



STUDIES ON EFFECTIVE SEGREGATION COEFFICIENTS OF IMPURITIES IN SILICON PULLED FROM MG-Si MELT

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Minimization of impurities content in Si, necessary for its application as semiconductor material, was performed by using directional crystallization of metallurgical grade Si (*n*-MG-Si) with 98 wt. % Si purity without intermediate stages. After pulling from melt, *n*-MG-Si goes into *p*-type Si with current carriers concentration (*p*) $\sim 10^{16} \text{ cm}^{-3}$ and Si has been purified practically from most of the impurities. The possibility of uncontrolled impurities removal from Si depends on impurities effective coefficient of segregation in Si. Therefore we have investigated the effective coefficient of segregation of unwanted impurities in Si crystals, obtained by pulling directly from MG-Si melt. In the presented article the effective segregation coefficient of major impurities in Si has been calculated and analysed in the dependence on the crystallization conditions. Effective coefficient of segregation makes possible estimate the capacity and efficiency of Si purification from impurities during crystallization from melt.

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presented in Si. Effective coefficient of segregation makes possible estimate the capacity and efficiency of Si purification from impurities during crystallization from melt. So the objective of the presented article is the investigation of effective coefficient of segregation of unwanted impurities in Si crystals, obtained by pulling directly from metallurgical grade Si (MG-Si) melt.

Introduction

Silicon technology has had a strong influence on the world economy over the past few decades, and presently is the driving force behind the revolution in semiconductor engineering applications. Silicon has advantages over other semiconductor materials because of its abundance on the earth, meeting most required criteria and having a number of better properties.^{1, 2} It is predicted to remain the prevailing semiconductor technology for the near future. The continual reduction of the size of Si devices has led to exponential increase in their quality together with an exponential decrease in the cost per function. The size reduction of bulk crystalline Si to the nanometre dimension expands the scope of silicon application. For example, nano crystalline Si becomes light emitting. Silicon technology is gradually moving into new applications as novel silicon-base nanotechnology. However further development of Si application requires further investigations in the direction of identification of behaviour of uncontrolled impurities in Si. The main criterion of Si suitability for application in semiconductor devices is its chemical purity. Therefore the problems connected with uncontrolled impurities removal from Si are very important.

Minimization of impurity contents of Si, intended for application as semiconductor material, is achieved by using many known traditional refinement methods, among them is crystallization from the melt. As a rule, it is applied on the final stage of technological process of purification of substances. However in given work a directional crystallization is used for direct purification of metallurgical Si without any intermediate stages. The possibility of removal of unintended impurities from Si depends on effective coefficient of segregation (*k*) of impurities

Experimental

The first step product of Si obtained by restoration from quartzite with reaction to carbon is metallurgical Si. *n*-MG-Si with $\sim 98 \text{ wt. \% Si}$ has been taken as initial material. Ample quantity ($\sim 2 \text{ wt. \%}$) of unwanted impurities Fe, Al, P, Ca, Cu, Mg, Mn, Ni, Ti has fallen one after the other into MG-Si from quartzite and restoring materials in time of restoration process. Carbon and oxygen has been presented in MG-Si too. The known Czochralski growth method of pulling crystals has been used for obtaining Si directly from MG-Si melt. Crystals have been grown from 48 mm diameter quartz crucible. Si crystalline rods with the length of 50 mm were used as the seeds. During the process of the crystal pulling the crucible with the mother melt revolved with the rate of rotation 45 and 10 revolutions per minute in opposite directions. The optimal effect of Si purification has been achieved at $\sim 0.25 - 0.30 \text{ mm per minute}$ rate of crystal growth. Such conditions provide the symmetry of temperature field at the crystallization front.

First the melting camera has been pumped off up to 10^{-4} mm Hg , and then washed by flow of argon. The fusion has been carried out in the argon atmosphere at a pressure of not more than 50 kPa. *n*-type MG-Si ($n \approx 10^{18} \text{ cm}^{-3}$) have been charged into the crucible. The volatile impurities actively evaporated from the surface of MG-Si have been removed from melting camera with equipped special apparatus for gas removing (gas-extracting arrangement). An argon supply and discharge of the working chamber was regulated so, that the pressure in the chamber remained constant at the level of 50 kPa.

The content of contaminating impurities in Si before and after the directional crystallization has been defined by X-ray diffraction method, micro X-ray spectral and emissive spectral analyses. Electrical properties and microstructure analysis of Si experimental samples have been implemented too. Effective segregation coefficient of detrimental impurities in Si at the crystal pulling from MG-Si has been determined on the base of established content of unwanted impurities in Si. *n*-MG-Si after pulling goes into *p*-type Si.

Results and Discussion

Mechanisms of impurity removal

At initial step of melting at low temperatures Si has been purified from mixture of those impurities which are more volatile than basic component. The melt had sufficiently large surface. So volatile impurities actively evaporated from the surface of Si melt at low temperatures and 10^{-3} mm Hg pressure. Their content is defined by pressure and composition of atmosphere in a processing chamber. At temperatures lower than Si melting temperature (1450 °C) impurities with less fusion temperature have evaporated too. On the next step of process temperature has increased by 50–70 °C higher than 1450 °C and Si melt stayed in liquid state certain time for removal (evaporation) of uneasily meltable impurities like Fe and Ti. Under the conditions of low pressure and high temperatures those impurities, which vapor tension is higher than one of Si (P, Al, etc.), have evaporated too.

It is known,³ that quantity of impurity (*m*), which vaporizes from open unit area of the melt (reflection of molecules from crucible walls is taken into account) is defined by:

$$m = \beta P \sqrt{\frac{M}{2\pi RT}} \quad (1)$$

where

P is the equilibrium pressure of impurity steam,

M is the molecular weight of impurity,

R is the gas constant,

T is the melting temperature,

and the coefficient β can be written as

$$\beta = \frac{156.6\alpha}{1 + \alpha d l^{-1}} \quad (2)$$

where

α is the condensing coefficient,

d is the crucible diameter, and

l is the height of walls of crucible above the melt.

Purification by evaporation has been effective for those impurities, which equilibrium pressure of steam exceeds one for Si. Those impurities which equilibrium pressure of steam

is higher then for the rest of the impurities vaporized easier at the identical conditions. The ratio of equilibrium pressure of steam for impurities and Si defines the degree of their partition. It follows from expression (1) that the vaporizability or ability to be removed of easy vaporable impurities from Si melt reduces in the row of $Mg > Ca > Mn > Al > Cu > Fe > Ni > Ti$.

Among a great number of foreign unforeseen electrically neutral impurities carbon and oxygen in Si attract attention. They get into semiconductors because of technology equipment (quartz crucible, heated graphite). Gaseous carbon and oxygen compounds products of the reaction have been removed by gas-extracting arrangement. At the same time refractory products have precipitated at the end of crystal. IR spectroscopy measurements of carbon distribution in Si have confirmed that carbon concentration increases at the end of a crystal. It indicates the enrichment of the melt with carbon due to segregation of carbon during the growth of the crystal. This cannot be explained only by the low distribution coefficient of carbon in silicon. It is also caused by collection of carbon in the melt in the result of chemical reactions of silicon with quartz and quartz with graphite. At the melt cooling carbide compounds are in isolated state. So, it is clear, that the carbon segregation process in silicon and the enrichment of the melt with carbon depend on the time of crystal growth process. Finally carbon has been removed with cut off part of Si crystal. It is remarkable, that Fe, Ca and oxygen promote the reduction of carbon solubility in Si.

MG-Si after pulling became *p*-type with current carriers concentration $\sim 10^{16} \text{ cm}^{-3}$ and has been purified practically from majority of impurities. Incidentally the impurities in MG-Si have obeyed to the procedure of purification in a variety of mechanisms because of different physical properties of impurities. During the execution of the metallurgical silicon purification process the quantity of Ca, Mn, Ni out of the whole collection of unwanted impurities has reduced so much ($< 0.001 \text{ wt. \%}$), that their concentration has been less of detection limit of applied methods of impurities determination.

The purification of silicon from Mg, Mn, Cu, Fe, Ni, Ti impurities have occurred mainly by segregation because of their small segregation coefficient in Si (10^{-4} – 10^{-6}). Equilibrium coefficients of distribution of Al and Ca impurities (k_0) in Si ($2.0 \cdot 10^{-3}$ and $8.0 \cdot 10^{-3}$ accordingly) are not sufficiently small for being removed from Si by directional crystallization. But saturation vapor pressure of Al and Ca is much more than one for Si. Thus their removal from melt surface into gaseous phase at high temperatures and afterwards by gas-extracting arrangement has been possible.

Effective coefficient of distribution of harmful impurities in Si at crystal withdrawal

It is known, that at the pulling of Si from melt impurities have redistributed between solid and liquid phases with certain ratio as mentioned above and this process is characterised by effective coefficient of segregation of impurity. *k* of impurities in Si for experimental samples has

been calculated on the base of experimentally established data of impurity composition. The dependence of k of impurities in Si on the pulling speed of crystals is shown in the Figure 1.

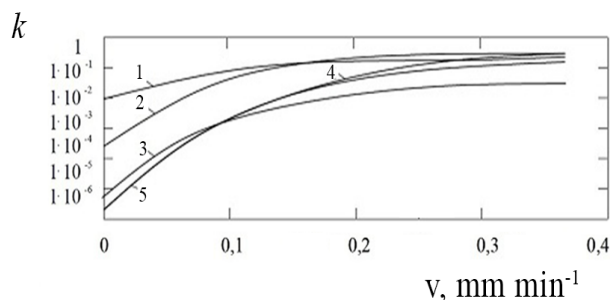


Figure 1. The dependence of effective distribution coefficients (k) of impurities in Si crystals on the pulling speed from melt. Impurities: 1 – Al; 2 – Cu; 3 – Fe; 4 – Mg; 5 – Ti.

The crystal Si pulling speed 0 mm min^{-1} belongs to the state of “equilibrium”, i.e. practically to very low pulling speed of crystal. For certain finite pulling speed magnitudes, k depends on the crystal pulling rate. It is remarkable, that equilibrium coefficient of distribution of majority of impurities in Si $k_0 < 1$. So as expected an increase in rate of crystal pulling results in k and at high pulling rates verge towards 1 (when quickly migrating separating phase is included) independently of magnitude of equilibrium coefficient of distribution of impurities k_0 .⁴ Data of effective coefficient of distribution of major impurities in Si corresponds to $k_0 \leq k \leq 1$ inequality. This result is in a good agreement with theory of Barton–Prima–Slichter.⁵ According to Barton–Prima–Slichter theory relationship between k and k_0 is defined by eqn. (3), at diffused transport of mass in δ layer (depth of melt near crystallization front-diffusion layer).

$$k = \frac{k_0}{k_0 + (1 - k_0)e^{-\Delta}} \quad (3)$$

where

$\Delta = v\delta/D$ is a dimensionless quantity, so called reduced velocity,

v is the solidification rate,

D is the diffusion coefficient of impurity

δ value depends on rate of rotation of crystal and changes in the range of $0.1\text{--}0.001 \text{ cm}$.

It can be seen from Eqn. (3), that in the first approximation k depends on the conditions of crystal growth processes i.e., solidification rate and rate of rotation of crystal (conditions of melt mixing). According to this theory when equilibrium distribution coefficient of impurities $k_0 < 1$, k increases at the growth of crystal pulling rate. While crystal is pulling from melt impurities with $k_0 < 1$ accumulate little by little in the melt because of they get into melt from crystallization front.

Accordingly impurities concentration at the surface exceeds their concentration in the melt. So $k > k_0$ and during the process of crystal growth the melt is progressively

enriched by impurities because of their bad solubility in solid phase. Therefore the end of crystal, where all residual impurities are concentrated, has always been cut off.

Impurity distribution along the ingot at crystal withdrawal

It is remarkable, that impurities are mainly concentrated at the end of Si crystal. Fig. 2 shows clearly that contaminated dark end parts of Si crystal.

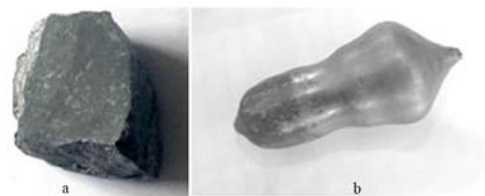


Figure 2. (a) Metallurgical Si and (b) Si crystal obtained by pulling from melt with 0.3 mm min^{-1} velocity.

The size of impure section reduces at the increase of the velocity pulling speed of crystal. It means that the effect of co-location of impurities at the end of crystal intensifies with growth of crystal pulling velocity. Impurity distribution along the crystal length during the crystal pulling from the melt is described by the following formula of Scheil.⁶

$$C = k C_0 (1 - g)^{k-1}, \quad (4)$$

where

$g = V_m/V_0$, g is the crystallized part of initial volume of melt;

V_m is the volume of crystallized phase,

V_0 is the initial volume of liquid phase,

when $g = 0$, impurity concentration in the melt C equates to its initial magnitude in the melt C_0 .

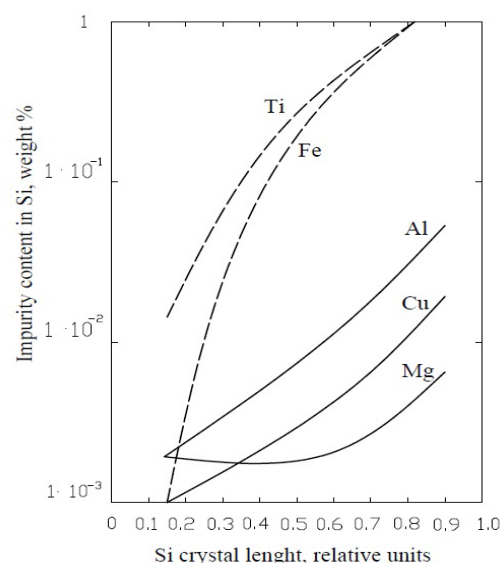


Figure 3. Dependence of impurities concentration in Si solid phase on the crystallized part of melt.

According to Eqn. (4) when $k < 1$ (at equilibrium during the process of crystal pulling, $k = \text{const}$) impurities concentration increases along the crystal length.

For majority of impurities in Si, $k \ll 1$, so Eqn. (4) can be written as Eqn. (5).

$$C \cong \frac{kC_0}{1-g} \quad (5)$$

where kC_0 is a constant. Eqn. (5) shows, that C is inversely proportional to the remaining part of melt. Dependence of impurity concentration in Si solid phase on crystallized part of melt is shown in the Figure 3.

Typical X-ray diffraction spectra have shown that obtained Si is single-phase. Consequently, there is only Si diffraction maxima on the diffractogram. Microstructure investigations has confirmed, that the tracks of different phase inclusions observed in initial microstructure of MG-Si almost disappeared after pulling Si crystal out of the melt. So crystal phase of Si is purer than liquid phase with irregular impurity distribution along length.

Conclusion

Thus Si and two or more liquid layers of slags, which differ by density, originate at Si melting and the purification of Si of impurities like Fe, Al, P, Ca, Cu, Mg, Mn, Ni, Ti take place by different mechanisms or their combination.

Concrete mechanisms processing at Si purification are defined by impurity-Si interactions and depend on impurity distribution coefficient between solid and liquid phases, degree of volatility, steam tension, melting temperature, specific weight, and other chemical properties of impurities. Because virtually all basic impurities in Si have distribution coefficient $k < 1$, their effective removal is carried out by pushing aside impurities into liquid phase.

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References

- ¹Green, M. A., Emery, K., Hishikawa, Y., Warta, W., Dunlop, E. D., *Progr. Photovoltaics: Res. Appl.*, **2015**, 23, 1.
- ²Khutsishvili, E., Khutsishvili, N., Kvirkvelia, B., Kekelidze, G., Nadiradze, L., Kekelidze, N., *J. Electr. Eng.*, **2015**, 3, 53.
- ³Sing, K. S. W., Everett, D. H. R., Haul, A. W., Moscou, I., Pierotti, R. A., Rouquerol, J., Siemieniewska, T., *Pure Appl. Chem.*, **1985**, 57, 603
- ⁴Martorano, M. A., Neto, J. B. F., Oliveira, T. S., Tsubaki, T. O., *Mater. Sci. Eng. B*, **2011**, 76(3), 217.
- ⁵Burton, J. A., Prim, R. S., Slichter, W. P., *J. Chem. Phys.*, **1953**, 21, 1987.
- ⁶Pfann, W. G., *Trans. AIME*, **1952**, 194, 747.

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