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Effect of crucible rotation on oxygen concentration during unidirectional solidification process of multicrystalline silicon for solar cells

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ABSTRACT

We studied the effects of crucible rotation on distribution of oxygen concentration in a crystal during the unidirectionally solidification process of multicrystalline silicon for solar cells. Oxygen concentration in the melt increased when crucible rotation rate was increased. Oxygen concentration in the silicon crystal was distributed inhomogeneously in the radial direction when crucible rotation rate was increased. This is due to suppression of oxygen transport. Consequently, less oxygen was transported from the crucible wall to the center of the melt. We found that oxygen concentration is small in the whole ingot and homogenized in the radial direction when crucible rotation rate during the solidification process is set to 1 rpm.

1. Introduction

The photovoltaic market has developed remarkably in recent years [1], and multicrystalline silicon now has a market share of more than 50% in all photovoltaic materials. Multicrystalline silicon is an important material for solar cells with the advantage of low-production cost. There are many impurities in a silicon crystal, such as oxygen, nitrogen, carbon and iron. The presence of oxygen causes SiO_2 precipitation [2], dislocations [3] and stacking faults [4], which decrease the conversion efficiency of solar cells. Boron and oxygen in silicon have also been reported to form boron–oxygen complexes, which cause light-induced degradation in solar cells [5]. These defects reduce the conversion efficiency of solar cells because they act as recombination centers of photocarriers. Therefore, control of oxygen concentration in a silicon ingot is important for improving the conversion efficiency of a solar cell.

In this study, we studied the effects of crucible rotation on distribution of oxygen concentration during the solidification process of multicrystalline silicon for solar cells.

2. Oxygen transfer

It is well known that oxygen is dissolved from a quartz crucible into the silicon melt and that it is transported in silicon melt by convection and evaporates from the melt surface [6]. It has been reported that the concentration of oxygen in the melt can be controlled by modifying melt convection in the case of the Czochralski method [7,8]. Oxygen is mainly transported by both convection and diffusion in the melt. Convection in the melt plays a key role for the distribution of oxygen concentration in the melt and a crystal. It has been reported that convection in the melt can be suppressed by rotation of a crucible [9,10].

The phenomenon of suppression of melt flow was explained by using the momentum equation (the Navier–Stokes equation) [9] as follows:

$$\frac{\partial u}{\partial t} = -u\nabla u - 2(\Omega k) \times u = (\Omega k) \times (\Omega k) \times r - \frac{1}{\rho}\nabla p + \frac{\mu}{\rho}\Delta u + g\beta(T - T_0), \quad (1)$$

where u, Ω, r and k represent vector of flow velocity, crucible rotation rate, position and unit vector along the growth direction,

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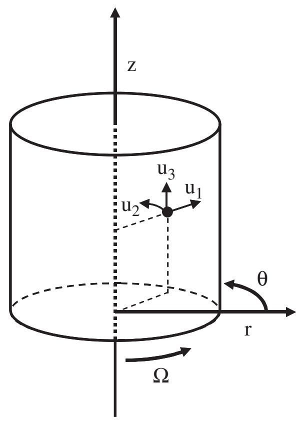

Fig. 1. Cylindrical coordinates in the unidirectional solidification method.

respectively, as shown in Fig. 1. The symbols ρ, β, g, p, μ and T are density, volume expansion coefficient of the silicon melt, vector of gravitational acceleration, pressure, viscosity of the fluid and temperature, respectively. Coriolis force is generated due to coupling of radial velocity and fluid rotation. The term $2(\Omega k)\times u$ in Eq. (1) represents a Coriolis force that is a cross product between vector of flow velocity and rotation. This term, which is called Coriolis acceleration vector, can be transformed:

$$\begin{aligned} a &= -2(\Omega k)\times u \\ &= -2\Omega(u_1 j - u_2 i), \end{aligned} \tag{2}$$

where i and j represent unit vectors of the radial component and azimuthal component, respectively. The symbols u_1, u_2 and u_3 are flow velocities in the radial direction, azimuthal direction and growth direction, respectively, as shown in Fig. 1. As a result, the radial component of the melt flow has a negative value and the azimuthal component has a positive value as in Eq. (2). Consequently, the radial velocity of the melt flow is decreased and azimuthal velocity is increased with increasing crucible rotation rate. Therefore, the radial velocity of the melt flow becomes small when crucible rotation is increased.

The contribution of melt convection to transport of oxygen in the melt is larger than that of diffusion. Hence, the total amount of oxygen transferred by melt convection becomes small when melt velocity decreases. The distribution of oxygen concentration becomes inhomogeneous in the case of small velocity of the melt in the radial direction during solidification.

3. Experimental procedure

Oxygen concentration in multicrystalline silicon grown by the unidirectional solidification method was measured by Fourier transform infrared spectroscopy (FTIR). The multicrystalline silicon used in the present study was grown by the following method [11]. Off-grade silicon feedstock was used in the present experiment. Carrier concentration of a grown crystal with a dopant of gallium was approximately $10^{16}\,cm^{-3}$. The crucible made of SiO_2 had been coated with a liner made of Si_3N_4, which prevents the ingot from sticking to the crucible. The raw materials were heated up to 1550 °C to stabilize the temperature of the melt for 2 h. After melting, the heater power was decreased to keep the temperature at a center of heater at 1450 °C. Then heater power was kept constant for 1 h prior to the start of growth. The heater was pulled up at a rate of 30 mm/h to solidify the silicon melt from the bottom to the top. The crucible rotation rates were set to 1 and 30 rpm during the solidification process. Argon gas was introduced at the top of the melt at a flow rate of 0.8 l/min under 0.5 atm pressure in order to avoid impurity incorporation of SiO and CO into the melt during the solidification process [12]. After the heater had almost reached the top of the furnace, the temperature was lowered at a rate of 300 °C/h to room temperature. The grown ingot had a cylindrical shape with a diameter of 10 cm and height of 10 cm.

The ingot was cut parallel to the growth direction into slices of 0.5 mm in thickness. Each sample was etched and polished before measurement by FTIR to remove the damaged layer formed by the cutting process. Sliced wafers were etched with a solution of hydrofluoric acid and nitric acid at the ratio of 1:13 for 10 min to remove the sawing damage. To obtain a mirror-like surface, the multicrystalline silicon wafers were polished with diamond particles of 0.5 and 0.3 μm in grain size, coordinated with water. Then the wafers were polished with alumina powder particles of 0.1 μm in grain size and deionized water. After polishing, the wafers were etched again using the same etchant as that described above for 3 min in order to remove the polishing damage.

FTIR measurement was carried out using an MFT-2000 (JASCO) at room temperature in air. The length of the infrared beam was set to 50 μm with a square shape. The resolution and number of accumulation of the spectrum were set to $4\,cm^{-1}$ and 182 times, respectively. The absorbance of interstitial oxygen was measured at $1106\,cm^{-1}$ [3]. Oxygen concentration was calculated from the peak height of interstitial oxygen calibrated by pure Czochralski and floating zone silicon wafers with calibration factors of $3.03\times10^{17}\,cm^{-3}$ [13].

4. Experimental results

Figs. 2(a)–(c) show distributions of oxygen concentration in the radial direction at heights 70, 50 and 20 mm from the bottom of the ingot, respectively. The abscissa shows the radius from the center of the ingot, and the ordinate shows the oxygen concentration. The concentrations of crystals with rotation rates 1 and 30 rpm are shown by open and closed circles in the figures. Oxygen concentration in the crystal at the crucible rotation rate 30 rpm showed an inhomogeneous distribution in the radial direction compared with that at the crucible rotation rate 1 rpm at 50 and 70 mm from the bottom of the ingot. At 20 mm from the bottom of the ingot, the concentrations in the two ingots were almost the same as shown in Fig. 2(c). Moreover, oxygen concentration near the top and middle of the ingot at the crucible rotation rate 30 rpm was larger than that at the crucible rotation rate 1 rpm.

5. Numerical calculations

In order to clarify the relationship between flow and oxygen concentration in the melt, we calculated oxygen concentration by using numerical calculations. The distribution of oxygen concentration was calculated using a global model [14]. Figs. 3(a) and (b) show the configuration and computation grid of a unidirectional solidification furnace and a zoomed-up view of the grid in the melt and crucible domains. Conductive heat transfer in all components and radiative heat exchange between all diffusive surfaces in the unidirectional solidification furnace were taken into account. Gas flow in the furnace was neglected. The value of 0.85 was used for the segregation coefficient of oxygen in these numerical calculations [6,15]. It was assumed that oxygen was dissolved from the crucible and evaporated at the melt surface. At the melt–crucible interfaces, the following equation, in which reaction between a liner made of Si_3N_4 and a crucible made of