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Abstract

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THE ROLE OF THE CATION OF AN ADDITIVE IN THE PROCESS OF SELECTIVE ETCHING OF KBr AND NaCl CRYSTALS

Selective etching of crystals occurs (with an appropriate choice of etchant) at the places where linear lattice defects (dislocations) emerge on the surface and at accumulations of point defects. The form of the pits obtained makes it possible to determine unambiguously what type of disturbance has occurred (see, for example, (1)). Etch pits were first associated with dislocations in (2), which was confirmed by other authors (3, 4). Theoretically, the formation of a pit at a dislocation was substantiated by Cabrera (5). Later, on the basis of these ideas, in (6–8) a mechanism was described for the formation of etch pits in LiF crystals.

The process of formation of an etch pit at a dislocation consists of the formation of a dissolution nucleus at the point where the dislocation intersects the surface, and the subsequent growth of the pit by the formation of kinks on the steps that make up the faces with high indices forming the pit, and by the motion of the kink along the step. Along with the formation of a kink, its "poisoning" (inhibition) takes place (9). As follows from (6–8), the etchant consists of two agents—a dissolving one and an inhibiting one. The orientation and shape of the pit are determined by the relative rate of these two processes. Dissolution is governed by the difference in the chemical potentials of the etchant and the crystal; inhibition, by the presence in the solution of cations or groups of atoms capable of being adsorbed at kinks and thereby slowing down or even stopping their motion.

N. F. Kostin et al. (10) believe that additives introduced into the etchant slow the dissolution of the crystal, which, in their opinion, is explained by "planar isomorphism" of the type of epitaxial deposits.

We have investigated the influence of various cations on the etching process of KBr and NaCl crystals. The same etchant base was used, consisting of chemically pure isopropyl alcohol and 1.4 vol.% distilled water. As additives, $PbBr_2$, $BaBr_2$, $CuCl_2$, and oleic acid were used. When 5.8 mg of $PbBr_2$ was added to 100 ml of the base (hereinafter denoted H), etchant H-1 was obtained for KBr crystals (see Fig. 1, insert to p. 329). The edges of the pits are oriented along [110] (in all experiments the cube face was etched); the tangential etching rate in the [110] direction at a temperature of 80° is 8.5 μ/min. Etchant H-1 is sufficiently active in the temperature range 20–80°, has a weak polishing action, and the etch pits on "fresh" and "old" dislocations do not differ from one another.

Etchant H-1 contains complexes $[Pb(H_2O)_4]^{2+}$, stable in nonaqueous solvents, and Br^- anions. During etching an exchange reaction proceeds, since excess Br^- anions appear:

$$[Pb(H_2O)_4]^{2+} + 4K^+ + 6Br^- \rightleftharpoons [PbBr_4]^{2-} + 4K^+ + 2Br^- + 4H_2O.$$

The equilibrium will be shifted to the right (the conventionally adopted stability constant of the complex $[PbBr_4]^{2-}$ in isopropyl alcohol is $10^{12\pm4}$). In addition to participating in this reaction, the Pb^{2+} cations will be adsorbed on the kinks that are formed. It is very probable that molecules of isopropyl alcohol will take part in this process (when H in the base of isopropyl alcohol is replaced by propyl, the etching properties do not change, but when isobutyl alcohol is used, etching is not observed—evidently the length of the alcohol molecule plays a role). The interaction of the processes of kink formation and inhibition leads to orientation of the pit along [110] (see (8)).

The Pb^{2+} cation was used in etching potassium halides in work (10). Its authors believe that in the presence of $BaBr_2$ and $CuCl_2$ etching does not occur, since there is no "planar isomorphism." We carried out experiments with these compounds in order to clarify the role of the cation in the etchant.

Etchant H-2, containing 22 mg of $CuCl_2$ per 100 ml of base H, reveals dislocations and cleavage steps on the surface of a KBr crystal at 80° after 2 min (Fig. 2, see insert to p. 329). The etch pits are oriented along [100], which is explained by the weaker ability, as compared with etchant H-1, to create kinks on steps, since the stability of the complex $[CuBr_4]^{2-}$ is 100 times less than that of the complex $[PbBr_4]^{2-}$. For this reason the etchant has no polishing action at all (cleavage steps are preserved). When the concentration of $CuCl_2$ in the etchant is lowered, the etch pits become smaller, and points of "random" dissolution appear on the surface because of the relatively excessive water content.

Etchant H-3 (5 mg of $BaBr_2$ per 100 ml of H), at 80° after 5 min, reveals dislocation outcrops on the (001) face of a KBr crystal, forming etch pits with edges oriented along [100]. To illustrate the reorientation of the pit as compared with etchant H-1, the KBr crystal after etching in H-1 was etched in H-3 at 80° for 2 min (Fig. 3, see insert to p. 329).

The role of the inhibitor was clarified in experiments with etchant H-1, to which oleic acid was added (in work (11) it was shown that fatty acids serve as good inhibitors). As the concentration of oleic acid increased from 0 to 0.7 g per 1000 ml of H-1, the etch pits in the KBr crystal, initially oriented along [110], became rounded and ultimately turned into round cone-shaped pits (which corresponds to scheme (8)).

Analogous experiments were carried out on NaCl crystals. Etchant H-1 was used. With a $PbBr_2$ content of 5.8 mg per 100 ml of base, round sharp-pointed pits were obtained.

At a $PbBr_2$ concentration of 1 mg per 100 ml, at 80° after 1 min, pyramidal etch pits oriented along [100] are observed (Fig. 4, see insert to p. 329). The same pits were obtained when NaCl was etched with H-1 containing 0.2 g of oleic acid per 1000 ml of solution.

According to our experiments, the process of pit formation consists of the formation of a dissolution nucleus and the subsequent growth of the pit through dissolution of the crystal substance around the dislocation line (in our case, by means of the formation of complexes with the cation of the additive). The dissolution mechanism consists in the creation of a kink on a step of monomolecular height (the step is directed along [100]) and the motion of this kink. The first process is affected by the difference in chemical potentials of the etchant and the crystal; the second, by the presence in the solution of a "poison" for step motion. Depending on the rate of these processes, the shape and orientation of the pit change. The rate of kink formation is greater in the presence of the complexes $[Pb(H_2O)_4]^{2+}$ than of $[Cu(H_2O)_4]^{2+}$ or $[Ba(H_2O)_4]^{2+}$. We believe that planar isomorphism does not exist during etching. When selecting the cation of an additive for the etchant, one should proceed from the complex-forming properties of the cation and from the reactions that may occur during etching.

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