ESD of nonthermal halogen atoms from In-doped (001)KBr

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Abstract

We have measured the kinetic energy distributions of neutral halogen atoms emitted due to electron-stimulated desorption (ESD) from In-doped (001)KBr single crystals. The concentration of In^+ in investigated samples varied between 10^{17} and 10^{20} particles/cm^3. The measurements were performed at target temperature of 150°C. In all cases the energy spectra consist of two peaks. The distribution of low-energy particles can be described by the thermal (Maxwellian) energy spectrum. Particles contributing to the second peak have nonthermal kinetic energies. The emission of halogen atoms having nonthermal energies decreases with an increase in the concentration of In impurities. At the same time, the emission of thermal particles does not seem to be sensitive to variation of In^+ concentration. At the temperatures of interest here, In^+ impurities are known to be very efficient traps for migrating holes but not to influence the migration of H-centers. The obtained results support the model of nonthermal halogen desorption which requires a long range diffusion of holes from the bulk to the surface as a necessary step of the process.

1. Introduction

The ESD of alkali halides has been a subject of numerous investigations during the last two decades [1]. It has been found that the flux of desorbing particles consists predominantly of neutral atoms of both solid components (alkalis and halogens) as well as neutral molecules and clusters. A small fraction of positive and negative ions has also been observed [2,3]. Most of the ejected neutral particles have low, thermal kinetic energies and are emitted with cosine-like angular distributions [4]. For several alkali halides, however, a considerable fraction of halogen atoms is ejected with nonthermal energies of approximately 0.3 eV. The angular distribution of these particles is peaked along the $\langle 001 \rangle$ direction for well defined single crystalline surfaces [4,5].

This contribution focuses on the desorption of halogen atoms with nonthermal energies. We will report here the experimental data obtained recently in our laboratory on ESD of In-doped (001)KBr crystals. These measurements enable us to determine the role of holes diffusion in the desorption of nonthermal halogen atoms. The electron–hole pairs are created in the initial steps of energy deposition by penetrating projectiles. They can be created anywhere in

the valence band of alkali halides, thus acquiring a rather wide distribution of initial kinetic energies [6]. For example, in KBr the width of the valence band is about 2.6 eV [7] so that, on average, the holes could have as much as 1.3 eV excess energy. Such holes are often called "hot holes" [8]. High initial energy makes "hot" holes very mobile providing an efficient transport mechanism of the energy deposited originally in the bulk of the crystal to the surface. In one of our previous papers we have shown that in order to describe properly the experimental dependence of the nonthermal Br yield on the energy of primary electrons impinging on (001)KBr, one should assume the mean diffusion length of carriers leading to desorption to be longer than 100 Å [9]. Unfortunately, no more direct evidence about a nature of such carriers could be drawn from that experiment. It is known, however, that the migration of holes can be altered significantly by monovalent mercury-like ion impurities (Tl^+, In^+, etc.) [10–12]. When added in minor amount, these ions occupy the alkali ion sites, thus, preserving the overall crystallographic structure of the crystal. At low temperature, the mercury-like impurities lead to a pronounced stabilization of electrons, holes and other defects near the ion impurity [10–12]. At elevated temperatures, however, only holes are effectively trapped on these ions [13–15]. In result, if diffusion of "hot" holes is indeed supplying the excitation to the surface which results in the emission of nonthermal atoms one can expect that the efficiency of this channel should decrease with the increase of the concentration of "hole

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traps". To verify this preposition we have measured the time-of-flight distributions and the total desorption yields of Br atoms emitted from 1 keV electron-bombarded (001)KBr samples having various concentrations of In ions.

2. Experimental

The details of the experimental setup have been described previously [16]. Briefly, the random-correlation time-of-flight (TOF) spectrometer with a flight path of 0.31 m was used to measure TOF distributions of neutral halogen atoms. Neutral atoms leaving the surface along the normal were ionized in an electron-impact ionizer and mass selected in a quadrupole mass spectrometer. The desorption was stimulated by a 1 keV electron beam directed at 45° with respect to the surface normal. The electron current was monitored by a Faraday cup and the spot size of the beam was determined by a CCD camera. Since it is known that the relative contribution of the thermal and nonthermal components depends on the current density of bombarding electrons [17], all measurements were done at the same electron current density. The samples were (001) single crystals of KBr doped with In concentrations ranging from 10^{17} to almost 10^{20} cm^{-3} as determined by an optical absorption technique. All the samples were mounted simultaneously on a sample holder and were cleaned by heating to 470 K in vacuum for several hours. The measurements were taken at 150°C to minimize the effect of In impurities on the diffusion of charge carriers and defects other than holes.

3. Experimental results and discussion

Time-of-flight distributions of Br atoms desorbed by 1 keV electrons from (001)KBr crystals doped with In are shown in Fig. 1. In general, two components are clearly visible in the spectra. The broad, temperature dependent peak can be fit by a Maxwell–Boltzmann distribution corresponding to a macroscopic surface temperature and is due to thermally emitted particles. The narrow peak with temperature independent maximum corresponding to a kinetic energy of approximately 0.25 eV is due to the ejection of hyperthermal particles. By integrating the areas under each of the peaks shown in Fig. 1 and by measuring the relative halogen desorption yield from all the samples, one can separate the total emission into the thermal and nonthermal components. The result is shown in Fig. 2. Clearly the thermal emission is barely influenced by the presence of indium. At the same time, the emission of nonthermal halogen decreases significantly with an increase in indium concentration.

1 keV electrons incident on alkali halide crystal create predominantly conduction band electrons and valence holes As we already describe in the introduction, the holes may have quite high kinetic energy and, consequently, they can diffuse over large distances in the crystal. Holes that arrive at the surface can neutralize surface halogen ion and lead to the emission of nonthermal neutral halogen atom. A detailed discussion of possible scenarios for surface halogen emission was given in Refs. [1,18].

The above model can be verified by checking whether the yield of nonthermal emission depends on the number of holes arriving at the surface. It is well known that mercury-like ions, like for example In$^+$, are very efficient hole traps. Two different mechanisms of hole trapping have been identified in the literature [10,11]. In the first process, In$^+$ traps a hole and is converted into doubly ionized In^{2+}. In^{2+} ions are stable, however, they can recombine with an electron or F-center. In result, an excited (In$^+$)* center is formed which can return to its ground-state electronic configuration by emission of a broad band luminescence with a peak energy around 3.0 eV in KBr. In the second channel, In$^+$ is first neutralized
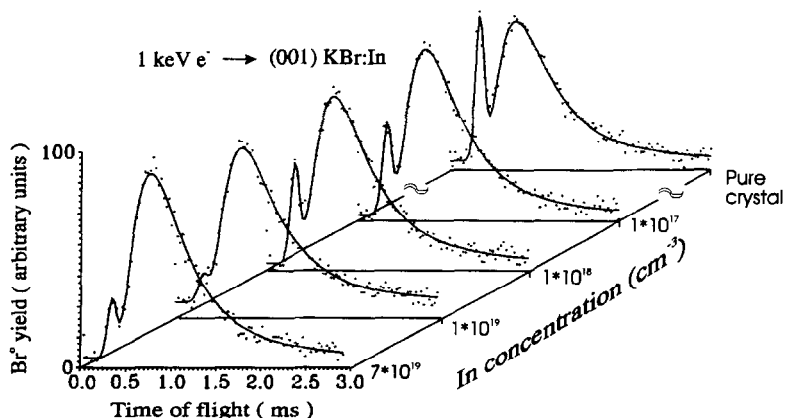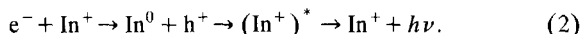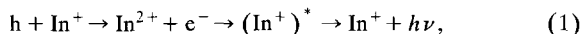

Fig. 1. Time of flight distributions of Br atoms emitted from 1 keV electron-bombarded, In-doped (001)KBr. The measurements were done at 150°C. Solid lines are plotted to guide the eye.

by trapping an electron. Neutral In^0 can be subsequently ionized to the excited state by recombination with a hole, and, finally, the process again results in the emission of radiation. Both processes can be summarized as follows:

$$h + In^+ \rightarrow In^{2+} + e^- \rightarrow (In^+)^* \rightarrow In^+ + h\nu, \qquad (1)$$

$$e^- + In^+ \rightarrow In^0 + h^+ \rightarrow (In^+)^* \rightarrow In^+ + h\nu. \qquad (2)$$

The doubly charged mercury-like ions are very stable in alkali halides. For example, the chemical determination of Tl^{2+} concentration indicates that Tl^{2+} ions are present up to 200–800°C depending on the host crystal [13]. On the other hand, it is known that if the temperature exceeds room temperature, the electron trapped in In^0 center is almost instantly thermally promoted to the conduction band [12]. Therefore, at the temperatures of interest in this paper only process (1) should be responsible for hole trapping.

It is visible in Fig. 2. that the emission of nonthermal atoms decreases with the increase of the concentration of In dopant. This observation is strong evidence that hole diffusion is indeed a necessary step for emission of athermal halogen atoms. We have also observed that the emission of nonthermal atoms decreases with the irradiation time for doped crystals, as presented in Fig. 3. For instance, the signal dropped to 50% of its initial value when the target of In-doped KBr (10^{19} cm^{-3}) was bombarded for 60 min with an electron beam with a current density of 20 μA/cm^2. The rate of decay decreases with a decrease
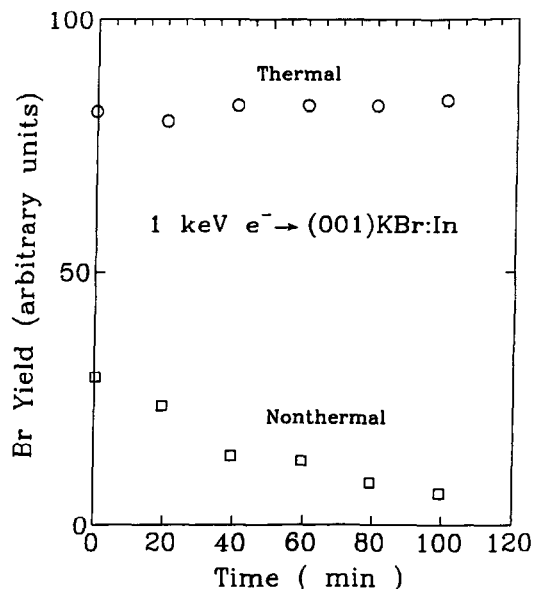
Fig. 3. Time dependence of the thermal and nonthermal Br° desorption yield electron-irradiated (001)KBr:In (10^{19} cm^{-3}). The measurements were done at 150°C. The sample was bombarded by 1 keV electrons with a current density of 20 μA/cm^2.

of concentration of indium and the nonthermal emission is constant from a pure sample. We believe that this phenomenon is caused by an increase of In concentration in the surface region due to removal of halogen and alkali atoms by bombarding electrons. During electron irradiation In impurities are not desorbed from the surface and, in result, their concentration will increase. The ESD of alkali halides is a very efficient process. A total desorption yield equivalent to 14 NaCl molecules atoms has been measured for NaCl single crystal at 300°C [19]. If we assume the desorption yield for KBr sample at 150°C of the order of 5 we can estimate that approximately 40 monolayers are removed during 1 min of electron bombardment. As a consequence, all In ions located in this volume will be accumulated in the surface zone and the concentration of In impurity in the surface region will be enhanced. This, in turn, will reduce the nonthermal emission due to the process described earlier. The initial yield of nonthermal emission can be recovered by annealing the crystal at 470 K for 30 min. Therefore, we assume that during annealing the excess In evaporate and/or diffuses into the bulk of the crystal and the initial In concentration is restored.

It is also visible in Figs. 2 and 3 that the yield of thermally emitted Br atoms is very weakly, if at all, dependent on both the In-concentration and irradiation time. The emission of thermal halogens is a secondary process with respect to the ejection of nonthermal particles. When the thermalized valence hole in bulk of alkali halide quickly localizes (self-traps) on a pair of lattice halide ions [20] they relax toward each other symmetri-
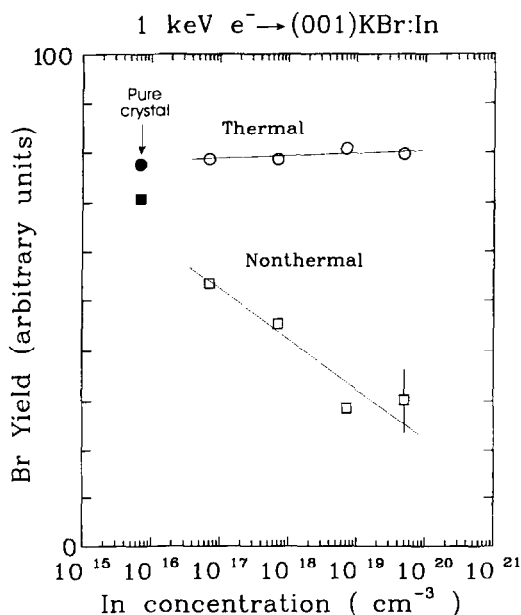

Fig. 2. Dependence of the thermal and nonthermal Br° yield on Indium concentration in 1 keV electron-irradiated (001)KBr:In single crystals. Black markers indicate results for pure sample. The measurements were done at 150°C. The solid lines are drawn to guide the eye.

cally along $\langle 110 \rangle$ in NaCl-type crystals forming so called V_k center. A self-trapped exciton (STE) results when an electron becomes bound to the site of the self-trapped hole. Such self-trapping occurs on a sub-picosecond time-scale [21] and can result in the emission of polarized light. This decay channel dominates at low temperature [22]. At higher temperatures STE can decay nonradiatively leading to the formation of F- and H-centers [20]. At the temperatures of interest in this paper, H-centers can migrate inside the crystal, arrive at the surface and the neutral halogen atom can desorb thermally [23]. The yield of thermally emitted halogen atoms depends on the diffusion range of the interstitial halogen atoms but also on the depth of deposited energy. In the doped crystals diffusing H-centers can be stabilized in the vicinity of a monovalent impurity at low temperatures [14,15]. This process is assumed to be responsible for the enhanced F-center coloration of irradiated In or Tl doped crystals [24]. Ashimova and Usarov have reported, however, that H_A centers (H-center trapped on impurity) are only stable below 110 K in In-doped KCl and below 90 K in In-doped KBr [15]. This observation indicates that mercury-like impurities become "transparent" to the diffusion of H-centers at high temperature. It is also very unlikely that the highest concentration of In used in our experiments, roughly 1 In atom to 10^3 lattice atoms, could influence the deposition of energy by primary electrons. As a consequence, one can expect that the emission of thermal halogens at high temperatures should not be altered by the presence of In impurities, which is indeed observed in our experiment.

4. Conclusions

The time-of-flight distributions of neutral Br atoms have been measured from electron-bombarded indium-doped (001)KBr single crystals at 150°C. It has been observed that the emission of nonthermal atoms decreases with the increase of indium concentration, while, the emission of thermal Br atoms is rather insensitive to the concentration of this impurity. It is known that In^+ ions are very efficient hole traps and are "transparent" to the diffusion of H-centers at elevated temperatures. These results strongly support the model in which diffusion of holes is a necessary step for nonthermal halogen emission.

Acknowledgements

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