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Specific Features of Multicrystalline Silicon Growth from High-Purity Commercial Silicon

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Abstract—The distribution of impurities in multicrystalline silicon (mc-Si) blocks grown at various velocities from refined commercial silicon by the Stochbarger method have been studied. It is established that the growth velocity V strongly influences the distribution of impurities along the block height. Growth at $V > 1$ cm/h leads to the breakdown of a crystallization front and the trapping of impurities. The results are explained by the concentration supercooling that arises when the growth velocity is increased above the critical level for a given type of initial material. The optimum rate for the crystallization with simultaneous effective purification of a commercial silicon from impurities has been experimentally determined.

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In recent years, multicrystalline silicon (mc-Si) has accounted for a significant percentage of materials for photoelectric converters [1]. In order to ensure the development of solar energy conversion engineering, in particular to solve the problem of silicon deficit on the world market, a promising direction is related to the production of mc-Si from refined commercial silicon using a technology [2] created at the Vinogradov Institute of Geochemistry (Irkutsk). The main criteria for evaluating the quality of silicon for photoelectric converters are the chemical composition and crystalline structure. The level of the electrical parameters of the semiconductor, which makes the fabrication of photoelectric converters expedient, is determined by the elemental composition, grain size, defect density, and types of grain boundaries [3]. The aforementioned mc-Si production technology employs crucibles made of silica with a thin protective silicon nitride coating. A disadvantage of silica crucibles is the reaction of the crucible material with melted silicon, which results in the saturation of a growing crystal with oxygen. In order to reduce this, it is necessary to increase the crystallization rate to the maximum possible level.

However, if a refined commercial silicon is used as the raw material, the permissible rates of crystallization are absolutely unacceptable for the proposed

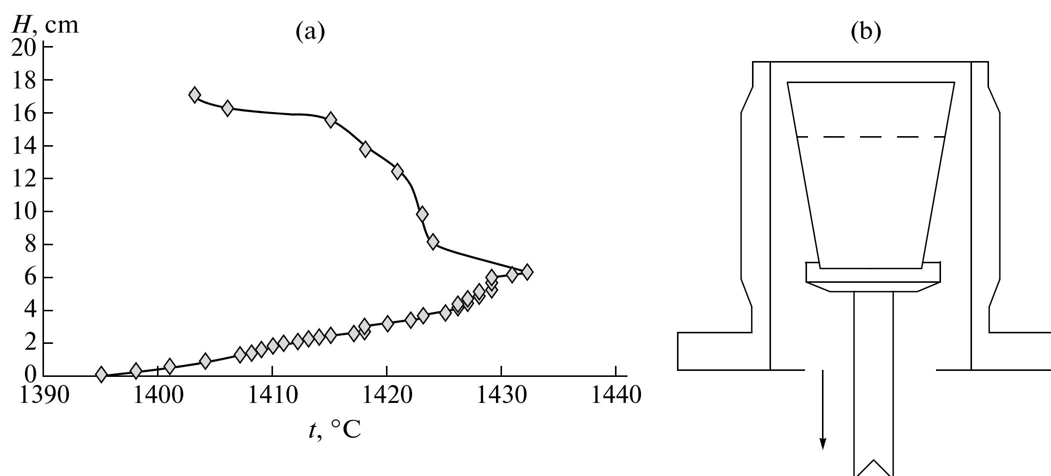

Fig. 1. (a) Axial profiles of temperature in an empty crucible occurring in the thermal field of a heater. Points below $H = 6$ cm correspond to temperatures measured at the bottom of crucible moved at a working velocity. (b) Schematic diagram of 620-ml crucible in the initial (upper) position ($H = 6$ cm) of driving rod relative to the heater (dashed line indicates an approximate level of silicon melt).

Table 1. Concentrations of impurities present in initial refined commercial silicon [$N \times 10^{-4}$ wt %]

Element	Al	Fe	Mg	Ca	Ti	Mn	Ni	Cu	Zr	B
Concentration	175	850	11	27	70	35	37	8	30	12

Table 2. Distribution of impurities along axis of mc-Si ingot [$N \times 10^{-4}$ wt %] (LOD = limit of detection)

Ingot	Element	Al	Cr	Mn	Fe	Ni	Zr
	LOD	2.0	0.2	0.03	1	0.2	0.04
A	Content of impurities in samples taken from various parts of ingot	4	0.2	0.03	4	0.2	0.05
		5	<+3	<+3	5	0.2	0.05
		2	0.3	0.03	4	0.2	0.04
		<+3	<+3	<+3	2	0.3	<+3
		<+3	0.6	0.03	4	0.6	<+3
		<+3	<+3	<+3	2	0.4	<+3
		3	<+3	<+3	3	0.4	<+3
		4	0.9	0.04	5	0.8	<+3
		4	0.2	0.03	5	0.5	<+3
		165	**6.9**	**61**	**1524**	**75**	**77**
	LOD	2	0.006	0.004	0.1	0.3	0.006
B	Content of impurities in samples taken from various parts of ingot	2	0.02	0.02	0.9	0.8	0.02
		5	0.07	0.02	1.2	0.9	0.01
		5	0.03	0.02	1.1	0.15	0.02
		8	0.02	0.1	3.3	0.24	0.14
		92	**5.9**	**53**	**1414**	**40**	**75**
		188	**9.7**	**96**	**2353**	**74**	**126**
		6	0.3	4.5	99	3.3	4.6
		8	0.05	0.2	5.4	1.1	0.3
		12	0.02	0.23	5.0	0.45	0.3
		5380	**143**	**1665**	**34 709**	**1472**	**1559**
	LOD	16	1	0.2	5	0.2	0.07
C	Content of impurities in samples taken from various parts of ingot	<16	<1	<0.2	<5	0.2	<0.07
		<16	<1	<0.2	<5	0.2	0.07
		18	**1**	**10.0**	**290**	**7.3**	**19.3**
		16	**1**	**7.9**	**177**	**5.9**	**14.0**
		<16	<1	1.1	20	0.8	1.5
		<16	<1	0.1	15	0.3	0.05
		26	**1**	**8.6**	**189**	**7.1**	**11.2**
		834	**30**	**296**	**6103**	**324**	**442**
		<18	<1	<0.2	<23	0.3	<0.1
		<18	<1	<0.2	<23	0.2	0.1

technology. When an ingot grows in the regime that corresponds to a chord of increasing fraction (f) of crystallized silicon, the segregation of an impurity that occurs in the melt at a given initial concentration C_0 corresponds to the effective distribution coefficient (k_{eff}) and is described by the following equation:

$$C = C_0 k_{\text{eff}}(1-f)^{k_{\text{eff}}-1}. \quad (1)$$

The well-known formula for k_{eff} shows that this value depends on several parameters [4]:

$$k_{\text{eff}} = \frac{k_0}{k_0 + (1-k_0)e^{-(V\delta/D)}}, \quad (2)$$

where V is the velocity of crystal growth from melt, δ is the diffusion layer thickness, and D is the diffusion coefficient of impurity in the melt. As can be seen from relation (2), the effective distribution coefficient (k_{eff}) differs from the value (k_0) determined as the ratio of impurity concentrations in the solid and liquid phases at equilibrium. Thus, the crystal growth takes place under nonequilibrium conditions, even at moderate rates of crystallization. For the impurities displaced by the crystallization front into the melt ($k_0 < 1$), the value of concentration immediately at the growth surface exceeds the level in the volume of melt. Therefore, $k_{\text{eff}} > k_0$ and, as the crystal growth accelerates, the impurity concentration at the interface increases and k_{eff} tends to unity. When the impurity concentration reaches the critical level, the impurity is trapped by the crystallization front. This phenomenon, called "concentration supercooling," is the main factor that hinders the possibility of mc-Si production from commercial raw materials at high rates.

In order to optimize the growth regimes, we have grown a series of mc-Si samples by the Stockbarger method at various velocities of crucible motion in the thermal field (Fig. 1). Other factors such as the axial temperature gradient (~5 K/cm), mass (1 kg), and the initial type of material remained unchanged. The crucible material was a glassy carbon that almost did not interact with liquid silicon and, hence, did not impose limitations on the process duration.

The elemental compositions of silicon samples were determined by the method of inductively coupled plasma mass spectrometry. The measurements were performed on a high-resolution double focusing mass spectrometer Element 2 (Finnigan MAT Germany). The impurities were concentrated by means of the autoclave decomposition of samples by hydrofluoric and nitric acid followed by distillation of the matrix element (MKP-03 setup, ANKON-AT-2, Russia). The task of determining analyts on a level of 10^{-8} – 10^{-4} wt % poses high requirements on the purity of reactants. For this reason, chemical treatments were carried out using Suprapur and Ultrapur grade acids (Merck, Germany) and deionized water with resistivity above 18.5 MΩ/cm prepared on an Elix=3/Mili-Q system (Millipore, France). The reliability of results

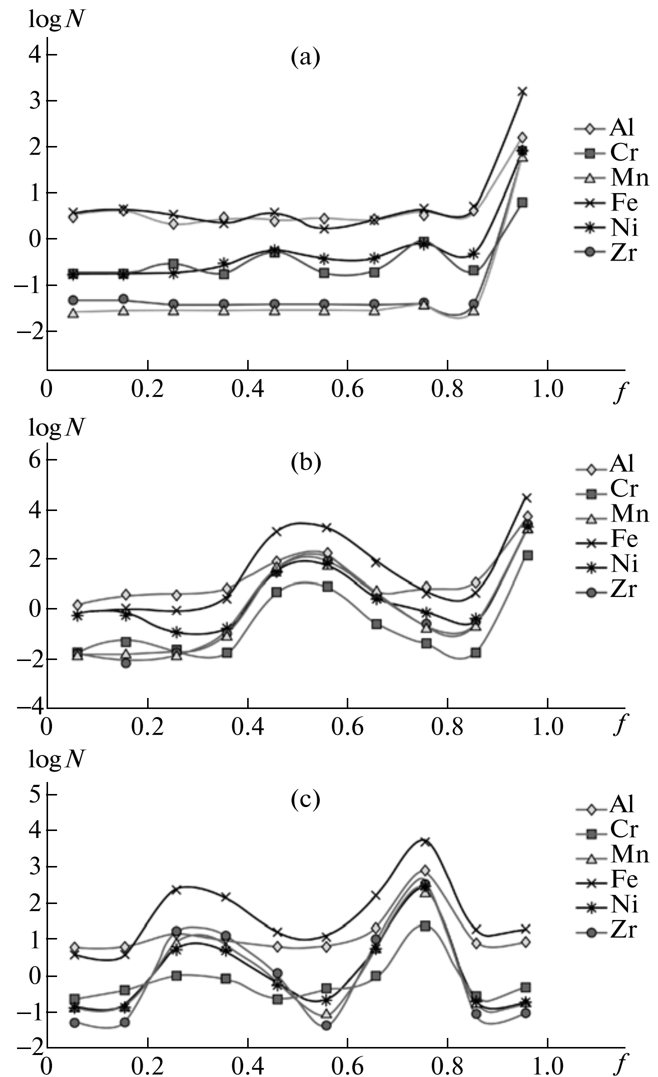

Fig. 2. Plots of concentrations of various impurities [$N \times 10^{-4}$ wt %] versus fraction f of crystallized silicon in ingots A (a), B (b), and C (c).

was checked by the method of additives and by reference to independently characterized samples of crystalline silicon (Kremnii Co., Shelekhov, Russia).

Tables 1 and 2 present data on the composition of initial commercial silicon and the results of determination of characteristic impurities in three ingots grown at various velocities. Ingots A, B, and C were obtained at V = 5, 10, and 15 mm/h, respectively. Figure 1 shows the profiles of these elements in the direction of silicon crystallization.

According to the results of chemical analysis, it can be concluded that normal growth in ingots B and C was violated and the crystallization front trapped impurities (concentration supercooling). An analysis of the data for ingot A, shows that the growth was accompanied by the effective purification of silicon from impurities. The upper (~10-mm-thick) part of the ingot,

where the impurity concentrations are several dozen or hundred times greater than in the main part, can be mechanically removed.

Thus, in growing mc-Si from refined commercial raw material by the Stockbarger method, one should take into account the high impurity content in the initial material. At relatively high growth velocities, this grade of raw material is susceptible to concentration supercooling, which sharply decreases the quality of the crystal. Thus, it is necessary to decrease the rate of crystallization.

On the other hand, the growth in silica crucibles may require the use of high velocities in order to avoid poisoning with oxygen ($k_0 > 1$), since even a protective silicon nitride coating on the inner walls cannot completely eliminate the interaction of the melt with silica. The experimentally determined optimum velocity of mc-Si growth from refined commercial silicon in glassy carbon crucibles was about 5–6 mm/h. The optimum velocity implied the formation of a desired columnar structure with simultaneous effective purification of silicon from impurities.

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