



Chemical stability of silicon nitride coatings used in the crystallization of photovoltaic silicon ingots. Part I: Stability in vacuum



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ABSTRACT

Photovoltaic silicon is currently grown in silica crucibles coated with an oxidized silicon nitride powder, which acts as an interface releasing agent between the silicon and the crucible. A series of experiments was performed to study the reactions between coating components under high vacuum, 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 reaction species from the inside of the porous coating to its surface and then their evaporation into the vapour phase.

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1. Introduction

The major part of photovoltaic silicon is currently produced by ingot growth from a melt. This implies the use of crucible materials in contact with molten silicon. In order to avoid sticking of solidified silicon on the crucible walls, photovoltaic silicon ingots are grown in silica crucibles 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. The minimum oxygen content corresponds to the one of the initial Si₃N₄ powder, usually lying in the range 1–2 wt%. In practice, this content is often increased up to 10 wt% in order to increase the cohesion of the coating [1,2] and its resistance to silicon infiltration [3,4].

Fig. 1 gives schematically the temperature cycle used during the silicon crystallization. In order to promote degassing, heating is performed under vacuum up to a temperature noted T*, then argon flow is introduced and the average temperature of Si is increased up to a plateau temperature T_{max} close to 1450 °C, higher than the melting point of Si (1414 °C). However, during this stage the temperature reaches 1500 °C at the top of the crucible. After several hours at the temperature plateau, the melt is slowly cooled

down in order to solidify silicon unidirectionally (from the bottom to the top). In practice, it is interesting to introduce argon at a temperature T* as high as possible in order to improve furnace degassing under vacuum without affecting the coating properties. The aim of this study is thus to determine the optimal value of T* and the influencing factors of this parameter. For this matter, experiments have been performed using coated silica substrates heat treated under vacuum with different temperature plateaux (between 1150 °C and 1380 °C), different durations and coating oxygen contents. The chemical composition and microstructure of the coatings after the experiments are characterized by mass loss measurements, by optical and scanning electron microscopies and by dispersion energy microanalysis. The results are discussed using an analytical, semi-quantitative, thermo-kinetic model.

In the Part II of this study [5] the stability of the coating under Ar flow and at high temperatures attained during the melting step will be studied.

2. Experimental procedure and materials

Vitreous silica substrates of different sizes (typically 50 × 50 × 5 mm³) supplied by VS Technologies have been used. For the coating, a slurry composed of a Si₃N₄ submicronic powder and polyvinyl alcohol dissolved in deionized water as a binder is first prepared. The slurry is applied to the surface of the substrate by spraying. The coated substrate is dried in order to remove the water and then heated up for two hours in air at temperatures

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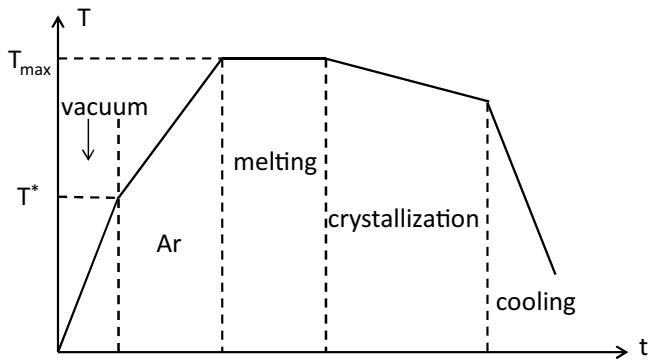


Fig. 1. Temperature cycle used in silicon crystallization furnaces.

Table 1

Measured oxygen concentrations C_0 , number of O moles per unit of volume n_0 and derived values of thickness e_0 of silica skin for typical coatings oxidized at 1000 °C and 1100 °C.

Oxidation temperature (°C)	C_0 (wt%)	n_0 (mol/m ³)	e_0 (nm)
1000	9	7.3×10^3	8
1100	21	1.5×10^4	18

in the range of 1000 °C–1100 °C in order to burn the binder and to oxidize the Si_3N_4 grains. The coating thickness ranges from 300 μm to 1000 μm depending on the number of spray runs. The silicon nitride powder supplied by UBE (SNE 10 grade) has a specific surface area of 11 m²/g and contains more than 95% of α - Si_3N_4 particles with roughly spherical shapes and a few β - Si_3N_4 needles. The particle diameter distribution is $d(10\%)$: 0.2 μm , $d(50\%)$: 0.5 μm and $d(90\%)$: 1.6 μm . The coating exhibits a microscopic porosity between individual Si_3N_4 grains and a macroscopic porosity formed by bubbles of some tens of microns produced by the spraying process as shown on Fig. 2. An average value of pore volume fraction, $\alpha_p = 0.67 \pm 0.03$, is calculated by measuring the coating weight and its geometrical volume. An equivalent pore

Table 3

z_{meas} values measured in experiments performed in vacuum by heating using a temperature ramp-up of 85 °/h to the temperature T_{max} followed by cooling.

Sample	C_0 (wt%)	T_{max} (°C)	z_{meas} (μm)
7	17.4	1150	0
8	9	1300	3–5
9	9	1380	30–50

radius is then derived from α_p and the specific surface area of the powder by approximating the pore network to an assembly of cylindrical pores with the same radius [3]. The pore radius thus calculated is $r_p = 115$ nm. Oxidation of the coating in air for 2 h leads to oxygen mass concentration C_0 (measured by the Inert Gas Fusion technique) that depends on the oxidation temperature as shown by the results in Table 1. In this study, C_0 is in the range of 6.7–17.4 wt% (see Tables 2 and 3). Oxygen introduced in the coating is in the form of an oxide skin around the Si_3N_4 particles. During oxidation, oxide bridges are formed at the areas of contact between particles, thus ensuring some cohesion to the coating as shown on Fig. 2c. From the values of C_0 and α_p , the number of O moles per unit of volume of the coating, n_0 , is calculated. In the context of the simple cylindrical pore model used to describe the pore network, n_0 values are converted into thickness values e_0 of the silica skin formed on the pore walls through the relation $n_0 = (4e_0\alpha_p)/(r_p V_M^{\text{SiO}_2})$ where $V_M^{\text{SiO}_2}$ is the molar volume of silica. Data of n_0 and e_0 for typical coatings oxidized during 2 h at 1000 °C and 1100 °C respectively are summarized in Table 1.

Experiments were performed in a graphite induction furnace under a vacuum of 10^{-4} – 10^{-5} mbar. In these experiments the temperature is raised up to T^* , then either it is kept constant at T^* during a plateau time t_{total} , or decreased rapidly to room temperature. For comparison purposes one experiment (experiment 6 in Table 2) was performed under argon flow. In this experiment, argon of commercial purity, containing a few ppm (in volume) of oxygen and humidity, was injected in the isothermal chamber with a flow of 2 L/min. The introduction of Ar was made after heating the sample under vacuum up to a temperature of 900 °C which is low enough to

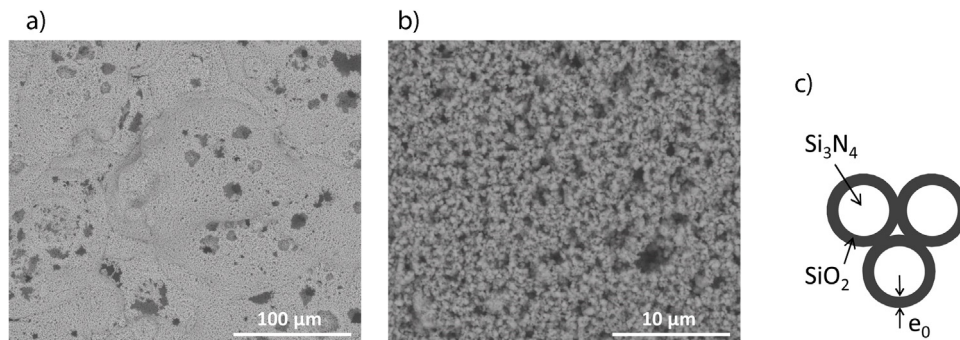


Fig. 2. The coating exhibits bubbles of several tens of microns in size produced by the spray process (a) and a submicronic porosity between silicon nitride particles (b). The oxidation treatment leads to the formation of an oxide skin with a thickness e_0 around Si_3N_4 particles and ensures the coating cohesion (c).

Table 2

Coating mass losses m_{los} , measured deoxidized depths z_{meas} , calculated evaporated thicknesses z_{ev} and total deoxidized depths z_{deox} for experiments performed under vacuum at constant temperature. All experiments have been carried out in high vacuum except experiment 6 performed under argon flow.

Sample	C_0 (wt%)	t (h)	T (°C)	m_{los}		z_{meas} (μm)	z_{ev} (μm)	z_{deox} (μm)
				(%)	(g/m ²)			
1	7	3	1200	~0.5	1.6	0	0	0
2	6.7	3	1300	8.75	29.7	60	11	71
3	9.5	3	1300	8.7	31.6	50	9	59
4	8.2	24	1200	8.3	27.0	20	15	35
5	16.8	24	1200	4.2	14.8	5	7	12
6 (Ar)	7.1	3	1300	~0	~0	0	0	0

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