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Influence of Sb doping on oxygen solubility in Si melt

X.-M. Huang, K. Terashima, H. Sasaki, E. Tokizaki and S. Kimura

Kimura Metamelt Project, ERATO, JRDC,
Tsukuba Research Consortium, 5-9-9 Tokodai, Tsukuba, Ibaraki 300-26, Japan

The oxygen solubility in liquid silicon, both undoped and Sb-doped, in equilibrium contact with SiO_2 has been analyzed after quenching by the SIMS technique in order to investigate the influence of antimony addition on the oxygen solubility. It has been shown that oxygen solubility in undoped silicon melt changes from $2.08x10^{18}$ to $2.29x10^{18}$ atoms/cm^3 upon temperature increases from 1447 to 1542°C. Addition of less than 1 at.% Sb caused practically no change in oxygen solubility, while addition of more than 1.3 at.% Sb appreciably increased both its level and its temperature coefficient.

1. INTRODUCTION

The incorporation of oxygen in silicon crystals during growth by the Czochralski technique has been investigated over the last 10 years, and studies include both experiments and theoretical calculations. Several recent papers dealt with investigations of the solubility of oxygen in liquid silicon in equilibrium with its oxide at elevated temperatures.[1-4] However, reported experimental data are not consistent.[2,3] One reason for the problems in obtaining reliable data on the silicon-oxygen system is the difficulty of quantitative analysis. Different measuring methods tend to give somewhat different results. With the SIMS (secondary ion mass spectroscopy) technique, however, measurements of oxygen concentration in polycrystalline samples quenched from silicon melt can now be carried out with sufficient accuracy.

Another reason possibly results from the different equilibrium conditions. According to the calculation of Ekhult and Carlberg,[2] oxygen solubilities are different in silicon melt with different equilibrium conditions: for example, oxygen solubility in liquid silicon is much lower in equilibrium with amorphous SiO than with SiO_2. Thus a carefully designed experiment promises reproducible data for oxygen solubility in silicon melt.

Until now all data were only on undoped silicon. But in fact, the investigation of properties of doped silicon is more meaningful from a practical viewpoint. Among n-type dopants, antimony is regarded to be important in the production of high-conductivity silicon wafers. The peculiarity of Sb in Si melt is that the amount of dopant introduced is considerable (a few at.%) due to the fact that antimony has a very small segregation coefficient (0.023).[5] Although it is said that oxygen concentration decreases quickly in heavily doped silicon crystal[6] and oxygen precipitation is much different from lightly doped or undoped crystals,[7] there is no data on the dependence of oxygen solubility on the concentration of Sb in silicon in equilibrium contact with SiO_2. In the discussion of ref. 1, it is suggested that oxygen solubility decreases with increasing antimony concentration without supporting data. As long as the influence of Sb on oxygen solubility remains a suspected cause for decrease of oxygen in Czochralski silicon crystals, an experiment must be carried out. Therefore, we investigated oxygen solubility in silicon melt and the influence of antimony addition on it.

2. EXPERIMENTAL

2.1 Sample preparation

To measure the solubility of oxygen in a silicon melt in equilibrium contact with silica, and to minimize the possible errors caused by the surrounding space, a combination of undoped or antimony-doped silicon and silica was prepared so as to insure complete contact with each other at high temperatures. An undoped or antimony-doped silicon rod 13 mm in diameter and 33 mm in length was charged in a 13-mm-inner-diameter silica ampoule with a flat bottom. The upper space in the ampoule was sealed with a silica rod with a slightly smaller diameter and it was welded completely to the inside wall of the ampoule after evacuation to the vacuum of about 10^{-6}torr. The evacuation was done to shrink the

softened ampoule at high temperatures and to complete the contact between the silicon melt and the ampoule wall. All the samples had been chemically etched before charging into the ampoules. The silicon rods used in undoped experiments were cut from a pure FZ crystal. Antimony-doped silicon rods were cut from some samples which were prepared by the following procedure. Two hundred grams of high-purity polycrystal silicon was placed into a crucible 50 mm in diameter and 60 mm in height and heated to the melt surface temperature of 1450°C under the vertical temperature difference of 50°C between the crucible bottom and the melt surface. It was kept in a molten state for about 30min, and then the appropriate amount of antimony was added into the crucible to achieve the nominal composition. It was kept at the same temperature for another 30min, cooled to 1350°C at a cooling rate of 200°C/h, and then cooled to room temperature at a cooling rate of 50°C/h. The nominal compositions of the samples were 1, 2, 3 and 5 at% Sb in Si. The purity of Sb was 6N.

2.2 Melting, resolidification and temperature measurement

The silica ampoule with a pure silicon rod or antimony-doped silicon rod inside was covered with a graphite holder, and heated to various temperatures in the range of 1426°C~1542°C for 90min in an Ar atmosphere. Fresh Ar was supplied at a rate of 1.5*l*/min. The furnace used in this experiment was a horizontal three-zone type. The temperature and its variation were measured using three 0.5-mm-diameter B-type thermocouples placed along the outer wall of the graphite holder at the two ends and the middle of the silicon rod. The thermocouples used in this experiment were calibrated by measuring melting points of Au, Pd and Sb. The variations of temperature monitored by the thermocouples during equilibration were within ±2°C for all the samples. The sample was quickly drawn from the furnace for quenching, after equilibration has been presumably attained in 90 minutes. Quenching rates of the samples were about 20°C/s. The duration for holding the temperature was determined by calculating the diffusion of oxygen atoms in the melt from the silica ampoule wall, using a diffusion coefficient of $1x10^{-4}cm^2/s$. Unfortunately, experimental data for the oxygen diffusion coefficient in silicon melt are not available, to the authors' knowledge. Thus the employed value for calculation was chosen on the basis that most common dopant elements have larger diffusion coefficients than that.[3,8] According to the calculation, the degree of saturation after 90 min was predicted to be 99.9%, even at the center of the melt, with the presently employed ampoule size.

2.3 Oxygen and antimony concentration measurements

The preparation of samples for SIMS was as follows: A 2-mm-thick slice from the middle of the quenched sample was cut with a diamond saw. The slices were ground and polished using a diamond grinder. As the quenched undoped samples were fragile, it was difficult to obtain large slices, but slices of heavily antimony-doped silicon samples were relatively easy to obtain as they were not very fragile. A piece about 4x4 mm^2 was cut from every slice for SIMS measurements and in order to obtain average values, every sample was measured three times at three different places. In SIMS measurement, IX 70S produced by VG Company was used, in which the primary ion source was Cs, acceleration voltage was 16KV, current was 0.5 μA, and the area of the primary ion beam was 300 μm in diameter. Standard samples for the measurement were silicon wafers, their oxygen concentrations were measured by FT-IR with a conversion coefficient of $3.03x10^{17}atoms/cm^2$.[9] Gas fusion analysis (GFA) was also carried out for some samples. The oxygen concentrations measured by SIMS were mainly discussed in this paper with occasional reference to the GFA data. The relative error of SIMS measurement was less than 5%.

The antimony concentrations were measured by both SIMS and ICP-ES (inductively coupled plasma emission spectrometry). Samples for ICP-ES measurement were taken from the remainder of the slices in proximity to the samples for SIMS. Every sample was measured twice to obtain average value.

Other impurities were not measured after the melting experiment since the initial purity was sufficiently high and the experimental procedure was believed to incorporate no additional impurities.

3. RESULTS AND DISCUSSIONS

According to the data in ref. 3, oxygen concentration only changed a few percent when cooling rate was varied from 2°C/s to 7°C/s, and data for oxygen solubility were indicated to be more accurate when

the cooling rate after equilibration was fast. Thus the cooling rates in this experiment were selected to be as fast as possible, about 20°C/s, which was much faster than those in ref. 3. According to the calculation from the diffusion coefficient of impurities in silicon melt, with the cooling rate of about 20°C/s, impurity atoms in silicon melt move only a few hundred microns before the melt is solidified. Every sample for SIMS measurement was measured three times at three different places which were separated by a few millimeters, so the values of the concentrations obtained here should be reliable. Detailed results are shown in Fig. 1.

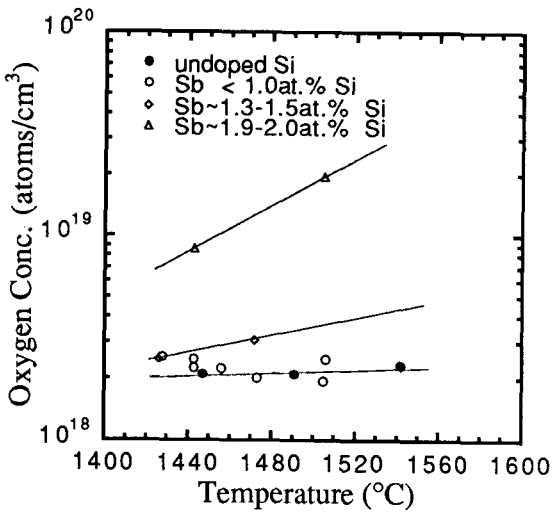

Fig. 1. Oxygen solubilities in Si melt measured by SIMS.

It can be seen from Fig. 1 that oxygen concentrations of undoped silicon samples range from 2.08×10^{18} to 2.29×10^{18} atoms/cm^3 over the temperature range of 1447°C~1542°C. This result agrees well with the experimental data in ref. 2. Oxygen concentrations of antimony- doped silicon samples range from 1.92×10^{18} to 19.48×10^{18} atoms/cm^3 over the temperature range of 1426°C~1506°C with various antimony concentrations. The real Sb concentrations measured by ICP and SIMS were ranged from 0.1 to 2.0 at. %. It is clear that the nominal concentrations and real concentrations are different, which will be discussed later.

Several other results can easily be seen from Fig. 1. (a) Oxygen concentration increases quickly with increasing antimony concentration when antimony concentration is higher than 1.3at.%. (b) The dependence of oxygen concentration on temperature is strongly correlated with antimony concentration. (c) There is no marked dependence of oxygen concentration on antimony concentration in the studied temperature range when antimony concentrations are lower than 1at.%. The oxygen concentration in this range is almost the same as in the undoped silicon.

In addition to the above results, another observation must be mentioned here. In every one out of twenty undoped silicon samples there was a greyish brown film between the solidified silicon and silica ampoule wall after it had been quenched. The film appeared to be amorphous SiO.

As mentioned above, the samples of antimony-doped silicon for oxygen dissolution experiments were cut from the mother samples, prepared by preliminarily melting silicon and doping Sb into it, and the mother sample was much larger than the sample used in dissolution experiment. Solidification of the mother sample began on the surface of the melt. Taking the segregation effect of antimony into consideration, one realizes that there should be a distribution of antimony in the crucible, with the highest concentration at the bottom. The Sb content in the middle part is, of course, lower than the average. It is not difficult to understand the difference between the nominal composition and the real composition.

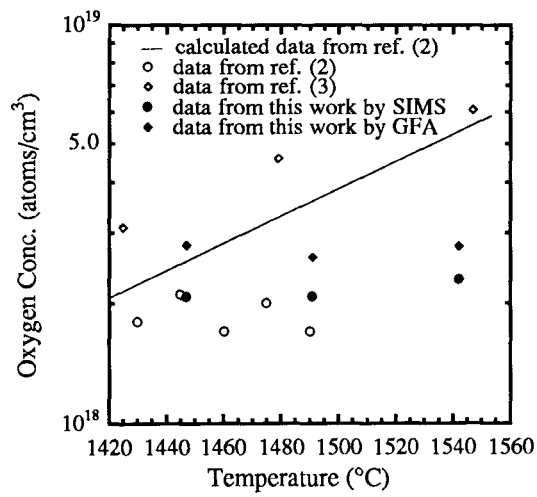

Fig. 2. A comparison of the dependence of oxygen solubility on temperature of undoped silicon melt.

Figure 2 is a comparison of the dependence of oxygen solubility on the temperature of undoped silicon. As a comparison, some values of oxygen

concentration obtained by GFA are also included. The result of measurement by SIMS is almost the same as that in ref. 2 in which the measuring method for oxygen concentration was also SIMS. But the data in this work obtained by SIMS and GFA are slightly smaller than the result in ref. 3 in which the measuring method was GFA, although the samples in all these studies were prepared by essentially the same method. It should be emphasized that with the SIMS technique, the result of this work and that in ref. 2 were consistent, and both were slightly smaller than the calculated result in ref. 2, while the result of this work and that in ref. 3 obtained with GFA are different and both are larger than the calculated result. In order to explain why the oxygen solubility in this work for undoped silicon was smaller than the result of calculation using thermodynamic data in ref. 2, it should be noted that a greyish brown film formed between the solidified silicon and the silica ampoule wall. It is probable that the equilibration was not complete between the molten silicon and the wall of silica ampoule, but partly contained amorphous SiO, which resulted in some reduction of oxygen solubility in the silicon melt.[2,10] Although there were slight discrepancies in results of different studies on oxygen solubility for undoped silicon, the conclusions based on the results of Sb-doped Si were consistent, since the difference in oxygen concentration between doped and undoped silicon was beyond the experimental error.

The enhancement of oxygen solubility by antimony addition in Si melt was beyond our prediction and is not easy to convincingly explain. It may, however, be explained by assuming a complex of Sb-O-Sb in the Si melt. Excessive oxygen dispersed in Si melt usually induces formation of SiO or SiO_2. However, if there is a tendency for Sb-O-Sb complex to form in Sb-doped Si melt, the excess oxygen may be consumed to form such complexes. In order for such a complex to form, Sb must be reasonably abundant. In addition, it is also suggested that the solubility enhancement is proportional to the square of Sb concentration. The experimental results indicate that the solubility does not appreciably increase when Sb concentration is below 1 at.%, and it is roughly proportional to the square of the Sb concentration above this value. However, whether or not such a complex exists in the Si melt remains to be verified.

We have discussed the reduction of oxygen concentration in heavily Sb-doped Si crystals grown by the Czochralski method. Three possible reasons have been given.[6,11] The first is the reduction of oxygen solubility in Si melt as the result of Sb introduction. The second is that Sb enhances the evaporation of oxygen (or oxygen-bearing species). The third is the decrease of the segregation coefficient of oxygen. Our experiment showed that Sb, when added at a concentration more than 1.3 at.%, does not decrease but increases the oxygen solubility in Si melt. Therefore the first possibility is now excluded.

4. CONCLUSIONS

Both undoped and Sb-doped silicon were melted in equilibrium with SiO_2 and quenched at a cooling rate of about 20°C/s. The oxygen and antimony concentrations were analyzed by the SIMS technique and/or by ICP-ES. It has been shown that oxygen solubility in undoped silicon melt changes from 2.08×10^{18} to 2.29×10^{18} atoms/cm^3 upon temperature increase from 1447 to 1542°C. The addition of less than 1 at.% Sb caused practically no change in oxygen solubility, whereas addition of more than 1.3 at.% Sb appreciably increased both its level and its temperature coefficient. The oxygen concentration can increase up to 19.48×10^{18} atoms/cm^3 when Sb concentration is 2.0 at.% in silicon melt.

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