cycle as seen in Fig. 1. Indeed, while the coating color is white before the experiment, it presents black and/or even green regions after the experiment indicating some modifications of its chemistry. One of the goals in this study was to examine the origin of these modifications.

To this end, a number of experiments were performed using coated silica substrates with different coating oxygen contents that were heat-treated under Ar flow at different temperature plateaus between 1300 °C and 1500 °C and different durations. The chemical composition and microstructure of the coatings after the experiments are characterized by mass loss measurements, optical and scanning electron microscopies as well as energy dispersion spectroscopy (EDS) microanalysis. The results are discussed using an analytical, semi-quantitative, thermo-kinetic model.

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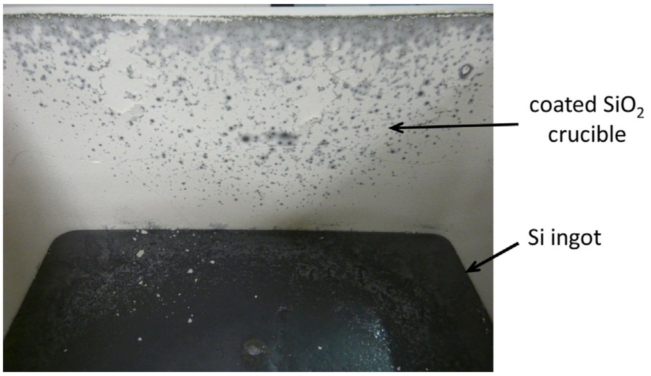

Fig. 1. View of the coating at the top of the crucible after a crystallization experiment (internal section of the crucible: 380*380 mm^2).

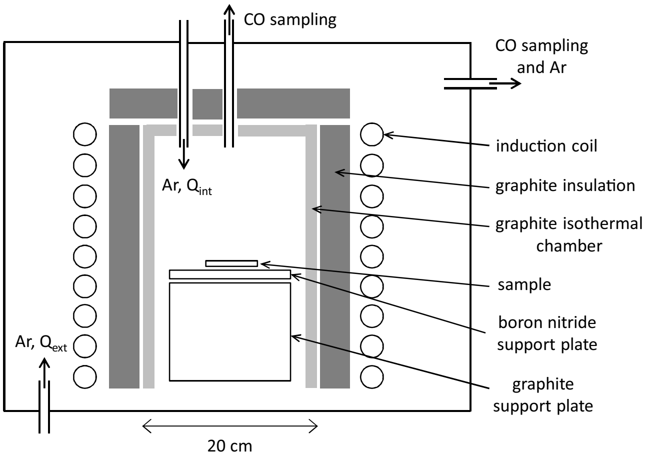

Fig. 2. Schematic drawing of the graphite furnace.

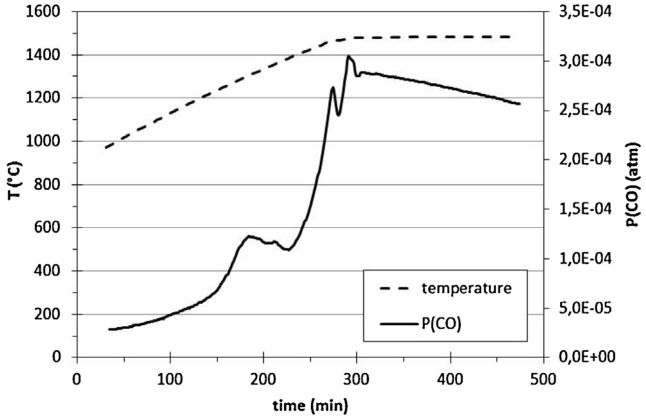

Fig. 3. Variation with temperature of CO partial pressure in argon in the isothermal chamber (experiment 8).

2. Experimental procedure and materials

Vitreous silica substrates of different sizes (typically $50 \times 50 \times 5\,\mathrm{mm}^3$) supplied by VS Technologies have been used. Coatings of several hundreds of microns thick have been fabricated starting from a α-silicon nitride powder with an average particle diameter of 500 nm. The coated substrates are submitted to oxidation treatments leading to oxygen contents CO between 7 wt% and 21 wt%. These contents correspond to silica skins around the nitride particles with a thickness e_0 lying from 6 nm to 18 nm respectively. The coatings are very porous, with average values of the pore volume fraction $\alpha_p = 0.67 \pm 0.03$, and pore radius $r_p = 115$ nm. When discussing the coating stability, it is convenient to use the parameter n_O, the number of moles of oxygen per unit of volume of the coating, which can easily be calculated from the values of the oxygen concentration and α_p. More details on the coating preparation and properties are given in [3] and in Part I of this study [4].

Experiments were performed in a graphite induction furnace depicted in Fig. 2. Heating is provided by electro-magnetic coupling between a graphite belt and a co-axial induction coil separated by an insulating graphite rigid felt. The atmosphere can be either high vacuum or circulating argon under one atmosphere. Argon is injected in the isothermal chamber (with a flow Q_{int}) and/or outside the chamber (with a flow Q_{ext}). Argon of commercial purity was used, containing a few ppm (in volume) of oxygen and humidity. The CO concentration in the gas is measured continuously at a given point inside and/or outside the isothermal chamber by pumping through a 6 mm internal diameter alumina tube at a rate 0.5–1 L/min and passing through the chamber of an infrared gas-filter correlation spectrometer. Fig. 3 gives a typical curve of the partial CO pressure P(CO) measured inside the isothermal chamber as a function of temperature.

In the experiments, the introduction of Ar is made after heating the sample under vacuum up to a temperature of 900 °C which is low enough to avoid any change in coating composition or microstructure (see Part I of this study [4]). Then, the temperature is raised up to a temperature plateau. After the experiment, the following characterizations are performed on the samples: (i) mass loss measurement performed using a standard laboratory balance with an accuracy of 0.1 mg, (ii) characterization of the chemical composition and microstructure of the coating surface by optical and scanning electron microscopies and by energy dispersion spectroscopy (EDS) microanalysis, and (iii) similar characterizations on polished cross-sections of the samples previously embedded in a resin. In the case of coatings which have lost their cohesion after the heat treatment, some particle agglomerates are taken off and analyzed by EDS.

3. Results

Table 1 gives the experimental conditions and results of isothermal experiments performed under argon flow at temperatures between 1300 °C and 1500 °C. The experiments have been carried out with $Q_{int} = 2$ L/min except for experiment 7 where $Q_{int} = 0$ L/min, and $Q_{ext} = 2$ L/min except for experiment 5 where $Q_{ext} = 15$ L/min. The last column presents top views of the samples taken at the end of the experiment. While in experiments 1 and 2 the coating surface has not changed at all, it appears as having "reacted" in the cases 3–6. The reaction is said "total" when it affects the coating over its whole thickness, otherwise it is "partial". The reacted areas have a grey/green color, except for the experiment 5 where they have a metallic aspect. The surface in experiments 7 and 8 is non-reacted except on the sides of the sample. As evidenced by the comparison of experiments 2 and 3, the coating transition from "non-reacted" to "reacted" occurs in a narrow domain of temperature (some decades of degrees). Moreover, when three hours at 1480 °C are needed in order to initiate reactivity (experiment 4), the reaction proceeds rapidly after, as verified in experiments 5 and 6 where the coating was affected by the reaction over its entire thickness. Note that the white areas on the macrograph of these experiments correspond to the silica substrate, which indicates that reactions in the coating led to contraction and cracking. Comparing experiments 4 and 7, it can be concluded that argon flow dispensed in the isothermal chamber favors reactivity. In contrast, the increase in oxygen content of the coating reduces reactivity (comparison of experiments 4 and 8). It