STRUCTURAL PERFECTION OF MELT-GROWN ALKALI HALIDE CRYSTALS

V. N. EROFEEV

Institute of Solid State Physics USSR, Academy of Sciences, USSR

The mechanisms of the dislocation formation during the melt-growth of alkali halide crystals have been analysed. The main plasticity parameters of NaCl and KCl crystals are measured at elevated temperatures. The Czochralski melt-grown NaCl and KCl crystals exhibited high structural perfection.

1. Introduction

Synthesis of alkali halide crystals with high structural perfection encounters many difficulties. The means to overcome these difficulties have not been developed so far, though constant efforts are being exerted in this direction.\(^1\)\(^-\)\(^3\) The present work deals with an analysis of the principal mechanisms of the dislocation formation in alkali halide crystals. The experiments are presented on the melt-growth of NaCl and KCl crystals of increased perfection.

2. Seed Dislocations

There are many causative factors giving rise to dislocations in a melt-grown crystal. The seed dislocations can be inherited by the crystal. Since the dislocation line cannot break down inside the crystal, it has either to form a closed configuration or to emerge on the surface. Therefore the seed dislocations grow into a crystallizing ingot. Not only individual dislocations but, also, small-angle boundaries and other dislocation defects can propagate from the seed.

As is known, Dash\(^4\) was the first to propose the technique to eliminate the inheritance process. Dash's technique yields good results in growing semiconductor crystals. In these crystals with a deep lattice potential relief the dislocations lie along the close packed directions (for instance, in Si these are the crystallographic directions \(\langle 110 \rangle\) in planes \(\{111\}\)). Figure 1 gives a
schematic presentation of a half-loop in Si, the places of the dislocation emergence on the sample surface are etch-pitted.\(^5\) We revealed the shape of dislocation half-loops by X-ray topography using Lung's technique\(^6\) (Fig. 2) as well as by the original method of selective chemical etching, proposed by us, that was subsequently employed for many materials and was termed the projection etching\(^7\) because after the etching there remains a trace from the dislocation line on the crystal surface corresponding to the dislocation

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Fig. 1. Etch pit shapes and the shape of dislocation half-loops in Si.

Fig. 2. Dislocation half-loops in Si revealed by Lung's method (×40).
projection on this plane. Figure 3 presents a micrograph of a half-loop. Figure 4 shows that said method enables one to reveal the dislocation microstructure too.

The deeper the lattice potential relief the stronger the dislocations tend to locate strictly in the relief valleys. Therefore, in semiconductors the seed

![Figure 3](image3.jpg)

**Fig. 3.** Configuration of dislocation half-loop in Si, revealed by chemical etching.

![Figure 4](image4.jpg)

**Fig. 4.** Microstructure of dislocations in Si, revealed by chemical etching.
dislocations can be cropped out due to the formation of a long thin neck, if they are not parallel to the axis of growth. Dash's technique is less effective in crystals with a low potential relief. In these crystals, firstly, dislocations do not lie along strictly selected directions and are not cropped out as the ingot grows; secondly, the dislocations are very mobile and pass into the crystal following the moving solid-liquid interface. Figure 5 presents, for comparison, the data on the dislocation velocities in crystals of different classes of material.\(^8\)\textsuperscript{1}\textsuperscript{-13} The velocity of dislocations in NaCl at \(T = 300\) K is 3 orders of magnitude larger than in Si at \(T = 773\) K at a constant stress \(\tau = 10\) MPa.

3. \textit{Thermal Stresses}

The structural perfection of melt-grown crystals is a function of the thermal conditions of growth giving rise to plastic deformation of the crystal. In this case, the nature of stresses can be different: nonuniform temperature distribution in the crystal causes the appearance of thermal stresses, a

![Diagram of dislocation velocity as a function of shear stress](image)

Fig. 5. Dislocation velocity as a function of shear stress: 1: Si, 773 K,\(^3\) 2: Ge, 673 K,\(^3\) 3: Nb, 473 K,\(^6\) 4: LiF, 300 K,\(^11\) 5: NaCl, 300 K,\(^12\) 6: Ag, 300 K.\(^13\)
discrepancy between the coefficients of thermal expansion of the crystal and the crucible (in the case of "container" techniques) gives rise to mechanical stresses, a discrepancy between the impurity and matrix atomic sizes gives rise to concentrational stresses. In the case of growth of pure crystals by pulling them on the seed (the Czochralski, Kyropoulos, Stepanov techniques) the main role is played by thermal stresses.

In our work,\textsuperscript{14} thermal conditions near the solid-liquid interface are investigated, and the distribution of axial and radial temperature gradients in a growing crystal is obtained by solving the steady state equations of thermal conduction using a computer, and from experimental measurements in NaCl crystals grown from the melt by the Czochralski method. Figure 6 represents schematically the distribution of an axial temperature gradient and the form of the temperature field in crystals with a convex towards the melt (Fig. 6a) and a concave (Fig. 6b) solidification front under actual conditions in the presence of heat loss from the side surface of the crystal. Solid lines show the isotherms whose geometry was determined from the experimental measurement of a radial temperature distribution. Dashed lines show heat fluxes. In a crystal with a convex solidification front, a maximum temperature gradient is observed not on the solid-liquid interface, but at some distance away from it. At such solid-liquid interface geometry, the heat fluxes due to release of the latent heat of crystallization appear to be focussed on the growth axis. Convergence of the heat fluxes towards the growth axis and, hence, an increase of the axial gradient slope at the moment that the isotherms undergo a full convex-to-concave transformation. So, the maximum magnitude and

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig6.png}
\caption{The behavior of the isotherms, heat flows and axial temperature gradient in the crystals with convex (a) and concave (b) solidification front.}
\end{figure}
position depend on the curvature of the initial isotherm, that is, on the curvature of the solidification front, and on the rate of this transformation, that is, on the cooling rate of a crystal (on the crystal size).

These conclusions are confirmed by the experimental measurements. Figure 7 represents the distribution of the axial temperature gradient along the crystal: the experimental data are solid lines, the calculated data are dashed lines. As the crystal radius is increased (2.5, 5 and 10 mm) and the solidification front curvature decreased, the magnitude of the gradient is decreased (curves 1, 2, 3) and its maximum position is displaced. In the case of a flat and concave front (curve 4) no peak is present.

A simultaneous determination of axial and radial gradients has shown that at the moment that the axial gradient has reached its maximal value, the radial gradient is zero (Fig. 8). To do this, differential thermocouples were grown in the crystal.

The temperature distribution in a crystal with a convex or concave solidification front must determine the thermoelastic stress fields in each case, because the stress source is the incompatibility of thermal deformations expressed by means of second derivative of temperature: \( \sigma = \alpha E L^2 (\partial^2 T / \partial z^2) \), where \( \alpha \) is a linear coefficient of thermal expansion, \( E \) is the Young modulus, \( L \) is a correction parameter depending on the cross dimensions of the crystal and on the geometry of the temperature field. It can easily be seen that the greatest value of \( \sigma \) corresponds to the case of a convex solid-liquid interface. The

![Graph showing experimental and calculated data on the axial temperature gradient dependence on a distance to the boundary interface as the crystal diameter increases and the crystallization front curvature decreases.](image-url)
The presence of the axial gradient maximum is also disadvantageous from the viewpoint of the distribution of the signs of the thermoelastic stresses arising in a growing crystal. The formation of the thermoelastic stress field can markedly be affected by the peculiarities of the radial temperature distribution, taking place in crystals with a convex solidification front. The presence of temperature maxima and minima restricts the occurrence of free thermal expansion of the adjoining layers and can give rise to essential thermoelastic stresses.

The qualitative conclusions are confirmed by the experimental observations. We have investigated the dislocation structure of alkali halide crystals grown from the melt by the Czochralski method, with respect to the solidification front shape. Figure 9 represents the dislocation density $\rho$ in KCl as a function of the magnitude of the solidification front sagging $\Delta H$ ($\Delta H=0$ is a flat front, $\Delta H>0$ is a convex front, $\Delta H<0$ is a concave front). As seen in Fig. 9 crystals with a flat solid-liquid interface have the greatest structural perfection.
The plastic deformation begins when the temperature gradients in the crystal are nonuniform and the arising thermal stresses exceed the yield point of this material. It is especially difficult to synthesize perfect alkali halide crystals. These crystals have a rather high melting temperature, low thermal conductivity (as compared with metals), low yield point (as compared with semiconductors), therefore when melt grown they have a great number of dislocations. A decrease of thermal stresses down to the yield point level is a complicated problem but at attaining this level dislocations will generate too, since the threshold stress \( \sigma_t \) for their formation is lower than the yield point value \( \sigma_y \). In Ge \( \sigma_t \) is smaller by one order of magnitude than \( \sigma_y \) and makes up approximately 0.15 MPa, \( \sigma_t = 0.6 \text{--} 0.9 \) MPa in Si, 0.5 MPa in InAs, 0.2 MPa in InSb, 0.07 MPa in GaAs.\(^{15}\)

In this work we present the measurements of the principal plasticity parameters of alkali halide crystals at elevated temperatures. The table gives the values of the yield point \( \sigma_y \), of threshold stresses for the dislocation motion \( \sigma_s \) and multiplication \( \sigma_m \), obtained in NaCl crystals. With account taken of

<table>
<thead>
<tr>
<th>( T, ^\circ C )</th>
<th>25</th>
<th>200</th>
<th>400</th>
<th>560</th>
<th>600</th>
<th>700</th>
<th>750</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \sigma_t, \text{ MPa} )</td>
<td>0.5</td>
<td>0.4</td>
<td>0.3</td>
<td>—</td>
<td>0.28</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>( \sigma_y, \text{ MPa} )</td>
<td>0.15</td>
<td>0.06</td>
<td>0.015</td>
<td>0.006</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>( \sigma_m, \text{ MPa} )</td>
<td>0.55</td>
<td>0.4</td>
<td>0.25</td>
<td>—</td>
<td>0.2</td>
<td>—</td>
<td>0.15</td>
</tr>
</tbody>
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these data an attempt has been made to minimize the action of the principal
mechanisms of the dislocation formation.

4. Crystal Growth Experiment

The NaCl and KCl single crystals were grown on a "dislocation-free"
seed. The single crystals, subjected to a prolonged isothermal anneal, were
used to cut samples, possessing large dislocation-free blocks. Thin long seed
crystals were prepared in such a way that they should terminate in a
dislocation-free surface. In order to avoid a thermal shock the seed was slowly
heated in the furnace. The crystal grew at a very small rate (2–3 mm/h) in a
thermal field with a minimal axial gradient and in the absence of a radial
temperature gradient. The heat removal from the crystallization site was
performed via a metallic stick, no water cooling was applied.³ The growing
crystal was immobilized, the furnace was rotated, the crucible with the melt
was lowered. The thermal conditions were selected such that the solidification
front should be flat. The grown crystal was cooled very slowly and uniformly
at a rate of 5–10⁰/ h.

These procedures made it possible to improve greatly the perfection of
alkali halide crystals. We obtained small NaCl and KCl crystals that did not
contain block boundaries and had the dislocation density lower by several
orders as compared with standard crystals (Fig. 10).

![Fig. 10](image-url)  
**Fig. 10.** Micrographs of etch pits in NaCl crystals: (a) standard melt-grown crystal;
(b), (c) crystals with small density of dislocations.
REFERENCES


