

ELECTRON MICROSCOPIC INVESTIGATIONS ON THE INHOMOGENEITY OF THE DISTRIBUTION OF DIVALENT DOPANT INCORPORATED INTO KCl CRYSTALS

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(Received December 15, 1971)

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1. Introduction

During the growth of crystals the trace poisons, present in a mother phase, build in into the crystal lattice where they directly produce point defects modifying the physical-chemical properties of the host crystals. In technical applications of crystals, the poison's modifying effect may be either desirable or undesirable. In either case, an important question is the homogeneity of the poison's distribution within the lattice from the point of view of the formation of other defects (dislocations, cracks etc.) during not only the growth but the technical treatment of crystals, too. The different electron microscopic methods are known to be very suitable and the most sensitive to the investigation of microdistributions of trace poisons [1]. In this paper, electron microscopic investigations are reported, which have given informations about the microdistribution of Pb or Sn dopants within KCl crystals.

2. Experimental

2.1. Producing crystals containing dopant of known concentration

From aqueous solutions, saturated with KCl at temperatures between 28 and 40 °C and doped with SnCl₂ or PbCl₂ in concentrations between $5 \cdot 10^{-3}$ and 2 mole %, KCl single crystals were grown by slow undercooling. Varying the rate of undercooling and the dopant content of the solution, KCl single crystals containing dopants in different concentrations were produced. After the growth, the total concentration of dopant (Pb or Sn) incorporated into the crystals was determined by polarographic analysis. The methods for growing and for polarographic analysis are not discussed here since they have already been described in detail in our earlier papers [2, 3].

The polarographic investigations mentioned above gave no informations concerning the microdistribution (whether atomic or segregated, homogene-

ous or not etc.) of the dopants present in the crystals. On the basis of earlier experiments it was expected that the incorporation of dopants into the crystals would not be uniform due to the growth rate fluctuations. [4, 5]

2.2. Surface gold-decoration technique

For the investigation of the microdistribution of incorporated dopant, the well-known surface gold-decoration method [6] was used. A test specimen of about $8 \times 4 \times 1$ mm³ size was fresh cleaved out from the KCl crystal for investigation. Then, thermal treatment at high vacuum has been applied to the specimen in a suitable, small molybdene band-furnace mounted into the chamber of a vacuum equipment (see F in Fig. 1). In the bottom of the band-

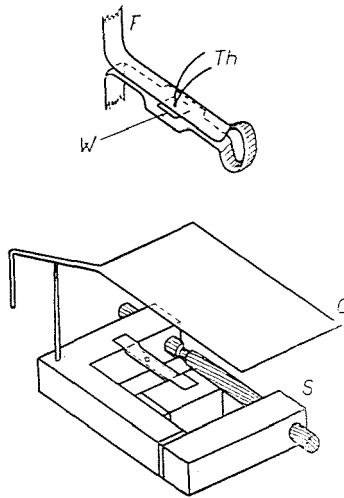


Fig. 1. Experimental arrangement in the vacuum chamber: F — band-furnace; W — small opening; Th — thermocouple; C — movable cover; S — source for evaporating gold and coal

furnace a small opening was cut to insure a free evaporation for one of the specimen's faces. To the upper part of the band-furnace a thermocouple was welded for reproducibly controlling the temperature. Between the source for evaporating gold and coal (S) and the band-furnace a nickel cover was employed, that could be moved by a magnet from outside.

Having produced a vacuum of about 10^{-5} torr in the chamber, the specimen placed into the band-furnace was heated and then slowly evaporated at 400 to 500 °C for 30 to 60 minutes. Then, having cooled the furnace to 120 to 150 °C gold of small quantity and coal as supporting film were condensed on the specimen. As it is known from earlier investigations [6], if the quantity of gold condensed was small enough the gold did not form a continu-

ous film on the surface of KCl but constituted small individual crystallites. Then, these small gold crystallites would be embedded into the matrix of coal film in their original places on the crystal surface.

Investigating the coal film in transmission in an electron microscope, the original arrangement of the gold crystallites on the crystal surface can be observed. Considering the cohesive energy of the atomic particles sitting in different surface positions [7], and the theoretical results concerning the evaporation and growth processes of crystals [8–12], on the basis of arrangement of gold crystallites informations can be obtained about the defect-structure of the crystals.

3. Results and discussion

In the process of building-down of a crystal face — in our case: evaporation of a crystal face in high vacuum — certain local surface conditions are of importance. Namely, there are places around which the cohesive energy of the ions forming the crystal lattice is smaller than in other spots. Such places are e.g. the intersection points of dislocation lines with the crystal face. Namely, the mechanical strain field around dislocations reduces the cohesive energy of the lattice elements. Around these intersection points of dislocations, characteristic surface figures consisting of (mono) atomic layers are formed during the slow evaporation of crystals [6]. The atomic layers creating the surface figures are traced (“decorated”) by the gold crystallites condensed on the crystal face.

The two transmission electron micrographs in Fig. 2 show such surface figures. In Fig. 2/a a series of concentric circles of atomic layers formed around the point of intersection of an edge dislocation is seen. These concentric atomic layers form together a small flat pit on the crystal face. Around screw dislocations where the atomic planes create a Riemannian surface, flat pits consisting of spiralling atomic steps appear. Fig. 2/b is an example.

If the evaporation has lasted long enough, the whole face (100) of the specimen gets covered by atomic steps due to dislocations intersecting the face.* During the building-down (evaporation) the atomic steps “move” away from their source places. The moving of the surface steps is influenced by all the surface positions around which the cohesive energy of the lattice elements (in our case: ions) is irregular. Such positions are e.g. the places where instead of regular particles, foreign ones (dopant atoms) are sitting in the crystal lattice. Because of the different atomic dimensions and electrical properties of the

* It is to be mentioned that besides the (mono)atomic surface steps, steps of polyatomic thickness may occur on the crystal face. But the frequency of the polyatomic steps is smaller than that of (mono)atomic ones. In the followings, presence of polyatomic steps will be generally neglected.

dopant particles, these foreign particles prevent the atomic surface steps from moving [13, 14]. This is the case for the KCl crystals containing divalent dopant, too.

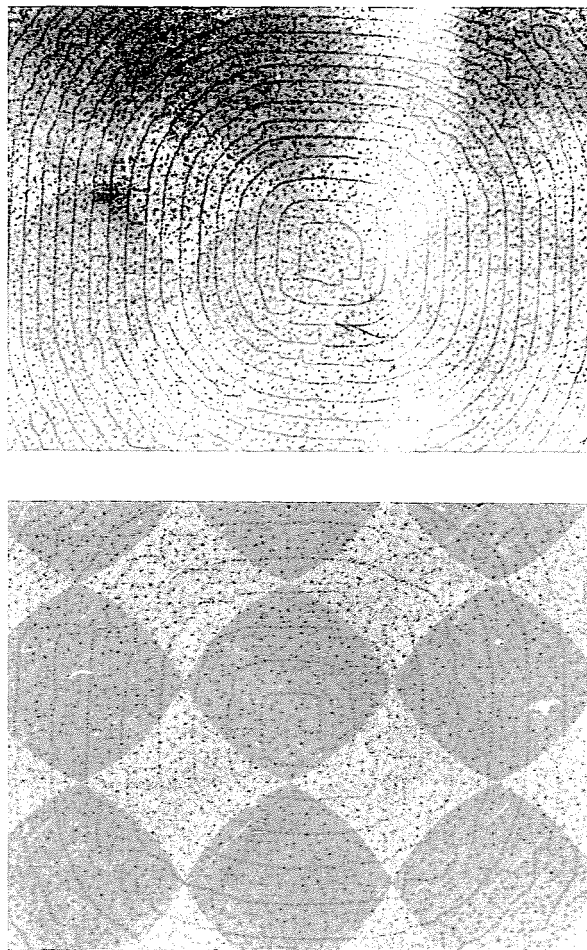


Fig. 2. Transmission electron micrographs of surface figures consisting of atomic steps formed around dislocations during the evaporation of KCl crystals (by surface gold-decoration technique), a) around an edge dislocation (magnification: $16000\times$); b) around a screw dislocation (magnification: $26000\times$)

If the dopants are present in the lattice in atomic distribution, and their concentration is small enough, then they prevent only the motion of individual atomic steps and this only locally. In this case, as an effect of the presence of foreign particles, small irregularities (zigzags) appear on the contours of the atomic steps (see the contours of atomic steps in Fig. 2). It was already proved

earlier that a relationship exists between the surface density of zigzags and the concentration of the divalent dopant incorporated into the crystals [15].

If the dopant concentration is great enough, a coagulation of dopant

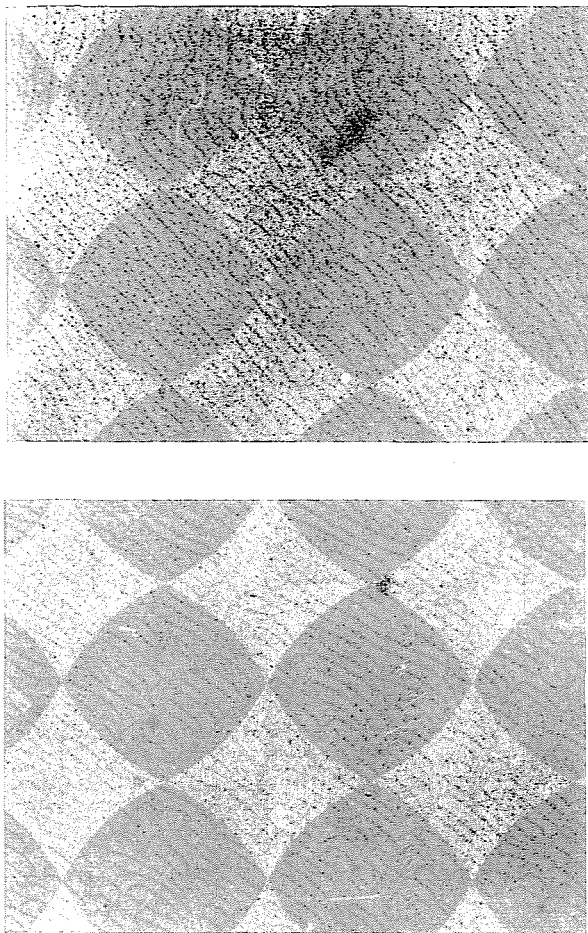


Fig. 3. Contour irregularities (zigzags) developed upon prevented motion of atomic layers (KCl with 0.26 mole % Pb): a) small zigzags (magnification: 35000 \times); b) zigzags disturbing several atomic steps (magnification: 35000 \times)

particles starts. The foreign particles of greater than atomic dimensions can already prevent the motion of several atomic steps all at once. So, great zigzags of polyatomic thickness can form. The different zigzags in Fig. 3 mark different stages of the dopant coagulation within the crystal. In several cases dark granules can be seen in the corners of zigzags. Their dimensions indicate that they are not the directly precipitated dopant particles but gold granulates

which condensed on dopant particles due to favourable nucleation conditions [11, 12]. Comparison of the two pictures demonstrates the spacing between two atomic steps to decrease in more poisoned areas.

For a great surface density of the foreign atoms or of the particles coagulated from them, these atoms or particles may collectively prevent the motion of shorter or longer sections of the steps rather than produce local zigzags in the step contours. In this case the moving velocity of atomic steps decreases

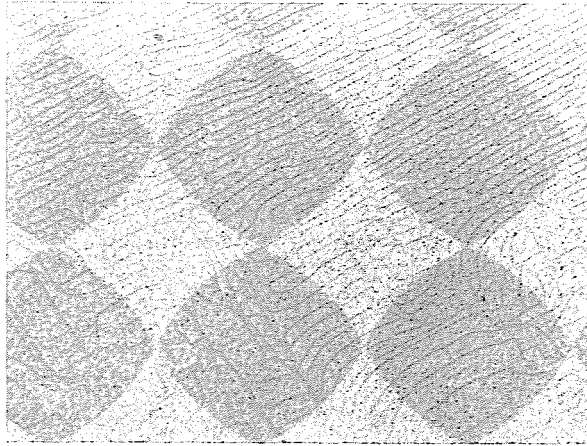


Fig. 4. Surface density of atomic steps on two areas containing dopants in different concentrations (KCl with $7.1 \cdot 10^{-3}$ mole % Sn). (Magnification: $16000\times$)

and the density of steps increases in the given area. Fig. 4 shows an example for this. Here the surroundings of the boundary between two areas containing dopants in different concentrations are seen. The difference in the density of atomic steps in the two areas is remarkable.

4. Conclusions

During slow evaporation of crystals in high vacuum the foreign atoms or particles present in the surface film of crystals influence locally or collectively the motion of atomic steps. From a comparison of the disturbing effects observed it appears that the dopants (Sn, Pb) within the KCl crystals are present in atomic distribution as long as their total concentration is small enough. Also in this case, areas of about $10^{-3} \dots 10^{-4}$ cm size are found where coagulated stages of dopants appear. This fact is an indication that the dopant concentration in these areas is over the average. In such areas a precipitation of dopants may have started during either the growth or the thermal treatment at the preparation of the specimen. Results of earlier optical investigations have led to the same conclusion [16].

As mentioned in item 2.1, development of more poisoned areas of crystals due to the growth rate fluctuation during the growth process was expected. Thus, the results of present electron microscopic investigations directly proved our expectations. Study of the relation between the growth conditions and the inhomogeneous dopant distribution is in progress.

The author is grateful to MRS. BÖSZÖRMÉNYI-NAGY and MRS. CSEH-SZOMBATHY for their assistance.

Summary

Electron microscopic investigations give information about the microdistribution of trace poisons within crystals. The investigations were carried out on KCl crystals grown from aqueous solutions doped with Pb or Sn, using electron microscopic surface gold-decoration technique. Differences observed in the evaporation structure of certain areas of a crystal face indicated inhomogeneities in the distribution of dopants incorporated into the crystal.

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