Ribbon-to-ribbon float zone single crystal growth stabilized by a thin silicon dioxide skin

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We have found that a thin silicon dioxide skin stabilizes the float zone in ribbon-to-ribbon single crystal growth. 40-μm-thick single crystal ribbons, oriented $\langle 100 \rangle$ and scanned in the $\langle 011 \rangle$ direction, were grown completely free of subgrain as well as grain boundaries. This surprising suppression of low angle grain boundaries may be related to a similar effect which has been seen in supported thick silicon on SiO_2 films.

It has been recognized for some time[1] that thin single crystal silicon ribbons are an ideal starting point for fabricating solar cells. Polycrystalline silicon ribbons[2] can be produced at high speed by melt spinning and rapid quenching. Conversion of these low-cost polyribbons to single crystal has been an important goal. This letter describes a method of remelting a polycrystalline ribbon and growing it into single crystal material in a ribbon-to-ribbon process. This aim is encouraged by the recent successes[3] which have been achieved in lateral zone melting recrystallization[4] of thick silicon on insulator films.

Recently it has been shown[3] that the low angle subgrain boundaries, which had plagued thin silicon on SiO_2 recrystallization, can be eliminated for the case of thick ($> 27\ \mu$m) polysilicon films. This suggests that unsupported but oxide encapsulated, grain boundary-free ribbons in the same thickness range might also be grown successfully, i.e., that thick *unsupported* ribbons might also be free of subgrain boundaries.

Previous efforts[5] in ribbon-to-ribbon recrystallization have concentrated on converting fine grain polysilicon into large grain silicon suitable for solar cells. A number of instabilities tend to frustrate the growth of single crystal ribbons by a float zone process. Prime among these is the hydrostatic instability of the rectangular liquid float zone. Inherently, surface tension forces tend to favor a spherical or cylindrical shape over the rectangular shape which is reqired for ribbon-to-ribbon growth, i.e., the liquid zone tends to ball up. In this letter we will show that the thin silicon dioxide skin, which forms naturally in an oxidizing environment such as air, stabilizes the float zone and permits subgrain boundary-free single crystal growth.

The geometry of our experiments is shown in Fig. 1(a). The instability is most severe at the edge of the float zone as illustrated in Fig. 1(b). According to the Young–Laplace equation,[6] the hydrostatic pressure induced by the curvature at the edge of the float zone is

$$P = \gamma(2/t - 1/R), \tag{1}$$

where γ is the surface tension of the liquid, t is the thickness of the ribbon, and $t/2$ is the radius of curvature imposed by the edge of the ribbon. A similar equation applies to the curvature on the surface of the float zone but the pressure must be the same in both cases by Pascal's principle. Since the face of the ribbon has very little curvature compared to the sharp curvature $2/t$ imposed by the edge, there must be significant cancellation between the two parts of Eq. (1). But $1/R$ can never be greater than $2/w$ where w is the width of the float zone. Therefore, significant cancellation in Eq. (1) requires that the width of the float zone w be narrower than the thickness t of the ribbon,i.e., stability requires

$$w \lesssim t, \tag{2}$$

a result which is perhaps intuitively obvious.

For thin ribbons, such a narrow float zone is difficult to achieve since it implies extremely steep temperature gradi-

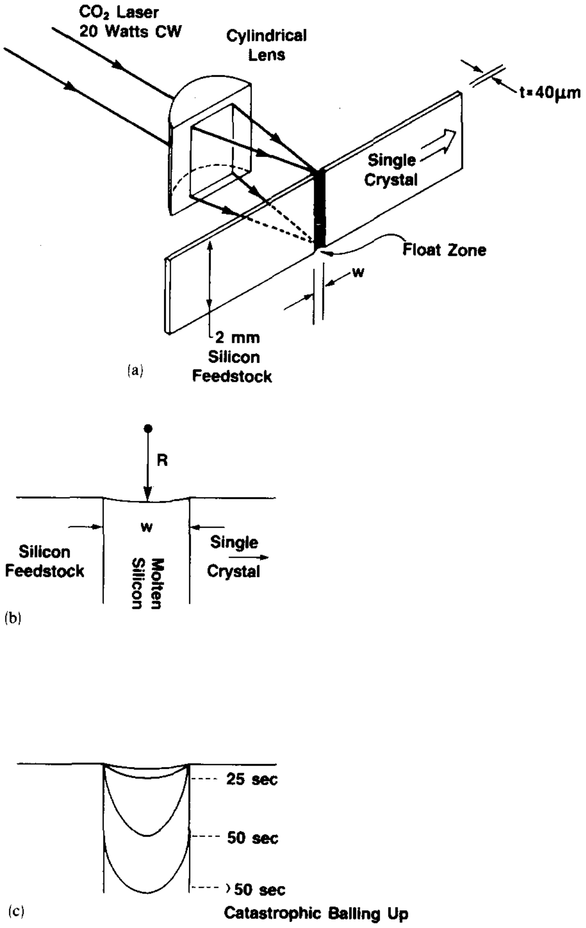

FIG. 1. (a) CO_2 laser beam is focused onto a silicon ribbon melting it completely edge to edge. The arrow shows the direction in which the ribbon is moved. (b) Close-up of the edge of the ribbon showing the curvature R which is caused by surface tension forces. (c) Development of the hydrostatic instability with time if the float zone remains stationary with respect to the ribbon.

FIG. 2. Photograph of self-emisison from the heated ribbon. The float zone spans the entire width (2 mm) of the ribbon. Liquid silicon is the dark central region.

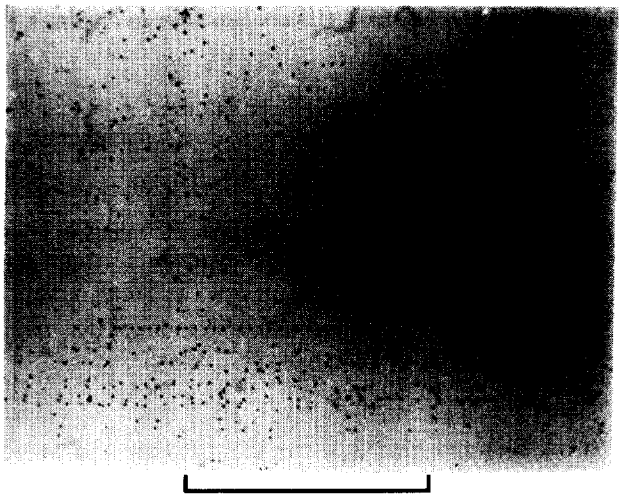

FIG. 3. Typical dislocation etch pattern of the recrystallized ribbon. There is no evidence of subgrain boundaries.

ents. It is perphaps for this reason that some of the more recent efforts[7] in ribbon-to-ribbon crystal growth now employ a geometry in which the edges of the polycrystalline feed ribbon remain frozen in order to provide stability to the molten region. Unfortunately that procedure is suitable only for growing coarse grain silicon rather than single crystal. This letter presents a different method for float zone stabilization which involves a thin silicon dioxide skin.

In our experiments, a 20-W continuous wave CO_2 laser is focused by a 10-cm focal length cylindrical lens to a line focus which was 120 μm wide as shown in Fig. 1(a). The feedstock silicon ribbon was cleaved from a commercially available $\langle 100\rangle$ wafer which was only 40 μm thick. The resulting ribbon was 2 mm wide, 40 μm thick, several centimeters long, and had a $\langle 100\rangle$ orientation on the face and a $\langle 011\rangle$ orientation along the long axis. A molten float zone was produced as illustrated in Fig. 2, which is a photograph of the rear face of the ribbon opposite the laser irradiated face. We found it necessary to raise the laser power significantly above the melting threshold in order to make the molten zone wider than the line focus beam width. This ensured that the melt front had spread away from the line focus into a region of weak laser intensity, thus preventing the lamellar radiative melt front instability[8] on the side of the ribbon facing the laser beam. Typically w equaled 200 μm.

The float zone was scanned by moving the ribbon under the fixed line focus of the laser beam at a speed of 0.2 mm/s. The recrystallized regions were 1 cm long, as limited by the scanning range of the ribbon which was mechanically supported at both ends. Since the feedstock was single crystal, the recrystallization might be regarded as a lateral *seeded* epitaxy.

The crystallographic defect structure was analyzed by Secco[9] etching. A series of dislocations was observed as shown in Fig. 3. These dislocations are the result of the severe thermal stress due to the change from melting temperature down to about 600 °C over a distance of only $\sim 150\,\mu$m. The same thermal stress induced dislocation pattern was formed in the single crystal feed ribbon even if it was heated to a temperature below the melting threshold. These dislocations could probably be eliminated by supplying bias heating to reduce the severity of the temperature gradient. In these experiments the line focus of the laser beam was the only source of heat.

No grain boundaries or subgrain boundaries could be observed over the 2-mm width and 1-cm length of the recrystallized regions. The sensitivity of the etch procedure in detecting grain boundaries was checked by monitoring the boundaries which were intentionally induced by thermal shock during growth. In addition, the observation of isolated dislocations in Fig. 3 assures that subgrain boundaries would have been seen if they were present.

A few experiments were repeated with ribbons oriented $\langle 111\rangle$ on the face and $\langle \bar{1}10\rangle$ along the length. The melt front became extremely faceted during growth and polycrystalline material resulted in contrast to the previous results. Doubtless some of the problems were due to the fact that $\langle 100\rangle$ and not $\langle 111\rangle$ is the minimum energy face[4] for an oxide covered surface.

The hydrostatic instability of the rectangular float zone was investigated by holding the float zone stationary with respect to the ribbon over an extended period of time. The result is illustrated in Fig. 1(c). The hydrostatic stability against balling up is only temporary. If the melt is held statinary at one spot the "balling up" instability will develop over a period of less than a minute. We interpret this as due to the viscous flow of the silicon dioxide skin in response to the tensile stress S which was necessary for hydrostatic stabilization.

In our geometry, inequality (2) is not obeyed since the ribbon is thinner than the width of the molten region. Therefore, the tensile stress in the silicon dioxide skin must be included in Eq. (1) in order to help cancel the sharp curvature $2/t$ imposed by the edge.

$$P = 2\gamma'/t - (\gamma' + Sd)/R\,, \tag{3}$$

where all the symbols have the same meaning as in Eq. (1)

except γ' is now the surface tension of the oxide covered liquid rather than the bare liquid, d is the thickness of the oxide skin (~ 200 Å), and S is the longitudinal tensile stress in the oxide skin in units of dyne/cm^2. Based on the 86° wetting angle[10] of the liquid silicon on SiO_2 and the known[11] surface tension of SiO_2 $\gamma' = 550$ erg/cm^2 in comparison to $\gamma = 719$ erg/cm^2, the bare liquid[12] surface tension.

Equation (3) may be solved for S under the assumption of significant cancellation between the two terms on the right-hand side. Assuming that $R = w$, a condition which occurs after the float zone is held stationary for several second, then

$$Sd \approx \gamma'(2w/t - 1). \tag{4}$$

Substituing the known values for γ', w, t, and d into Eq. (4), $S \approx 2\times 10^9$ dyn/cm^2.

The time scale for significant viscous flow is given by $\tau \sim \eta/S$, where η is the viscosity of the silicon dioxide and S is the stress it is experiencing. Reference 11 gives the viscosity of SiO_2 as $\sim 5\times 10^9$ poise at 1412 °C, the melting temperature of silicon. Therefore the time scale for significant deformation $\tau \approx 2.5$ s which is in reasonable agreement with the time scale given in Fig. 1(c) for the collapse of the stationary float zone. Therefore, the model of a float zone stabilized by the mechanical tension of a thin silicon dioxide skin is consistent with known values of surface tension and viscosity.

Under dynamic conditions of crystal growth with a moving float zone no tendency toward "catastrophic balling up" was observed. Single crystal silicon ribbons encapsulated in a thin silicon dioxide skin were produced. There was no evidence of subgrain boundaries for $\langle 100\rangle$ ribbons scanned in the $\langle 011\rangle$ direction. This is in distinction to $\langle 111\rangle$ ribbons scanned in the $\langle \bar{1}10\rangle$ direction which resulted in low quality polycrystalline material.

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