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Impurity Distribution in Multicrystalline Silicon Growth

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Abstract—This paper presents experimental data on the growth of multicrystalline silicon with tailored electrical properties using starting silicon of purity better than 99.999 at %. Our calculations demonstrate that the effective distribution coefficients of Fe-group impurities decrease with increasing impurity concentration in the starting charge.

Keywords: multicrystalline silicon, directional solidification, effective distribution coefficient

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INTRODUCTION

Multicrystalline silicon (mc-Si) is justly thought to be a basic material for solar cells [1]. The key factor that limits the progress of solar power conversion is the cost of semiconductor silicon. In this context, considerable potential is offered by upgraded metallurgical-grade silicon (UMG-Si), of purity from 99.9 to 99.999 at %, as regions of solid solutions of impurities in silicon are approached [2, 3]. One key issue is knowledge of the maximum allowable impurity concentrations in UMG-Si that ensure particular properties of mc-Si. To resolve this issue, it is necessary to find physical means of reducing the initial impurity concentration in UMG-Si in the mc-Si growth process, that is, to determine the effective distribution coefficients of impurities. Directional solidification entails impurity segregation and the formation of the macro- and microstructure of the ingot. As shown earlier [3–5], the directional solidification of silicon with an initial purity of 99.76 at % fails to ensure a reduction in the concentration of impurities to the level of their solubility limit in the structure of mc-Si, necessary for efficient operation of solar cells. Subsequent experiments used silicon of purity better than 99.99 at %.

The purpose of this work is to study the effect of the iron-group impurity concentration in the starting charge on the effective crystal–melt distribution coefficients of the impurities in multicrystalline silicon growth.

EXPERIMENTAL

The kinematic parameters preset for the growth of mc-Si ingots (Table 1) using starting charges of various compositions (Table 2) meet the following requirements: (1) the crucible–melt–crystal system should be rotated at the minimum rate sufficient for azimuthal leveling of the thermal field [4] and (2) the crucible–melt–crystal system should be translated across a temperature gradient zone at a speed no higher than that at which constitutional supercooling develops on the interface [5].

In this study, we compared our experimental conditions for the preparation of mc-Si form silicon of preset composition and the experimental conditions in the growth of mc-Si from MG-Si metallurgical, unrefined silicon in Martorano et al. [2]. To ensure purity better than 99.99 at %, the starting growth charges 2–4 were prepared using semiconductor silicon (99.99999+ at %) and a master alloy. Doping of silicon ensured p-type conductivity and resistivity of at least 0.5 Ω cm in the last-grown layer of the resultant ingot. The master alloy had the form of powder prepared using the surface layer of a directionally solidified ingot from charge 1. Table 2 presents not only the compositions of charges 1 (99.76 at %) and 2–4 (99.99 to 99.999 at %) but also data on the content of several impurities in MG-Si and their solubility limit in solid silicon [2]. The composition of MG-Si was determined using glow discharge mass spectrometry [2]. Blanks in Table 2 are due to the fact that there are no data for Ge and Co impurities.

Quantitative chemical analysis of master alloys and mc-Si layers grown from charges 1–4 was conducted by inductively coupled plasma mass spectrometry (ICP MS) [5]. Figure 1 schematizes how the mc-Si ingot was divided into 11 tentative transverse layers, from which samples for analysis, numbered in the order of the solidification of the layers, were taken. In the case of the ingot grown from charge 3, the data were averaged over three samples taken from different

Table 1. mc-Si growth conditions

Material	mc-Si from MG-Si [2]	mc-Si from experimental silicon charges
Si charge weight, kg	0.54	1
Temperature gradient, K/m	2000	500
Growth rate, m/s	5×10^{-7}	1.39×10^{-7}
Crucible rotation rate, rps	No rotation	1/300
Ingot length, m/diameter, m	0.11/0.034	0.1/0.07
Growth interface	Concave	Flat

Table 2. Content of major elements in the starting charges for mc-Si growth and their solubility limit C_s [2]

mc-Si	C, ppmw (10^{-4} wt %)					
	Fe	Ni	V	Ge	Mn	Co
MG-Si [2]	2850	90	15	–	58	–
Charge 1	850 ± 195	37 ± 7	60 ± 12	1 ± 0.32	35 ± 7.4	70 ± 8.4
Charge 2	7.82 ± 2.7	0.29 ± 0.08	0.3 ± 0.09	0.01 ± 0.003	0.06 ± 0.019	0.17 ± 0.03
Charge 3	7.06 ± 2.4	0.26 ± 0.07	0.66 ± 0.19	0.02 ± 0.006	0.12 ± 0.038	0.44 ± 0.08
Charge 4	3.49 ± 1.19	0.21 ± 0.06	0.22 ± 0.06	0.01 ± 0.003	0.05 ± 0.016	0.15 ± 0.027
C_s [2]	0.3	4.2	0.18	Unlimited	0.29	0.76

azimuthal positions of each layer. In the other mc-Si ingots, one sample was taken in each layer.

RESULTS AND DISCUSSION

Martorano et al. [2] studied the impurity distribution in mc-Si ingots using a model in which there was a diffusion layer in front of a growth interface moving at a preset rate. Their results indicate that, at a slow directional solidification rate, the purity of the starting MG-Si (99.7 at % purity) and the roughly equal contributions of the convection and diffusion mechanisms to mass transport allow one to use the complete melt intermixing approximation in calculating the effective impurity distribution coefficient. In this approximation, the impurity concentration in an ingot is determined by its initial concentration in the melt, C_0; the fraction of melt solidified, f; and the effective distribution coefficient, k, which is independent of the impurity concentration according to the Pfann equation [2, 6]: $C = C_0k(1 - f)^{k-1}$.

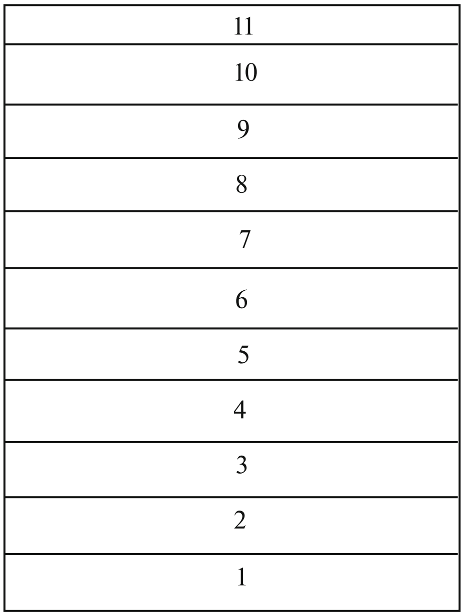

Fig. 1. Schematic of how the mc-Si ingot was divided into layers.

In analyzing the impurity distribution in ingots 1–4, we restrict ourselves to this approximation, because we think that we deal with approximately equal contributions of the convection and diffusion mechanisms to mass transport. This is indirectly supported by the crystal growth parameters used: (1) the ratio of the temperature gradient to solidification rate for MG-Si ($G/V = 4 \times 10^8$ (K s)/m^2) is comparable to that of the silicon of compositions 1–4 ($G/V = 3.6 \times 10^8$ (K s)/m^2); (2) crucible rotation at a rate of 0.2 rpm has an insignificant effect on the shape of the growth interface and the convection structure and rate [4].

Since there are considerable uncertainties in determining trace impurity concentrations in the ingot, the Pfann distribution (1) is also given at $C_0 \pm \Delta$, where Δ is the uncertainty typical of the ICP MS method in the corresponding range of concentrations of a particular element. The uncertainty in determining the initial

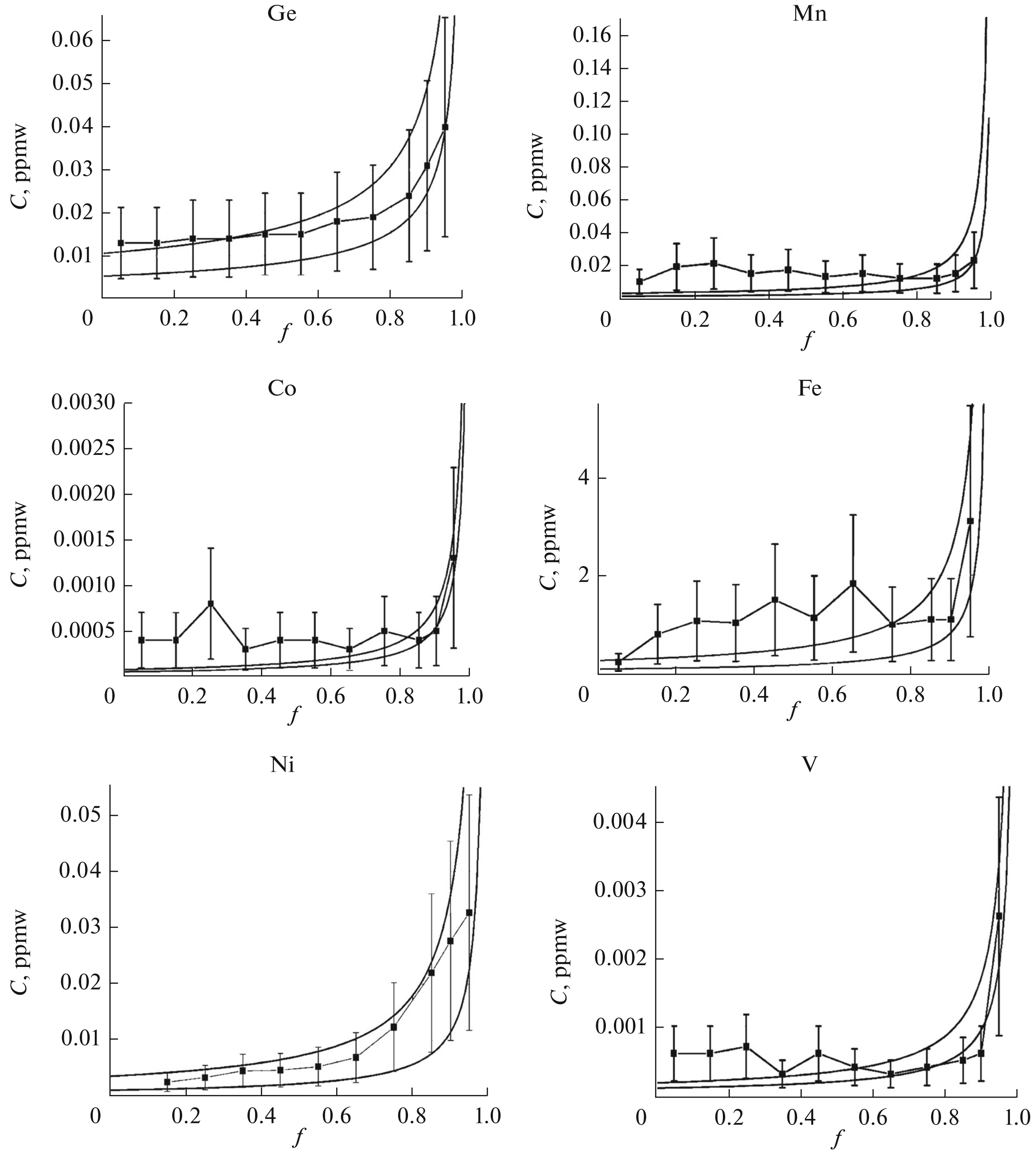

Fig. 2. Ge ($k_{\text{eff}} = k_0 = 0.33$), Mn, Co, Fe, Ni, and V impurity distributions (ppmw, or 10^{-4} wt %) along the mc-Si ingot grown using charge 3; *f* is the fraction of melt solidified.

impurity concentration, which is orders of magnitude higher, is lower than that in determining the concentration of the impurity in the ingot, especially when C_0 is evaluated from the impurity concentration in the master alloy. The impurity distribution coefficient was adjusted so that curves *1* at $C_0 - \Delta$ and $C_0 + \Delta$ remained within the ranges that included the uncertainty in impurity concentration measurements in the bottom and top parts of the ingots, respectively (Fig. 2). Figure 2 shows the Ge, Mn, Co, Fe, Ni, and V impurity distributions in ingot 3, which illustrate the effect of diffusion mass transport.

The nonmonotonic variation of the impurity concentration with increasing *f* in some of the plots may be due to local concentration fluctuations in the boundary layer as a result of incomplete melt intermixing in the free convection regime. Local features of the boundary layer are also influenced by the crystal growth mechanism. Silicon on the growth interface has both atomically smooth {111} close-packed sur-

Table 3. Effective impurity distribution coefficients in mc-Si growth from MG-Si [2] and using charges 1–4

mc-Si	k					
	Fe	Ni	V	Ge	Mn	Co
MG-Si [2]	0.0004	0.0015	–	–	0.002	–
Charge 1	0.002	0.006	0.00004	0.33	0.001	0.00001
Charge 2	0.025	0.012	0.0020	0.33	0.030	0.0005
Charge 3	0.03	0.015	0.0012	0.33	0.017	0.0002
Charge 4	0.05	0.020	0.0030	0.33	0.035	0.0006

faces and atomically rough surfaces (any other crystallographic planes). Strong supercooling on the {111} faces leads to high tangential growth rates. The replacement of grains with low reticular density by those with high reticular density (or vice versa) sharply changes impurity segregation conditions [6].

Table 3 lists the effective distribution coefficients of Ge and Fe-group impurities. Blanks in Table 3 are associated with either impurity detection limits or the fact that there are no data on the concentration of a particular element [2]. Comparison of the C_0 data in Table 2 and the k data in Table 3 suggests that there is a correlation demonstrating that, with decreasing initial impurity concentration, the effective distribution coefficient of the impurity rises.

One possible physical interpretation of this finding is that the incorporation of an impurity particle into a lattice already distorted by another particle requires large work. Elastic interaction between impurity particles reduces their solubility in the solid phase and the impurity distribution coefficient at high concentrations [7]. If the liquidus and solidus lines at low impurity concentrations are rectilinear, k is independent of C_0. In Tables 2 and 3, this can be seen for Ge, which forms a continuous series of solid solutions with silicon. It can be seen that the $k = 0.002$ reported by Martorano et al. [2] for Mn impurities is inconsistent with this behavior. It is worth noting that MG-Si contains considerably more impurities (especially Fe) than does charge 1. It seems likely that, in this case, there is some feature of the physicochemical interaction between different impurities when these are incorporated into the structure of the ingot, which favors the capture of one of them by the growing crystal. Moreover, in crystal growth from MG-Si and silicon of compositions 1–4, the growth interface had different shapes, which was probably a consequence of the differences in the geometry of the crucible–melt–crystal system. A concave growth interface favors the capture of impurities by the growing crystal [5].

On the whole, to prevent an increase in the effective distribution coefficient of an impurity, it is necessary to (1) reduce the growth rate and (2) ensure an external influence enhancing convective heat and mass transport and leading to more effective melt stirring.

CONCLUSIONS

Our results on the distribution of Fe-group impurities demonstrate that reducing their concentration in the starting silicon to their solubility limits or a lower level leads to an increase in their effective distribution coefficients. To prevent an increase in the effective distribution coefficient of an impurity in going to purer starting silicon, it is necessary to change mc-Si growth conditions.

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