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ANOMALOUS RESISTIVITY PROFILES IN LONG SILICON CRYSTALS GROWN BY THE CZOCHRALSKI METHOD

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Anomalous resistivities have been observed in the upper portions of Czochralski-grown silicon crystals 15–25 inches long. Several experiments have shown that the anomalies are due to the presence of thermal donors. These donors are formed in regions that are far enough from the growth interface in each crystal to spend appreciable periods at temperatures in the 300–500 °C range before crystal growth is completed and the system cooled to room temperature.

Dislocation-free silicon crystals up to 3 in. in diameter and 30 in. long are being grown by the Czochralski method in our production facility as a source of wafers for device processing. The crystal boules are pulled from a silicon melt that is contained by a fused silica liner.

These crystals often exhibit anomalous resistivity profiles. Typical examples of these profiles for both p-type, boron-doped crystals and n-type, phosphorus-doped crystals are illustrated in figs. 1 and 2, respectively. The resistivity measurements were made along the outside of the crystal boule with a two-point probe. Since the current flow is distorted near the ends of the boule, valid measurements cannot be made within 2 in. of each end. (Some crystals were cut into two sections before the resistivity was measured, so that the end effects lead to a gap in the data at the break between the sections.) The resistivity at the lower end of each crystal varies in the manner expected from the distribution coefficients measured for shorter crystals, but at about 10 in. from the bottom there is an abrupt increase in resistivity for the p-type crystal and a smaller but also abrupt decrease in resistivity for the n-type crystal.

In annealing experiments on silicon containing high concentrations of oxygen, Fuller and Logan[1]) and Kaiser, Frisch, and Reiss[2]) found that thermal donors involving oxygen were formed by annealing at 300–500 °C and removed by annealing at temperatures above 500 °C. On the basis of these results, the resistivity anomalies in the long crystals are proposed to be due

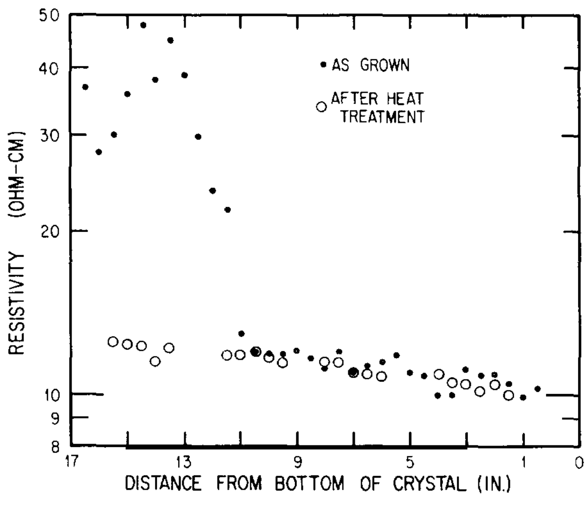

Fig. 1. Variation of resistivity with distance for typical boron-doped silicon single crystal 2 inches in diameter.

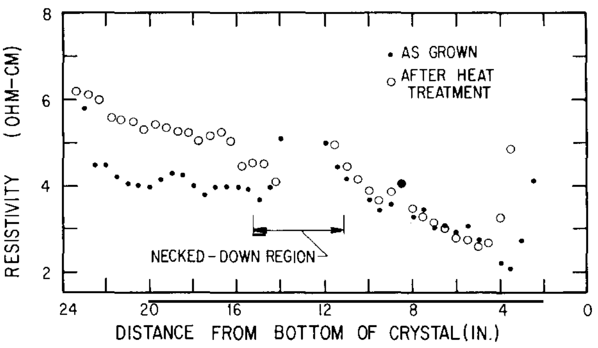

Fig. 2. Variation of resistivity with distance for phosphorus-doped silicon single crystal. The crystal diameter was initially 2 in. After 11 in. of growth the diameter was decreased to 1/16 in. and then increased to 2 in. for the final 9 in. of growth.

to formation of oxygen donors; oxygen is incorporated in the crystals during growth as a result of the reaction between the silicon melt and the fused silica liner. These donors are formed in portions of the crystals that are far enough from the growth interface (in this particular case, more than about 10 in.) to spend appreciable periods at temperatures in the 300–500 °C range before crystal growth is completed and the system cooled to room temperature. In p-type samples, the thermal donors compensate the boron acceptors, thereby reducing the carrier concentration and increasing the resistivity; in n-type samples, these donors are added to the phosphorus donors, increasing the carrier concentration and decreasing the resistivity. The increase in donor concentration inferred from the resistivity change was 7×10^{14} cm^{-3} for the p-type crystals and 8×10^{14} cm^{-3} for the n-type crystals, well below the maximum change of 2×10^{16} cm^{-3} reported by refs. 1 and 2.

Three types of experiments were performed to confirm the hypothesis of thermal donors: first, post-growth annealing experiments in which the resistivity anomalies are eliminated; second, temperature measurements as a function of distance from the growth interface; and third, experiments in which the temperature profile of the crystal puller is altered to keep the temperature of any part of the crystal from falling below 600 °C before the system is cooled to room temperature.

The data for resistivity versus crystal length after heat treating the boules for 4 hr at 650 °C are also given in figs. 1 and 2. The after-heat-treat resistivity varies in a manner expected from the distribution coefficients for boron and phosphorus measured for shorter crystals. The disappearance of the resistivity anomalies can be attributed to the removal of the thermal donors, which according to the data of Fuller and Logan[1]) would require much less than 4 hr at 650 °C.

During the growth of several crystals, the experimental procedure described by Brice and Whiffin[3]) was used to measure the temperature at the seed end of each crystal as a function of length of material grown. This technique does not directly yield a temperature profile, which is a plot of the temperature as a function of position along the crystal at a fixed time. However, the method does yield a profile if it is assumed that the temperature of a particular point at any time depends only on its distance from the solid–liquid interface, and not on its distance from the top of the crystal*. A 2 in. diameter cylinder of single crystal silicon 2 in. long, with a 3/16 in. diameter hole drilled through the center, was used as a seed. A quartz sheath containing a platinum/platinum–13% rhodium thermocouple was placed in the center hole. The output from the thermocouple was recorded with a stripchart recorder during growth. The large seed was dipped into a 4 kg melt and single crystal growth was continued for about 3 in. After 3 in. of growth each crystal examined became twinned and then polycrystalline. The change from single crystal to twinned crystal to polycrystalline material should not affect the temperature profiles and macroscopic heat flow conditions. Crystal diameter was maintained by varying the pull rate. Temperature profiles were measured for boron- and phosphorus-doped crystals grown at various seed and crucible rotation rates.

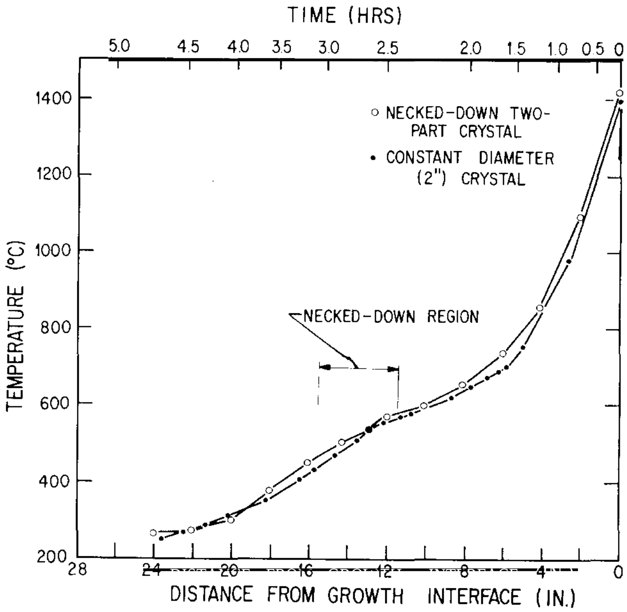

Fig. 3. Temperature at the seed end versus distance from the solid–liquid interface for a constant diameter crystal and a necked-down two-part crystal.

The longitudinal temperature profile for a 26 in. long, 2 in. diameter boron-doped crystal is shown in

* This assumption was verified by comparing the temperature data measured at 2 in. and 4 in. along a 4 in. long seed. For both thermocouples the temperature plotted as function of distance from the interface was the same.

fig. 3. It can be inferred from the data that approximately the top 12 in. of crystal dropped below 500 °C before crystal growth was completed, and that portions of the crystal remained below 500 °C for as long as 2 hr. According to the results of Fuller and Logan[1]), a substantial concentration of added donors could be generated in the top portion of the crystal during this time. The results depicted in fig. 1 can be explained on the basis of this model.

The temperature data for a necked-down two-part crystal are also given in fig. 3. The diameter of this crystal was initially 2 in. After 11 in. of growth, the diameter was reduced to $\frac{1}{2}$ in. and then increased to 2 in. for the final 8 in. of growth. The profile in this instance is almost the same as that of the constant diameter crystal. It is apparent that the temperature profile is dependent on the thermal environment dictated by the puller rather than on the crystal diameter. The resistivity profile plotted in fig. 2 is that of a crystal grown under "neck down" conditions. The upper portion shows a change in resistivity indicative that the temperature dropped below 500 °C, yet the overall profile is quite similar to that of a constant diameter crystal.

In order to verify that donor formation occurs in portions of a crystal that are in the 300–500 °C range, several crystals were grown in a puller which had been modified to maintain the entire length of the crystal above 600 °C until cooling to room temperature. The resistivity profiles obtained in this case indicate that no thermal donors were formed, since the as-grown profiles are not anomalous and do not differ significantly from profiles measured after post-growth annealing at 650 °C.

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