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SUPERCOOLING OF A MELT AND CRYSTAL GROWTH BY THE CZOCHRALSKI METHOD

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In the present work, in studying the growth of crystals by the Czochralski method, it was established for the first time that, under the growth conditions considered, supercooling of the melt plays the determining role in the formation of the structure and in the distribution of impurities in crystals. This is established both for germanium and silicon crystals, which were the initial objects of investigation, and for crystals of aluminum, copper, iron and, apparently, all other comparatively pure substances capable of crystallizing. All subsequent work was carried out mainly on aluminum. The principal results of the work are set forth below.

1. In an asymmetric thermal field, a crystal, in the absence of rotation, inclines toward the cold side of the field. On a longitudinal section of such an aluminum crystal, doped with Cu^{64} in an amount of 10^{-4}%, grown without rotation at a pulling rate of 2 mm/min, etching in an aqueous NaOH solution reveals two adjacent regions, etched differently, extending in the direction of crystal growth (Fig. 1a). The region facing the "cold" side of the field, dark in the photograph, is etched deeply, while that facing the "hot" side is etched weakly. On the cold side of the field the crystal captures more impurity than on the hot side. This phenomenon is explained by the unequal supercooling of the melt on different sides of the field—stronger on the cold side than on the hot side. This can be seen in the photograph in Fig. 1b of a longitudinal section of an aluminum crystal doped with Cu^{64}, 10^{-4}%, grown without rotation with a 7-minute stop at point 1′. In Fig. 1c an autoradiogram of the same crystal is presented. The inclination, indicated by the dotted line, is relatively small for the stopped crystal.

When a crystal is pulled, the interface rises above the initial level, and the higher it rises, the greater the pulling rate of the crystal. Its edge facing the hot side of the field is drawn up higher than the cold edge. The inclination of the interface, determined by this greater drawing-up of the hot edge, increases with increasing pulling rate. The higher the interface rises, the more strongly the melt is supercooled, and the crystallization proceeds at a relatively lower temperature and at a higher rate. Owing to the greater drawing-up of the interface at the hot

Fig. 2. Change in the state of the melt upon rotation. $CDBA$ and CDB_1A_1 are the positions of the crystal before and after rotation; BA and B_1A_1 are the positions of the interface before and after rotation

Figure 1: Fig. 2. Change in the state of the melt upon rotation. $CDBA$ and CDB_1A_1 are the positions of the crystal before and after rotation; BA and B_1A_1 are the positions of the interface before and after rotation

edge, the supercooling gradient at the hot edge of the interface is smaller than at the cold edge. Therefore crystal growth proceeds unequally on different sides of the field. On the cold side of the field crystallization proceeds at a higher rate; here the crystal is formed with a less perfect structure and with greater capture of impurity than on the hot side.

2. If, in the course of growth, the crystal is turned through 180° (by half a revolution), then it assumes a new position, shifting in the direction of the turn and changing its inclination to the opposite one (Fig. 2). Upon turning, the region of the crystal which had been facing the cold side of the field, the "cold" region, will penetrate into deeper layers of the melt from the hot side. The region of the crystal that before the turn faced the hot side of the field, the "hot" region will rise above the surface of the melt on the cold side, carrying the melt along with it. Thus, as a result of the rotation, the degree of supercooling of the melt on the hot side of the field decreases, while on the cold side it increases. Consequently, immediately after rotation, crystal growth on the cold side of the field accelerates, while on the hot side, conversely, it slows down, until the previous steady state of the melt (before rotation) is reached.

Figure 3a shows a photograph of a longitudinal section of an aluminum crystal doped with Cu^{64}, $10^{-4}\%$, grown without rotation, with rotations through 180° at points $I, II, \ldots, VI$; Fig. 3b shows a radiogram of the same section. The transition region is marked by the appearance, on the longitudinal section of the crystal, of a wedge-shaped area, light on the radiogram (Fig. 3b) on the side of the wedge apex, lighter than the "hot" part of the main region of the crystal formed under steady-process conditions, and dark on the side of the base of the wedge, darker than the "cold" part of the main region of the crystal. This difference is also readily established from the degree of etching (Fig. 3a) of the transition region in comparison with the region of the crystal formed under steady-process conditions.

Fig. 2. Change in the state of the melt upon rotation. $CDBA$ and CDB_1A_1 are the positions of the crystal before and after rotation; BA and B_1A_1 are the positions of the interface before and after rotation.

3. If the rotation of the crystal is carried out continuously, then the crystal contains no regions formed under steady-process conditions; instead, the transition regions merge into one continuous band extending through the

volume of the crystal in the form of a helix. This continuous band consists of two adjacent layers that differ in structure and impurity content.

The etching pattern on the longitudinal section of a crystal grown with rotation at a rate of 1/2 revolution per minute and a pulling rate of 2 mm/min (Fig. 4a) is composed of repeated instances of an elementary pattern representing an individual transition region under intermittent rotation (cf. Fig. 3a).

The helical macroinhomogeneity arising in the rotating crystal appears externally as the formation of a spiral on its cylindrical surface. The pitch of the spiral S is determined by the ratio of the total rate of crystal pulling v_1 and lowering of the melt surface in the crucible v_2 to the number of revolutions n of the crystal per unit time,

$$S = f\left(\frac{v_1 + v_2}{n}\right).$$

On the side of the lower slope, a weakly etched helical layer adjoins the crests of the spiral turns. The depressions between the crests correspond to a strongly etched helical layer.

The hot bands, light in the photograph (Fig. 4a), often overlap and become isolated in the central part of the crystal. Isolation in the form of a central core is also characteristic of the cold bands and is yet another, highly distinctive, type of inhomogeneity characteristic of crystals grown with rotation. Directly adjacent to the edge of the hot region of a crystal grown without rotation (Fig. 1a) is a narrow band, dark in the photograph, strongly etched similarly to the cold region of the crystal. A narrow band also adjoins the edge of the cold region of the crystal; it is darker in the photograph and etched more deeply than the main cold region.

Both edge bands owe their origin to the relatively stronger supercooling of the melt at the edges of the melt surface.

Fig. 1

Fig. 3

Fig. 4

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This edge effect on a longitudinal polished section of a crystal grown with rotation (Fig. 4a) is manifested in a narrowing of the "hot" bands toward the edge of the crystal and a widening of the "cold" bands. At the very edge of the crystal the hot regions end in a narrow point (cf. also Figs. 3a and 3b). The hot bands are "undercut" also because they form at places where the crystal narrows (on the hot side of the thermal field), which, as will be seen from the next section, is accompanied by supercooling of the melt at the edges of the crystal.

4. If the initial pulling rate of the crystal is decreased, the crystal invariably increases in diameter. With the opposite change in the pulling rate, the crystal narrows. These external changes in dimensions are accompanied by a profound change in the structure of the crystal.

Figure 4b shows a photograph of a longitudinal polished section of an aluminum crystal grown with rotation at a rate of 2 rev/min. At an unchanged pulling rate (2 mm/min in the upper part of the crystal), the bands of inhomogeneity arising in the crystal as a result of rotation run at approximately the same distance from one another (1.7 mm), forming over a time of approximately ~ 0.65 min. When the pulling rate is decreased (at point *aa*) to 0.5 mm/min, i.e., by a factor of 4, the distance between the bands changes disproportionately little at first, and moreover is smaller at the edge of the crystal (1.4; 1.2; 1.0; 0.8; ⋯mm) than in the central part (respectively 1.5; 1.5; 1.2; 1.1; ⋯mm). This indicates that, at the beginning of the transient process, the growth rate considerably exceeds the rate of rise of the crystal and, consequently, the interface surface descends, and more so in the central part. The higher growth rate of the crystal at the center indicates greater supercooling of the melt beneath this central region than at the edges of the crystal. The region of the crystal that formed from the more supercooled melt is marked on the longitudinal polished section by the appearance of a "cold" cone I—I—I, penetrating into the "hot" region.

When the pulling rate is changed in the opposite direction (from 0.5 to 2.0 mm/min, see Fig. 4b), the beginning of the transient process is marked by a considerable lag of crystal growth behind its rise, and this lag is greater at the center of the interface surface than at its edges. The interface surface, consequently, rises. The sagging of its edges indicates greater supercooling of the melt at the edges in comparison with the central part. In the structure of the crystal this is marked by the formation of a "hot" cone penetrating into the "cold" region of the crystal.

The indicated transient processes are caused by a disturbance of the heat balance in the melt-crystal system. When the pulling rate is decreased, the volume of metal crystallizing per unit time decreases and, consequently, so does the amount of heat of crystallization released. As a result, there is a deficiency of heat passing through the crystal. The crystal cools somewhat, which entails an increase in the supercooling of the melt in the central part of the interface surface. When the pulling rate is increased, the amount of heat of crystallization released increases, as a result of which an excess of heat passing through the crystal is created. The crystal heats somewhat, as a result of which the supercooling in the central part of the interface surface decreases.

From the discussion of Fig. 4b it follows directly that any change in the pulling rate of the crystal (as well as stops–Fig. 1) leads to a considerable aggravation of inhomogeneity in the structure and in the distribution of impurities in the crystal.

5. The elimination of structural and impurity inhomogeneities in crystals

should be sought in the creation of a symmetrical thermal field and in the establishment of all causes leading to its distortion and, consequently, to nonuniform supercooling of the melt at the interface surface.

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Note: Figure translations are in progress. See original paper for figures.