FORMATION OF AN INTRAGRAIN DISLOCATION SUBSTRUCTURE DURING THE GROWTH OF NaCl SINGLE CRYSTALS FROM THE MELT

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FORMATION OF AN INTRAGRAIN DISLOCATION SUBSTRUCTURE DURING THE GROWTH OF NaCl SINGLE CRYSTALS FROM THE MELT

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1. Within weakly misoriented grains of alkali-halide single crystals grown from the melt there are usually dislocations, more or less uniformly distributed, sometimes called growth dislocations. The relative role of the possible mechanisms of their formation is discussed in a number of works, on the basis of the dependence of dislocation density on growth conditions ([1]) and of variations in the dislocation distribution both within the ingot ([2,3]) and inside an individual grain ([4]). All the observations of the dislocation structure required for this are carried out on specimens which, after growth, have undergone a certain heat treatment (usually annealing in a more or less homogeneous temperature field near the melting point and slow cooling to room temperature). Under these conditions the dislocations possess considerable mobility, sufficient for the structure formed during growth to be very strongly changed as a result of glide, climb, and interaction; apparently, attempts to fix the growth structure by quenching should lead to still greater changes, since the low thermal conductivity and high plasticity of alkali-halide crystals inevitably lead to intense multiplication of dislocations. Thus, the dislocation structure usually observed (the density, distribution, and configurations of the dislocation lines) is the result of the superposition of a large number of different factors; it is quite unclear to what extent it corresponds to the growth structure and to what degree the results of its study can be used to elucidate the mechanism of dislocation formation during the growth process.

In the present work it has been found that, under cooling conditions which apparently provide the closest approximation to those occurring during the growth of single crystals (sufficiently slow cooling of the ingot in the field of the temperature gradient existing in the crystallization furnace), there appears a very distinctive, previously unobserved, “labyrinth” structure of dislocation distribution, arising (as will be shown below) under strictly defined growth conditions.

2. NaCl single crystals were grown by the Czochralski method ([5]) and by

Fig. 4

Figure 1: Fig. 4

the method described in (6); after separation from the melt they were cooled directly in the crystallization furnace. On etching with glacial acetic acid of cleavages along the cleavage planes (100) in crystals grown along [001] and [011], a characteristic dislocation substructure was found, typical examples of which for different orientations are shown in Figs. 1 and 2.

In contrast to the pattern usually observed in artificial single crystals of the NaCl type, the pyramidal etch pits inside subgrains here are not arranged chaotically, but form clusters in the form of relatively wide rows, aligned approximately along [010] and [001], independ—

···regardless of the crystallographic orientation of the ingot axis, and creating a peculiar labyrinth pattern.

Layer-by-layer chemical polishing and etching showed that the clusters consist of spatially curved dislocations forming irregular three-dimensional networks, mainly with triple nodes (see Fig. 4). The dislocation networks are arranged in approximately flat layers, whose thickness corresponds to the width of the rows of etch pits (see Figs. 1 and 2); moreover, these layers (the "walls" of the labyrinth) have a clearly expressed tendency to be located in the cleavage planes {100}.

Fig. 4. Configuration of dislocations in a substructure layer (projection onto a cleavage plane perpendicular to the plane of observation and parallel to the investigated row of etch pits). The nodal points are indicated by circles; dotted lines indicate cases in which dislocations are arranged parallel to the observation surface, when the lines are not revealed by the etching method.

The average thickness of the spatial network along the normal to the plane of Fig. 3 is 25 μ.

The indicated substructure is practically insensitive to the growth rate in the interval 3-48 mm/h, but it clearly depends on the magnitude of the temperature gradient near the phase boundary. With a decrease in the axial temperature gradient, the distances between the rows of etch pits increase, the total dislocation density decreases, and at a certain sufficiently small gradient ($\sim$ 15 deg/cm under our conditions) only randomly scattered etch pits are observed in the field of view, not forming any regular structure.

One of the most interesting features of the substructure is its thermal instability in a homogeneous temperature field. Annealing in a gradient-free furnace at temperatures above 450° leads to a relatively rapid disappearance, within the volume of the specimen, of the ordered layers of dislocation networks; in this process the decrease in dislocation density is not accompanied by their displacement in space between neighboring layers, but is the result of interac-

Figure 1

Figure 2: Figure 1

Figure 2

Figure 3: Figure 2

tion of dislocations within the given layer. Since annealing in a gradient-free temperature field is a usual stage accompanying crystal growth, this instability apparently was the reason why the dislocation substructure described here had not been observed until now.

3. At present, five mechanisms have been proposed for the formation of dislocations in crystals growing from the melt (^{7}): 1) propagation of dislocations from the seed into the growing crystal; 2) improper coalescence of dendrite branches protruding into the melt; 3) relaxation of stresses caused by changes in the lattice parameter due to sharp composition fluctuations; 4) "engulfment" of planar accumulations of vacancies; 5) relaxation of thermal stresses. Although a number of features of the observed substructure make it possible to estimate the possible relative role of these mechanisms in its creation, none of them can be excluded *a priori*.

Fig. 1. Growth direction [001]. *a*—23×; *b*—region marked by a rectangle in photo *a*, 196×

Fig. 2. Growth direction [011], 23×

Fig. 3. *a*—gradient annealing according to the regime: heating, holding, cooling; dislocation density $\rho = 1.8 \cdot 10^6$ cm^{-2}; *b*—gradient annealing according to the regime: heating, cooling, $\rho = 1.3 \cdot 10^6$ cm^{-2}; *c*—initial structure of the specimen, $\rho = 4 \cdot 10^4$ cm^{-2}, 53×

The first three mechanisms listed "act" or are a consequence of processes occurring directly at the surface of the growing crystal in contact with the melt; the remaining two can be realized only behind the crystal–melt surface, in the already formed solid phase. Proceeding from this fundamental difference between the two groups of possible causes, one of them can be excluded by the following experimental arrangement. A NaCl specimen, cleaved in the form of a square prism from a piece of a carefully annealed crystal (i.e., one not containing the substructure under consideration), is fastened in the crystal holder of a crystallization apparatus and, after slow heating of the furnace, is introduced into the melt. After a certain holding time, contact with the melt is broken, and the temperature in the furnace is lowered to room temperature at the same

Figure 3

Figure 4: Figure 3

rate as in cooling grown single crystals. Such an experiment thus imitates only that part of the process of obtaining a single crystal which is associated with its cooling after growth (with the exception of the stage of heating the specimen from room temperature, which, under real growth conditions, is naturally absent), and makes possible the action of only the last two of the above-listed mechanisms of dislocation formation.

Investigation of cleavages of NaCl specimens showed that heat treatment of this type (in a sufficiently large temperature gradient) invariably leads to the formation within the grains of a labyrinthine substructure, completely analogous to that observed in grown crystals. This result excludes the mechanisms of the first group from among the possible causes of formation of the labyrinthine substructure.

Analogous results were obtained in gradient annealing of KCl, KBr, and LiF specimens.

4. In Fig. 3a and b typical results are shown for gradient annealing of NaCl specimens under the following two regimes: a—heating for 30 min to 675° (at the lower, hottest end of the specimen), holding at this temperature for 1 hour, cooling for 30 min; b—heating and cooling at the same rates, but without holding. Both regimes give approximately the same increase in dislocation density (cf. with the initial structure, Fig. 3c), but b leads to a chaotic distribution of etch pits, whereas a causes the appearance of a distinct labyrinthine structure. This result indicates that the process of formation of the dislocation substructure is not associated with the mere fact of lowering the specimen temperature and, consequently, cannot be explained within the framework of the mechanism of vacancy supersaturation and trapping of vacancy disks.

Thus, the only possible mechanism of formation of the dislocations participating in the observed effect is the relaxation of thermoelastic stresses caused by the inhomogeneity of the temperature field in the crystal. This point of view is additionally confirmed by the results of annealing NaCl specimens in a linear temperature field (with a constant temperature gradient dT/dz along the z axis of the specimen), i.e., under such conditions in which, as is known ([8]), thermoelastic stresses are absent. Independently of the magnitude of dT/dz, the holding time, and the cooling rate, annealing under these conditions is never accompanied by the appearance of a labyrinthine substructure.

Moreover, a substructure previously created in the specimen is destroyed in this case in exactly the same way as under gradient-free annealing.

The data presently available are still insufficient for a reliable judgment about the kinetics of formation of the observed substructure. However (see Fig. 3), it is clear that the stages of dislocation generation and of their arrangement into labyrinth walls are separated in time. Annealing according to regime a leads to an increase in the degree of formation of rows of etch pits with increasing holding time. This means that the formation of rows is associated with the motion (apparently, mainly by climb, since below 480° a substructure does not arise in NaCl) of dislocations and their rearrangement into clusters of a definite geometry.

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