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Heat and Mass Transfer during Crystal Growth

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Quality of semiconductor and oxide crystals which plays an important role for electronic devices is grown from the melts is significantly affected by the heat and mass transfer in the melts during growth by using Czochralski crystal growth systems. This paper reviews the present understanding of phenomena of the heat and mass transfer, especially melt convection from the results of flow visualization by using X-ray radiography to the details of numerical calculation needed for quantitative modeling of melt convection. Characteristics of flow instabilities of melt convection with a low Prandtl number are also reviewed by focusing on the instabilities of baroclinic, the Rayleigh-Benard and the Marangoni-Benard from points of view of temperature or rotating effects during crystal growth. The origin of the baroclinic instability is reviewed based on geostrophic hydrodynamics, and it is discussed whether silicon flow is completely turbulent or has an ordered structure. Mass transfer in silicon melt is also discussed in the paper from microscopic point of view by molecular dynamics simulation using Stillinger-Weber potential.

KEYWORDS: silicon, continuum mechanics, 3-D time-dependent, flow structure

1. Introduction

The Czochralski (Cz) and/or hiridontaal bridgeman (HB) crystal growth technique are widely used and accepted for fabricating high-quality substrates for silicon (Si) VLSIs, gallium arsenide (GaAs) monolithic and integrated circuit devices, and optical devices. It is well known that the breakdown voltage of oxide layer grown on Si substrates depends on the growth conditions under which the Si crystals were grown, such as the crystal pulling speed or the temperature distribution in the growth furnace. For GaAs case, temperature distribution near solid-liquid interface modifies distribution of dislocation which affects threshold voltage of source-drain current in transistors. Stress field in crystals modified by flow of melt makes inhomogeniety of reflective index in oxide crystals. The melt convection should be controlled from the point of view mentioned above. However, difficulty of the control has been found because actual flow has been hard to monitored for semiconductor or oxide melts on account of opaque melts. So far, the distribution of impurities and point defects in grown crystals, which affects the degradation of the breakdown voltage for silicon devices, is dependent on the amplitude of temperature fluctuation at solid-liquid interface. The fluctuation is mainly caused by the flow instability which contains laminar or turbulent flows. Therefore, the origin of the flow instability should be clearly clarified, so that it can be controlled to obtain high-quality crystals. Several possibilities of the instabilities have been reported in the CZ crucible, for example Rayleigh-Benard and baroclinic instabilities by using model fluids. To confirm the origin of the instabilities, visualization would be essential for correct understanding of the flow of actual molten silicon itself. Numerical simulation using a global heat and mass transfer model has been proposed as a useful way to analyze flow velocity and temperature distribution throughout a furnace.

The purpose of the present paper is to introduce hierarchy of possible flow instabilities in an actual CZ system. The origin of flow instability will also be discussed based on fluid dynamics from the points of view of experiment based on flow visualization and theory by using numerical simulation. Microscopic topics on mass transfer in silicon melt is also understood in the last part of the paper. Viscosity of silicon melt which governs mass transfer has been reported to have anomaly near the melting point. However, molecular dynamics simulation of the melt obtained a conclusion without anomaly even under super-cooled condition. Now, the discrepancy is on the way of discussion because the melt near the melting point plays and important role for solidification.

2. Numerical technique

Numerical simulation was carried out using a control volume method with three-dimensional geometry. Time-dependent calculation was also performed by using ADI or STABCG method as a matrix solver. Governing equations are expressed in eqs. (1-3). When effect of axial or cusp shaped magnetic fields was taken into account, Lorentz force was included in eq. (3).

\[
\frac{\partial \rho}{\partial t} = \nabla (\rho u) = 0, \quad (1)
\]

\[
\rho \frac{\partial \Phi}{\partial t} + u (\rho \nabla \Phi) = \nabla (\Gamma \nabla \Phi) + S, \quad (\Phi = u, T, c), \quad (2)
\]

\[
S = - \nabla P + F (= \rho g) + f, \quad (3)
\]

where, \(\rho\), \(t\), \(\Gamma\) are density, time and diffusivity for the valuables such as velocity, temperature and impurity concentration. When oxygen transfer in the silicon melt was taken into account in the calculation, the following assumption of equilibrium concentration and flux was adopted at the boundaries such as melt-crucible and melt-gas.
\[ o = 3.99 \times 10^{23} \exp(-2.0 \times 104/T) \text{atoms/cm}^3 \]  
(4)

\[ q = h(O(\text{melt}) - O(\text{gas})) \]  
(5)

3. Temperature and rotation effects to convection modes

Three-dimensional numerical simulation is going to become a potential tool to investigate origin of flow instabilities. From the above point of view, several innovative research on fluid flow of semiconductors have been reported to clarify three-dimensional structure of convection of molten semiconductors\(^1,2\). This session introduce the result on confirmation of spoke pattern formation in silicon melt from numerical simulation. Figures 1 (a) and (b) show birds eye views of temperature contours and velocity vectors on the plane of 5 mm below the surface.

![Figure 1. Birds eye views of temperature contours (a) and velocity vectors (b).](image)

If the flow mode is exactly axisymmetric azimuthal velocity component should not be observed. However, alternative modulation of azimuthal velocity component which is almost one order magnitude smaller than radial velocity can be observed. The lines indicated by A and B are corresponding place in Figs. 1 (a) and (b). It can be easily recognized that fluid is ascending from inside of the melt and spreading out in the azimuthal direction along line A, although it descending into inside of the melt. Additionally, temperature in the ascending part is higher than that in the descending part. These result leads us to understand that cell structure is confirmed which is originated by the Rayleigh and/or thermocapillary Benard instabilities.

From the above results, we are able to conclude that the spoke pattern is formed in silicon melt in a CZ crucible. Additionally, we can conclude that the pattern is penetrated in the bottom of the silicon melt although it has been thought to be terminated just beneath the surface for the case of oxide melts. The reason of the increase of penetration depth may be attributed to the large flow velocity. Since silicon melt has small viscosity, the Grashof number which contains viscosity becomes large. Consequently, the flow becomes inertial flow dominant. This means that the large momentum of fluid transfers from surface to the bottom readily. Therefore, the pattern reaches from the surface to the bottom. The origin of the pattern is thought to be both the Benard\(^3\) and/or thermo-capillary\(^4\) instabilities, although it is difficult to identify which instability is dominant because reported values of temperature gradient of surface-tension which originates surface-tension-driven flow have some sort of ambiguity. Therefore, it is important to obtain reliable value of the temperature gradient of surface tension which produces thermocapillary flow.

Numerical simulation on flow instability was reported to clarify three-dimensional flow structure by assuming as axisymmetric flow is relaxed, i.e., the three-dimensional flow problem was solved using a finite difference method\(^5\). The temperature boundary conditions of the melt, which strongly affect the flow mode\(^6\), were set to be axisymmetric to identify origin of non-axisymmetric profile. The data obtained by the global calculation are semi-quantitatively identical to the data measured by the thermocouples. We previously reported that the flow becomes axisymmetric at a relatively high \(\Delta T = 55 \text{ K} \) for the small crucible case: \( H = 3.8 \text{ cm} \), \( \omega_c = -1 \text{ rpm} \), \( \omega_s = 1 \text{ rpm} \), \( R_c = 3.75\text{m} \), and \( R_s = 1.8 \text{ cm} \). The \( \Delta T \) is measured between crystal and crucible wall. In the present calculation, \( \Delta T \) is reduced to 45 K to change the boundary conditions to those of the non-axisymmetric case. The calculated velocity vector from rotational view point with the same angular velocity as crucible rotation rate and from stationary point of view are shown in Figs. 2 (a) and (b), respectively. Wavy structure with wave number of two in azimuthal direction can be recognized. It is also clarified that the vortices are penetrated into the bottom.

4. Magnetic fields effect

Magnetic fields have been thought to be suppress velocity of fluid flow although direct observation of fluid
flow has not yet been carried out. The author's group succeeded in the direct observation of molten silicon convection by using X-ray radiography method under axial magnetic field\(^7\). Two sets of X-ray sources and cameras are inserted between them to set the sources and cameras closely for clear visualization.

Figure 2. Calculated velocity vector (a) from rotational view point with the same angular velocity as crucible rotation rate and from stationary point of view (b).

Figure 3 shows relationship between flow velocity and strength of magnetic fields. Solid circles and broken lines represent experimental result and numerically calculated by using three-dimensional calculation\(^7\). The calculated result agrees well with experimental except low magnetic fields. Trend of the reduction of flow velocity sometimes has been explained by a concept of "magnetic viscosity", however, the concept does not directly express fluid motion. Fluid motion of molten silicon is able to express by "magnetic number" contrary to the magnetic viscosity. The concept is based on the inertial flow regime, therefore, thickness of velocity boundary layer near crucible wall is almost constant with and without magnetic fields.

Figure 3. Magnetic field dependence of flow velocity of silicon.

5. Impurity concentration

Silicon single crystals with 2-inch diameter were grown in two kinds of crucibles as follows. A crucible without a carbon sheet was used in case I, while a crucible with a carbon sheet attached at the bottom was used in case II to prevent oxygen dissolution to the silicon melt as shown in Fig. 4. All experiments were performed in the same conditions: starting materials (300g) 3.5-inch diameter crucible, crystal rotating rate of 3 rpm, and similar heater power. Crucible-rotation dependence of oxygen concentration at the center of the crystals grown by the two different crucibles is shown in Fig. 5. The experimental results are indicated by broken lines while the numerical results are plotted by solid lines. Open and closed circles represent the results obtained respectively from the crucibles with and without a carbon sheet. The figure indicates an abrupt increase in oxygen concentration between 4 and 6 rpm crucible rotation rates for the normal crucible (case I). Flow visualization using X-ray radiography clarified that the flow mode of the melt was axisymmetric below a 4 rpm crucible rotation rate, while the mode was non-axisymmetric above 6 rpm. Boundary condition at the bottom of the crucible for oxygen concentration was imposed as eq. (6),

\[
\frac{\partial c}{\partial n} = 0,
\]

where \(c\) is oxygen concentration and \(n\) is a normal component perpendicular to the bottom of the crucible.

Figure 5 indicates that the oxygen concentrations in the crystals grown from the crucible with a carbon sheet (case II) are less than those in the crystals grown the crucible without a carbon sheet (case I). Discrepancy in the concentration between cases I and II is dependent on the crucible rotation rates. The discrepancy is about 25% of the total concentration for a low crucible rotation rate, while the value for a high rotation rate is about...
45% of the total concentration. This rotation rate dependence of the discrepancy clarifies that only the ratio of the area between the crucible bottom and the total contact area between the melt and a crucible is not able to simply explain the variation of oxygen concentration in the grown crystals, since the ratio was always constant even when the flow mode changed from axisymmetric to non axisymmetric.

Figure 4. A carbon coated crucible (case II).

The absolute values of the numerical results are slightly larger than those of the experimental results. This discrepancy of the absolute value may come from unknown parameters such as segregation coefficient, evaporation rate at the free surface and dissolution rate at the melt-crucible interface used in the present numerical simulation. However, the ratio of the concentrations of oxygen obtained crystals grown in crucibles with and without a carbon sheet is nearly the same in both the numerical and experimental case. Let us return to the abrupt increase of oxygen concentration between 4 and 6 rpm, as shown in Fig. 5. There are two mechanism to explain this increase. The first is the pumping effect due to crucible rotation. Forced convection from the crucible bottom to the crystal appears when the crucible and crystals rotate. This upward flow just beneath the solid-liquid interface carries melt with high oxygen concentration from the bottom of a crucible to the crystal/melt interface. The second mechanism is the formation of a vortex structure produced by baroclinic instability at high rotation rates.

Contributions of these effects on oxygen transfer in the melt can be estimated from the concentration differences of cases I and II at various crucible rotational rates. Case I contains effects of pumping flow and vortex flow, while case II only contains vortex flow for high crucible-rotation rate since the crucible bottom was coated by a carbon sheet.

Figure 5. Crucible rotation dependence of oxygen concentration.

About 25% of oxygen in the crystals, i.e., the difference between 45 % increase for case I and 20 % increase for case II of the oxygen concentration for the non-axisymmetric case was attributed to the pumping flow, since mass transfer of oxygen by the pumping flow is suppressed in case II by coating the crucible bottom and axisymmetric flow was almost suppressed. It can be also estimated that the 20% of oxygen in the crystals is transferred from side wall by the vortex flow.

The value of 25% for oxygen transfer by pumping flow is less than the ratio of the bottom area to the total contact area between the melt and the crucible, which is about 40%. Therefore, this discrepancy clarifies that only the ratio of the area between the crucible bottom and the total contact area, i.e., the bottom and the wall at which the silicon melt and the crucible are attached to each other, can not simply explain the variation in oxygen concentration in the grown crystals, since the ratio was constant even when the flow mode changed from axisymmetric to non-axisymmetric.

Single silicon crystal with 2-inches diameters were grown under vertical magnetic fields from 0 tesla to 0.3 tesla to observe their oxygen concentrations. Two kinds of heating systems introduced in Figs. 6 (a) and (b) were employed to modify the flow pattern in the melt. The heating system in Fig. 6 (a) makes the temperature distribution at the bottom of the crucible cold, while the system in Fig. 6 (b) makes the temperature at the bottom hot. In this paper, we call the first system type A and the second system type B. All experiments were performed under similar conditions. The experiments were performed with 300g of starting materials within a 4-inch diameter crucible. The crystals were rotated at 3 rpm, and had similar heater power. The rotating rate of the crucible was set at -1 rpm. The pulling rate of the crystals was kept at 1 mm/min. The oxygen concentrations in grown crystals were measured using an infrared
absorption method (FTIR) at room temperature.

Calculated oxygen concentrations from the center of the crystals grown from the melt with a height of 5 cm are indicated in Fig. 6 (a) by a solid line. The experimental results are indicated by a broken line for type B heating system. The absolute values of the numerical results are slightly different from those of the experimental results. This discrepancy may be due to unknown parameters such as the segregation coefficient, evaporation rate at the free surface, and the dissolution rate at melt-crucible interface used in the present numerical simulation. The anomaly of the oxygen concentration for both the experimental and numerical results was observed at 0.1 tesla. The anomaly can not be observed for type A heating system as shown in Fig. 7(b) while the solid line indicates calculated results and the broken line indicates experimental results. The anomaly can be attributed to the formation of the Benard cell, since the strength of the magnetic field in which the anomaly was observed was almost identical to that in the formation of the Benard cell. Oxygen concentration decreased again above the magnetic fields because the oxygen diffuses to the top of the melt and evaporates into the gas phase.

6. Molecular dynamics

A diffusion constant and viscosity in a silicon melt are calculated using molecular dynamics simulation based on the modified Stillinger-Weber interatomic potential in the temperature range from 1550 K to 1900 K. Temperature dependence of the calculated diffusion constant which is expressed in Fig. 8 can be expressed using the following equation,

\[ D = \langle (x - x)^2 \rangle / t \]  

(7)

Viscosity of the silicon melt, which correlates to the diffusion constant, is also estimated using Eyring's relation. The calculated viscosity correlates well with experimental data which were obtained by an oscillating cup method except in the temperature range from 1550 K to 1750 K. The result indicates that no anomaly of diffusivity or viscosity can be found near the melting point.
Figure 8. Calculated self-diffusivity of molten silicon.

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