Journal of Crystal Growth 492 (2018) 18–23

Contents lists available at ScienceDirect

Journal of Crystal Growth

journal homepage: www.elsevier.com/locate/crys

Towards graphite-free hot zone for directional solidification of silicon

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ARTICLE INFO

Article history:
Available online 11 April 2018
Communicated by T. Paskova

Keywords:
A1. Characterization
A1. Impurities
A1. Directional solidification
A1. Semiconducting silicon
B3. Solar cells

ABSTRACT

The reduction of SiC, Si_3N_4 and transition metals impurities in directionally solidified Si ingots poses one of the crucial challenges in the solar cells production. Particularly strong contamination comes from the graphite parts in the hot zone. Therefore, we selected three massive ceramic materials to replace graphite, developed the novel design of the crucible support and cover and compared the crystals grown in them with ingots from the standard graphite design. The experiments were performed for phosphorus n-doped silicon of G0 size. The ingots were compared with respect to O- and C-content, metal impurities, resistivity and lifetime. The superior performance of TiC relative to other ceramics was observed, particularly due to the lower concentration of substitutional carbon in Si ingot (up to 2.6 times) and the higher minority carrier lifetime of (up to 4.4 times) with narrow red zones.

1. Introduction

In the solar cells production, there is a compelling need for a cost-effective technology that can improve the ingot quality and increase the yield. For progress towards these goals, it is important to control the level of carbon impurities in ingots in order to prevent the formation of SiC, which might result in wire breakage during wafer slicing and in rendering the long lifetimes. In a typical industrial furnace, solar-grade polysilicon is loaded in a nitride-coated quartz crucible placed inside a graphite susceptor, and the crucible is covered with a graphite plate. In general this setup is surrounded by carbon based heaters and insulation. All materials present in the hot-zone could be the source of ingot contamination. So far, the reduction of impurities was a subject of many scientific studies that proposed solutions for crucibles, coating and feedstock of various purity and price. Nevertheless, only a few studies were devoted to the search for material alternative to graphite that will prevent the formation of SiC from the reaction between SiO, which evaporates from the melt due to the reaction of the liquid silicon with the SiO_2 crucible, and graphite parts. At the same time, the new ceramic parts should sustain high working temperatures in oxidative ambience, they should be low in metallic impurities, be free of health risks and should have sufficient mechanical strength/durability. All those properties in one are barely obtained by graphite parts, which were chemically vapour deposited with a layer of SiC, W or e.g. Mo and their alloys [1,2]. For example, the limited damage tolerance and insufficient fracture toughness [3] of SiC coating on graphite due to their different expansion coefficients can limit SiC coating applications, while e.g. the other proposed material W presents acute health hazard. Moreover, all W compounds should be regarded as highly toxic [4]. Further on, although the Mo melting point is 2623 °C, Mo rapidly oxidizes at temperatures above 760 °C, making it unsuitable for use in oxidative ambience [5] such as during directional solidification processes (DS) of silicon. Therefore, there is still an urgent need to find better solutions.

The present study is focused on identifying carbon-free massive ceramic material for the crucible cover and support in a DS G0-sized setup. For this purpose, we selected three advanced ceramics out of eight, adjusted a design of the crucible support and the growth process to the ceramics material properties. The properties of the grown n-doped Si ingots were compared with the ingots from the standard graphite design with respect to O- and C-content, metal impurities, resistivity and lifetime. Phosphorus n-doped silicon feedstock was selected for this study as it is believed to be the material of the future that can increase the solar cell efficiency by up to 25% relative [6].

The first very encouraging results are presented and the strengths and weaknesses of various ceramics in comparison to graphite are discussed.

2. Feasible ceramic materials

As mentioned above, we searched for carbon-free massive ceramic material that is chemically stable at high working

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https://doi.org/10.1016/j.jcrysgro.2018.04.010
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Nomenclature

Cp	specific heat capacity [J/kg/K]
T	temperature [K]

Greek symbols

α	thermal expansion coefficient [10^{-6}/K]
ε	emissivity [-]
ϕ	porosity [%]
λ	heat conductivity [W/mK]
σ_B	bending strength [MPa]
σ_{TS}	tensile strength [MPa]
σ_C	compressive strength [MPa]
ρ	density [kg/m^3]
ρ_{el}	spec. elec. resistivity [$\mu\Omega$m]

temperatures in oxidative environment, has low concentration of metallic impurities (in particular Ti, Fe, Cr, Cu and Ni [7–9]), has sufficient mechanical strength/durability with low brittleness, has sufficient heat conductivity, is free of health risks and at the same time is affordable.

The following eight ceramic materials were considered: sintered silicon carbide (SSiC), nitride bonded silicon carbide (NSiC), recrystallized silicon carbide (RSiC), tantalum carbide (TaC), tantalum nitride (TaN), titanium carbide (TiC), vanadium carbide (VC) and tungsten carbide (WC). Properties of these ceramics are given in Table 1. For example, the values of thermal conductivity of SSiC, TiC and graphite are similar at temperatures near the melting point (T_m) of silicon, i.e. these materials are good heat conductors. On contrary, at lower temperatures $T \ll T_m$, TiC behaves as a moderate conductor. Very low heat conductivity of NSiC would hamper the heat removal from silicon during solidification, making NSiC unattractive for DS applications. Moreover, NSiC ceramic is typically accompanied with the high content of metallic impurities, such as Al and Y. Due to chemical instability of WC and TaN and their low maximum working temperatures in oxidative environment, i.e. $T_{max} = 811$ K for WC and $T_{max} = 700$ K for TaN, these ceramic materials were eliminated from further considerations. An additional criterion to exclude ceramics is also a high metallic content, like in WC of Co and Ni. Furthermore, VC has significant health risk, and TaC and TaN materials are excluded for commercial usage due to their very high material prices.

Summarizing the above considerations, three massive ceramic materials: TiC, RSiC and SSiC were identified as the most feasible constructive materials to replace standard graphite parts in the hot zone, in this study particularly the crucible cover and the support.

3. Experimental

The DS growth of silicon was performed in a G1-size furnace equipped with a side KRIST*MAG*® magnetic heater [12] and common top and bottom resistance heaters. In order to investigate the influence of the ceramic purity on the ingot quality we chose the G0-size where the ratio of ceramics surfaces to the volume of silicon is high. Hence, the maximum of impurities should be incorporated in the small ingots. The series of experiments was performed using ultra clean fused silica crucibles in the dimension $8 \times 8 \times 6$ cm^3, filled with 0.9 kg phosphor-doped solar grade silicon feedstock and completely surrounded by the ceramic and graphite as a benchmark, respectively (Fig. 1). For all set-ups we used the same T profile, similar cycle time and growth rate of ca. 1 cm/h. In all growth experiments, the melt was exposed to double frequency downwards travelling magnetic field with frequencies $f_1 = 20$ Hz and $f_2 = 200$ Hz. The experiments were repeated in each set-up at least twice to assure siliconizing of fresh graphite and ceramic parts as in the real DS process. Samples were obtained from vertical cuts and for impurity analysis from the middle and the very last-to-freeze parts of the final ingots.

The shape of the solid-liquid (s/l) interface in silicon ingots of all sizes was obtained from striation morphology analysis using lateral photo-voltage scanning method (LPS) [13]. Minority carrier lifetimes were measured on polished non-etched and non-passivated surfaces by the microwave detected photoconductivity method (MDP) [14] using the laser wavelength of 980 nm, the pulse duration and transient duration of 1 ms, respectively. Specific resistivity was obtained using 4-probe method. FTIR spectroscopy was applied to find out the distributions of substitutional carbon (C_s) concentration and interstitial oxygen

Table 1
Selected properties of graphite and technical ceramics. Price is given for p.a. quality of materials.

Property	Unit	Material							
		Graphite [1]	RSiC [11]	NSiC [11]	SSiC [11]	TaN [11]	TiC [11]	WC [11]	TaC [11]
ρ	[kg/m^3]	1750	2550	2795	3125	14,300	4800	15,600	14,200
ϕ	[%]	16	19	11	<3	<5	<1	<1	<3
σ_B	[MPa]	55	80	180	400	–	290	250	350
σ_{TS}	[MPa]	32	–	–					–
σ_C	[MPa]	100	–	650	>2500			2700	
E-Modul	[GPa]	9.8	240	240	400		495	615	510
Hardness	[-]	100 HR5/40	–	–	26 GPa	30 GPa	32 GPa	9 Mohs	17 GPa
α	[10^{-6}/K]	4.6	4.8	4	4.5		7.4	5.5	6.3
$\lambda_{@300;\ 1500K}$	[W/mK]	81*; 34*	23; -	23; -	145*; 37*	3.2; -	14*; 37*	110; -	22; -
$\rho_{el@293K}$	[$\mu\Omega$m]	14	–	–	10^{-9}–10^{0}	0–140	0.2–0.7	0.27	0.2–0.3
$Cp_{@293K}$	[J/kg/K]	1197	–	–	672		560	39.8	190
$\varepsilon_{@423;\ 923K}$	[-]	0.8	0.83; 0.96	0.83; 0.96	0.83; 0.96		0.62; 0.7	0.85	0.5
T_{max}	[K]	2273	2073	1773	2173	700	2273	773	2773
Price [10]	[€/kg]	70	281	–	281	3800	465	281	2840

* Heat conductivity was measured at IKZ using Laser Flash technique (LFA).