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Problems in Growth of 4-Inch Wide Silicon Ribbon Crystals

Masatoshi MATSUDA and Ekyo KURODA

Central Research Laboratory, Hitachi Ltd.,
Kokubunji, Tokyo 185

Ribbon crystals with 4-inch width are grown using a specially designed rectangular heater. Wide ribbons crack spontaneously during crystal growth or handling. Thermal stress in crystals is calculated using the observed temperature distribution in crystals. It is clarified that larger maximum shear stress is concentrated around the center of the crystal in wider ribbons. Local thermal stress leads to residual stress, which is the main reason for spontaneous cracks in these ribbons.

§1. Introduction

A practical way to achieve low-cost silicon solar cells is to produce ribbon crystals directly from a melt. This eliminates cutting and polishing losses. A detailed discussion of crystal growth techniques and of the crystalline, electrical and mechanical characteristics of silicon ribbon crystals has been presented elsewhere.[1–4] In a previous paper,[5] 3-inch wide ribbon crystals were grown by controlling temperature distribution at the die top strictly. These 3-inch wide ribbons cracked very little, however almost all 4-inch wide ribbons cracked during crystal growth or handling.

Crystals deform elastically up to yield stress (σ_m) and then deform plastically with dislocation formation. When an applied stress exceeds fracture stress (σ_f), crystals crack. Temperature dependence of σ_f is very small compared to that of σ_m. σ_m decreases with temperature rise, so that thermal stress results in cracking rather than dislocation formation under about 700°C.[6]

In this paper, the reasons for large residual stress in wide ribbons are discussed by measuring the temperature distribution and calculating the maximum shear stress in crystals during growth. The thermal stress varies greatly in the width direction and leads to local plastic deformation. This deformation then causes residual stress in the crystal. As crystals grow and their temperature becomes lower, they fracture.

§2. Experimental

Ribbon crystals were grown using graphite die by the edge-defined film-fed growth technique.[7] The apparatus was designed to produce wide ribbons as shown in Fig. 1. Growth was performed by resistance heating in an Ar ambient. A rectangular heater, which contained two carbon plates 60 cm long and 6.5 cm wide, was used to realize better thermal uniformity. The temperature of the melt in the die was controlled using a thermocouple placed under the graphite crucible holder. Temperature balance at the die top was achieved using a flow of Ar gas which flowed through quartz tubes located at the die edges.

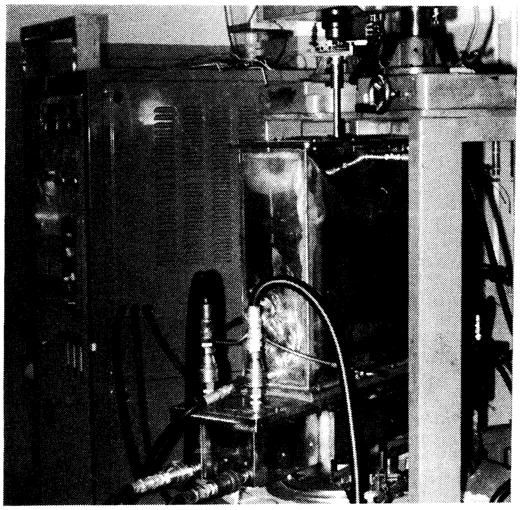

Fig. 1. Rectangular furnace with water cooled chamber and view-port.

Temperatures in the melt and in the crystal were measured by a Pt–PtRh thermocouple inserted in a quartz capillary during crystal growth.

§3. Results

A 4-inch wide ribbon crystal is shown in

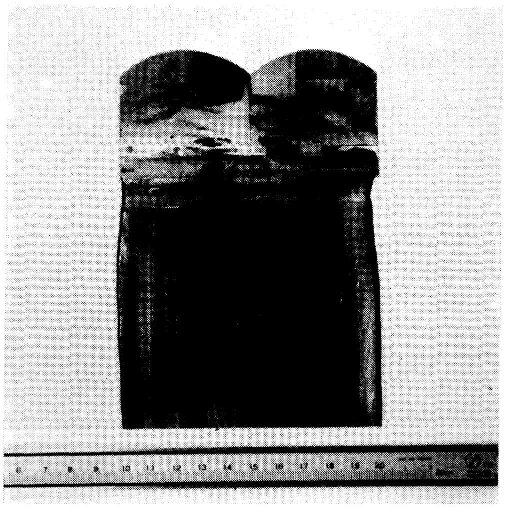

Fig. 2. 4-inch wide silicon ribbon crystal. A spontaneous crack is shown in the open circle.

Fig. 2. The seed was composed of two silicon wafers and the grown ribbon crystal was cracked in the space between the two seed wafers as shown by the open circle. This cracking is considered to be due to a strong stress concentrated at the point where this space and the grown crystal meet. Residual stress in the crystal was calculated from the split width and split length and crystal width.[8] It was 10–50 kg/mm^2 in the five specimens.

There are two causes for this ribbon crystal cracking. One is spontaneous splitting into a few pieces during crystal growth. This occurs when crystals have non-uniform shapes such as locally thin parts and small spaces as mentioned above. Here, the residual stress is concentrated in the non-uniform area. The other case is spontaneous shattering into small pieces during handling after crystal growth. Shattering occurs with uniformly shaped crystals grown from one wafer seed. The fine cracking indicates that the crystals had great amounts of residual stress.

The temperatures in the melt and in the ribbon crystal were measured continuously during crystal growth. A thermocouple with 50 μm diameter, which was covered with a quartz capillary having a 0.6 mm outer-diameter, was used in order to measure the crystal temperature exactly. This eliminated the heat conducted by the thermocouple. The thermocouple junction was mounted under the seed. The die top space was 1.0 mm and growth rate was 2.5 mm/min. A crystal grown for measuring the temperature is shown in Fig. 3. Figure 4 shows observed temperature distribution during crystal growth. Temperature gradients in the melt and in the ribbon crystal near the growth interface were 31°C/cm and 150°C/cm, respectively.

When the temperature gradients in solid and liquid at the growth interface are dT_s/dy and dT_l/dy, respectively, then the continuity of the

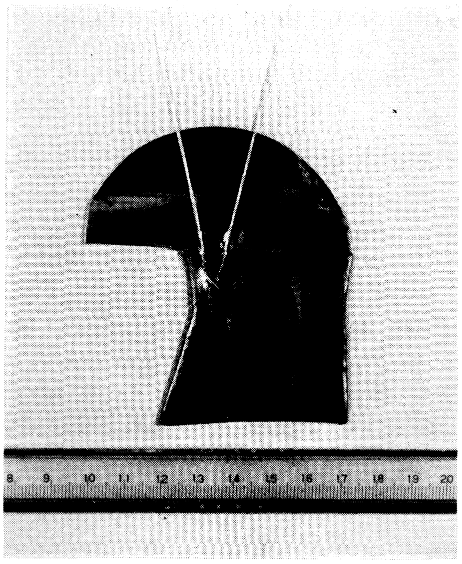

Fig. 3. Crystal grown to measure temperature distribution.

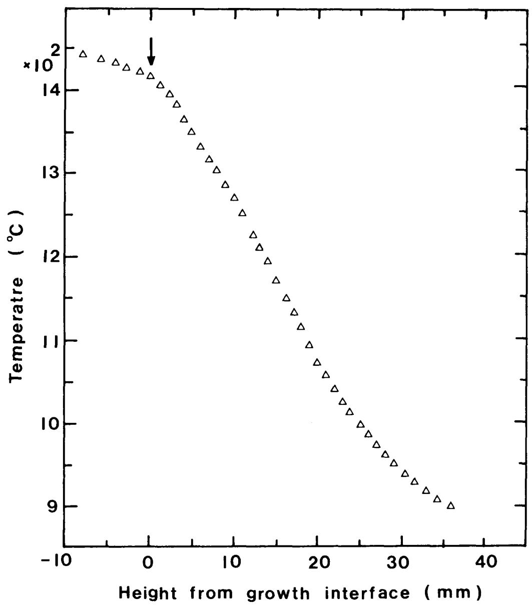

Fig. 4. Temperature distribution in the melt and on the ribbon surface.

heat flux requires:

$$K_s\frac{dT_s}{dy}=K_l\frac{dT_l}{dy}+Lv. \quad (1)$$

Here, K_s and K_l are the thermal conductivities of solid and liquid, respectively. L is the latent heat of solidification and v is the growth rate.

Next, the following values were substituted in this expression: $K_s=0.22$ J/s cm deg;[9] $K_l=0.6$ J/s cm deg;[10] $L=4.1\times10^3$ J/cm^3;[11] and the observed thermal gradients mentioned above. Then, $K_s(dT_s/dy)$ becomes 33 J/s cm^2 and $K_1(dT_1/dy)+Lv$ is 36 J/s cm^2. This good coincidence means the temperature distributions in liquid and solid can be accurately measured.

§4. Discussion

Thermal stresses in the growing ribbon are calculated using the observed temperature distribution. Crystal temperature can be regarded as uniform in the horizontal direction but varies greatly in the vertical direction.

The coordinate system used in this study is shown in Fig. 5. Ribbon thickness is very small with respect to length and width. Therefore, thickness can be neglected and a two dimensional equation can be used to calculate thermal stresses. The other basic assumptions in the theoretical formulation are that the material behaves elastically at all times, that the material is isotropic, and that Young's modulus (E) and the thermal expansion coefficient (α) are independent of temperature. Then the stress components σ_{ij} are obtained from the stress function $\phi(x, y)$ which is a solution to the following differential equation:[12]

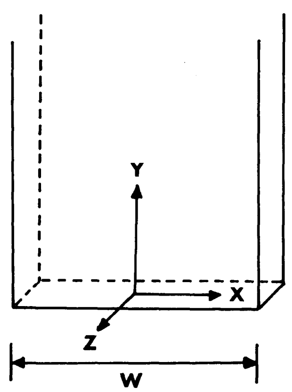

Fig. 5. Coordinate system.

$$\frac{\partial^4\phi}{\partial x^4}+2\frac{\partial^4\phi}{\partial x^2\partial y^2}+\frac{\partial^4\phi}{\partial y^4}=-E\alpha\frac{d^2T}{dy^2},$$

$$\sigma_{xx}=\frac{\partial^2\phi}{\partial y^2},\quad \partial_{yy}=\frac{\partial^2\phi}{\partial x^2},\quad \sigma_{xy}=-\frac{\partial^2\phi}{\partial x\partial y}. \quad (2)$$

The boundary conditions of the stress components are that

$$\sigma_{yy}=\sigma_{xy}=0;\quad y=0,$$

$$\sigma_{xx}=\sigma_{xy}=0;\quad x=\pm\frac{w}{2}, \quad (3)$$

where w is the ribbon width. Analytic solutions of eqs. (2) and (3) are approximately expressed as[4]

$$\sigma_{ij}=\alpha E\frac{d^nT}{dy^n}f_{ij}(w);\quad n\geqq 2. \quad (4)$$

In the present analysis, maximum shear stress is used to evaluate the stress acting on the crystal:

$$\tau_{max}=\sqrt{\left(\frac{\sigma_{xx}-\sigma_{yy}}{2}\right)^2+\sigma_{xy}^2}. \quad (5)$$

τ_{max} along the ribbon width in 4-inch wide crystals is shown in Fig. 6. It is found that the distribution of τ_{max} is small in the width direction at heights of 1.6 and 3.2 cm from the growth interface. However, a large stress concentrates around the center of crystal at the growth interface. This stress results in local plastic deformation.

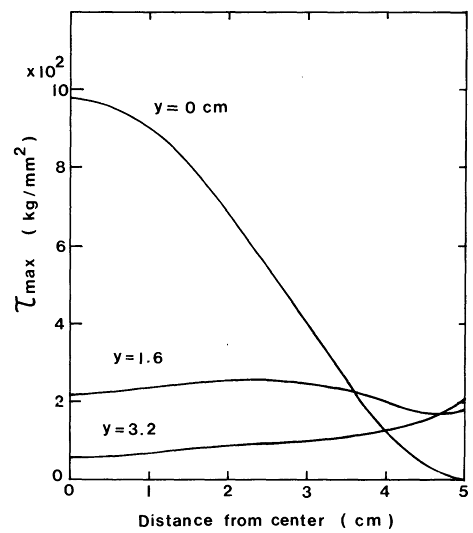

Fig. 6. Distribution of maximum shear stress along the ribbon length and width in a 4-inch wide ribbon crystal.

Next, τ_{max} along the width at the growth interface was calculated for crystal widths from 1 to 5 inches and results are shown in Fig. 7. It should be noted that the τ_{max} of 4-inch wide ribbons is 40 times larger than that of 2-inch wide ones. Non-uniform stress greatly increases with crystal width and leads to local plastic deformation.

On the other hand, crystals are always annealed during crystal growth. However, all of this local deformation can not be annealed out because of the fast growth rate and the large non-uniform thermal stress. As a result, wide crystals easily crack due to residual stress remaining in grown crystals.

Finally, it is described three methods to prevent spontaneous cracking in ribbon crystals. The first method is to grow uniformly shaped crystals. The stress concentrates on the place where thickness and width are non-uniform, and crystals are easily cracked. Grown crystals should be uniform in shape.

The second is to anneal out the residual stress. An after-heater is placed above the die top to remove the residual stress in the grown crystal.

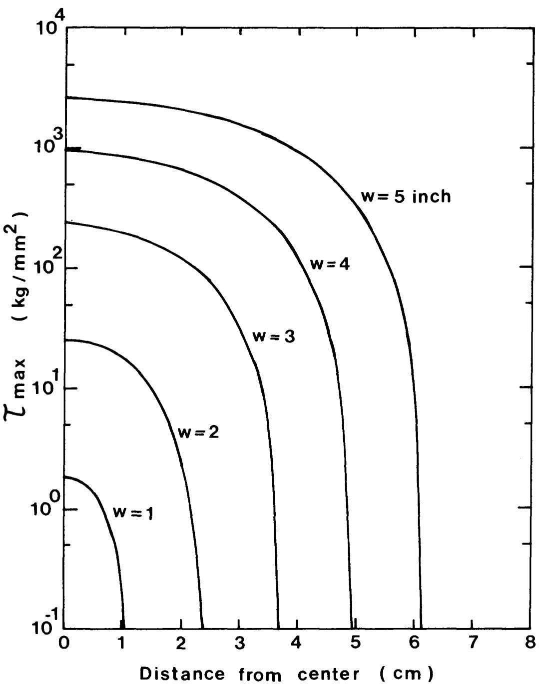

Fig. 7. Distribution of maximum shear stress along the width for various ribbon widths.

The third is to produce thermal stress free crystals. The main contribution to the thermal stress is the vertical temperature profile. According to eq. (4), if the vertical temperature profile is linear, stress free crystals are grown.

§5. Conclusion

Ribbon crystals with 4-inch width are grown by controlling the temperature distribution at the die top. Crystals less than 3-inch wide hardly crack but most crystals with 4-inch width crack spontaneously. The calculated thermal stress results indicate that maximum shear stress acting on the central part of the crystal increases with crystal width. Furthermore, residual stress is caused by this large thermal stress, which is the reason for easy cracking of wide ribbons.

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