

Surface Topography Dependent Desorption of Alkali Halides

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Electron-stimulated desorption of the (100)KBr surface has been investigated in vacuum with noncontact atomic force microscopy and mass spectroscopy. It has been found that both desorption components (K and Br) show oscillatory dependence on the electron dose with the oscillation amplitude decaying gradually. These results correspond with periodically varying, as a result of a layer-by-layer desorption, surface topography. It is proposed that the surface terrace edges act as traps for excited F centers diffusing in the crystal. The oscillating density of terrace edges varies surface recombination/reflection rates for the F centers and modulates the balance between surface and bulk deexcitation of the crystal.

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Desorption induced by electronic transitions (DIET) has attracted wide interest of the scientific community for several decades [1]. First of all, it is of great importance from a fundamental point of view to understand details of the energy conversion processes following local excitations of the solid which are responsible for a multitude of effects as defect creation, radiation damage, luminescence, and particle emission from solid surfaces. Furthermore, all those DIET related phenomena have many important consequences in the technology of devices containing semiconductor/insulator junctions, processes induced by the solar radiation in space ices, radiation damage of optical materials, nuclear waste storage, etc. In particular, recent investigations of the electron-induced desorption (ESD) and photon-induced desorption of alkali halides made it possible to establish a theoretical model describing diffusion processes responsible for transfer of excitation from the bulk to the surface [2]. However, the influence of the surface topography on the desorption process remains so far unknown.

In alkali halides the energy of impinging electrons is primarily deposited in the form of hot electron-hole pairs which initiate either the nonthermal desorption process at the crystal surface [3] or the formation of Frenkel defects (F and H centers) in the bulk. The diffusion of Frenkel defects and their recombination with the surface lead to emission of both halogen and alkali atoms with energies described by the Maxwellian formula (thermal desorption). The recombination of the H center with the crystal surface can be understood easily. The surface halogen adatom produced by the H center is weakly bound (0.14 eV according to Ref. [4]) and no specific surface sites are needed for desorption. In contrast, the mechanisms of recombination

of the F center with the crystal surface are not yet clear [4]. Kubo *et al.* [5] have found that during electron irradiation of a NaCl(100) crystal, at the temperature of 120 °C, F centers are accumulated at the crystal surface. Optical excitation (within the F band) of these centers leads to emission of alkali atoms. Puchin *et al.* [6] has performed total energy and adiabatic potential energy surface (APES) calculations for the F center at the surface of (100)NaCl. They have found that the F center in the ground state cannot initiate desorption of an alkali atom at the perfect surface because of the energy deficit of ~ 2 eV. According to the same theoretical work the $2p$ -excited F center could have sufficient energy to facilitate the desorption but, as shown by the APES study, an energy barrier for such a transition should inhibit the desorption process. As a result of these findings low-coordinated surface sites like terrace edges, kinks, and corners have been examined and it has been concluded that alkali atom desorption is likely to occur preferentially at these low-coordinated sites [6].

Recently it has been demonstrated that stimulated desorption of alkali halide crystals proceeds in a layer-by-layer mode [7,8] by growth and linking of pits (of monoatomic depth) on the (100) crystal surface. Therefore, during the ESD experiment the surface density of low-coordinated sites oscillates as a function of the radiation dose. The present experiment has been performed in order to demonstrate the crucial role of low-coordinated surface sites in the electron-stimulated desorption of the alkali halide crystal.

In our experiment we have used quadrupole mass spectroscopy (QMS), time-of-flight spectroscopy (TOF), and noncontact atomic force microscopy (NC-AFM). KBr crystals were cleaved in air and subsequently put into a

vacuum system. The base pressure in the system is 2×10^{-8} Pa. The crystals, kept at the temperature of 130°C , have been irradiated with a 1 keV electron beam (with current of $0.2 \mu\text{A}$ and the spot of $\sim 0.2 \text{ mm}^2$) scanned over the area of $\sim 2 \text{ cm}^2$. Prior to the AFM measurements irradiated crystals have been kept in vacuum for several hours to allow for decharging of the surface. The AFM scans have been done at room temperature. In a single experimental run both desorption signals (K and Br) have been recorded as a function of time.

The QMS signals as a function of the irradiation dose are presented in Figs. 1a and 1b. Both (Br and K) desorption fluxes show damped oscillations with a period corresponding to a dose of $\sim 20 \mu\text{C}/\text{cm}^2$ ($1.25 \times 10^{14} e/\text{cm}^2$). At the beginning of irradiation, however, the potassium component is relatively low and increasing, whereas the initial desorption signal of bromium is very high and decreasing rapidly. After a dose of $\sim 2 \mu\text{C}/\text{cm}^2$ both K and Br signals oscillate almost parallel.

The TOF spectroscopy has been used to check velocity distributions of desorbed atoms. The TOF spectrum could be measured every 10 s and sets of the spectra vs irradiation dose have been recorded for both K and Br. It has been found that from the very beginning of irradiation the

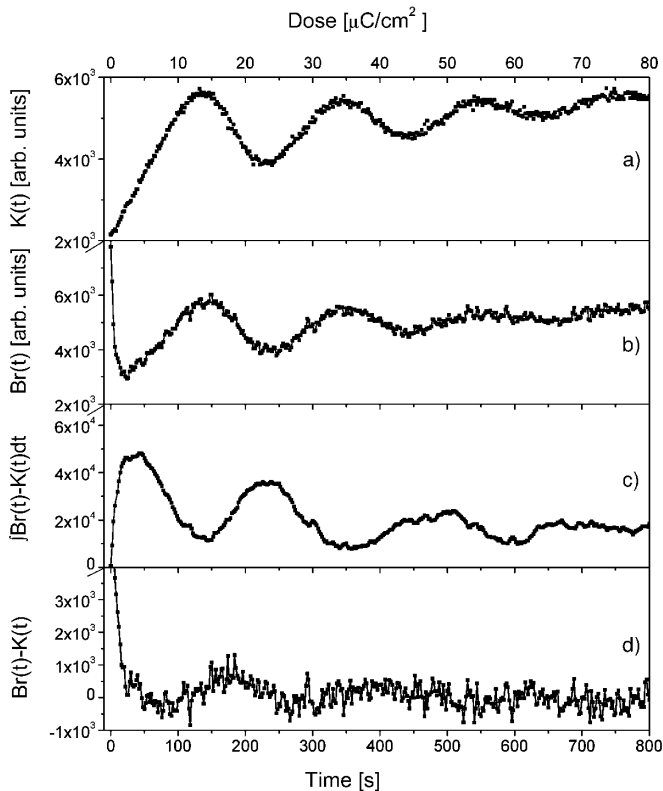


FIG. 1. The desorption signals during ESD of (100)KBr as a function of the electron dose, normalized under assumption of stoichiometric desorption after a long time: (a) the K signal; (b) the Br signal; (c) the number of F centers stored in the crystal; (d) the difference between the Br and the K signal.

Br TOF distribution has a typical double structure [3], the nonthermal component with a maximum around 0.3 eV and the thermal component characterized by macroscopic surface temperature, whereas the K TOF spectrum has the Maxwellian shape only. It is quite striking that only the Maxwellian components of desorption oscillate with the electron dose. In contrast, the nonthermal component is independent on the dose. For our QMS measurements we have chosen such experimental conditions (temperature and low current density) that the nonthermal component constitutes an insignificant fraction of the total Br signal. The TOF measurements have proved that the desorption fluxes shown in Figs. 1a and 1b are representing a single desorption process from the very beginning of the electron irradiation.

The NC-AFM images of the irradiated KBr surface, taken for small increments of the irradiation dose, indicate that one period of oscillation corresponds to removal of a single monolayer. Examples of such AFM images measured at the irradiation doses required to obtain the first maximum and the subsequent minimum of the desorption curves (see Fig. 1) are presented in Fig. 2. It has been found that the K desorption signal is correlated with the edge density on the surface. The maximum efficiency of the process occurs for the surface where islands of monoatomic height account for $\sim 50\%$ of the surface area (as seen in Figs. 2a and 2b). In such a state the density of edge atoms reaches about 5% of the total atom density in the KBr(100) monoatomic layer ($0.92 \times 10^{15} \text{ cm}^{-2}$). The minimum efficiency of the desorption process is observed for a flat surface with a few small pits of monoatomic depth

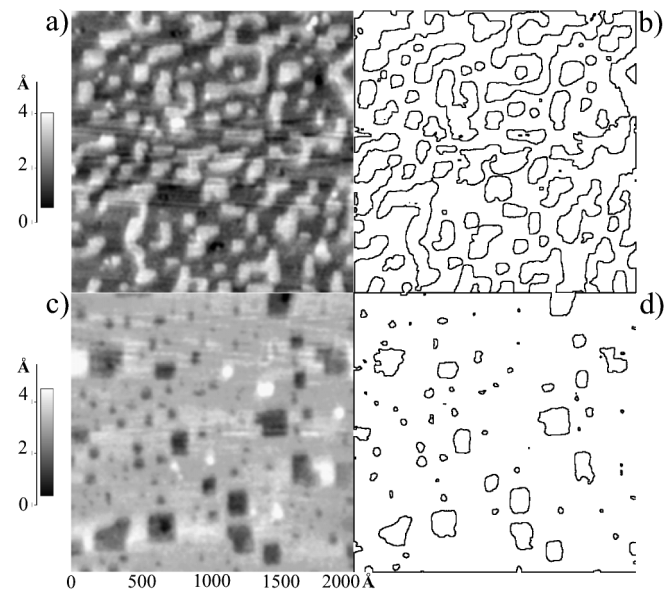


FIG. 2. NC-AFM images of the (100)KBr surface bombarded by 1 keV electrons. (a) The image if the irradiation has been stopped at the desorption yield maximum and (b) corresponding surface step distribution. (c) and (d): Analogous images if the irradiation has been stopped at the desorption yield minimum.

(as seen in Figs. 2c and 2d) which corresponds to the density of edge atoms of $\sim 1\%$.

Since our desorption is a steady-state process the periodic modulation of desorption fluxes has to be an effect of changing branching ratio between these deexcitation paths which initiate atomic emission and those paths which do not. In the crystal bulk, a keV electron creates a large number of valence-band electronic excitations, i.e., electron-hole pairs and free excitons (electron-hole plasma). In an ionic solid, which is characterized by strong electron-phonon coupling, such primary excitations are quickly localized by self-trapping in time of the order of 10 ps. This process is associated with the drastic lattice deformation. Subsequent evolution of self-trapped excitations leads to the formation of separated H - and F -center pairs (primary Frenkel pairs) [9]. As a result of thermally assisted diffusion these centers can recombine to a so called “ π -luminescent” state of the self-trapped excitons and decay with the emission of a ~ 2.5 eV photon [10,11]. However, in the surface proximity a concurrent deexcitation channel is possible; the H center and the F center may decay separately through recombination with the surface causing the emission of a halogen atom and an alkali atom, respectively. It should be noticed that the diffusing H center (which is essentially an interstitial atom on an anion sublattice) does not result in surface erosion—after the emission act the perfect crystal surface is restored. It is the diffusing F center which induces changes in the surface topography.

At this point we emphasize that, at temperatures of our experiment, the processes involved in alkali atom desorption are rather fast and last no longer than 10^{-6} s [2,5,12]. This implies high mobility of F centers. On the other hand, the initial Br signal is much higher than the K signal until irradiation time of 20 s is exceeded (see Figs. 1b and 1c). This indicates that a significant fraction of F centers is accumulated in the crystal in immobile form not causing alkali atom emission.

It has been found previously that the ground state F centers are immobile, whereas excited and relaxed F^* centers can easily diffuse in the crystal [13–15]. In the recent paper Salminen *et al.* [15] have demonstrated that initially uniform F center concentration in electrolytically colored KBr crystal can be modulated, if the crystal is exposed to 518 nm light which is within the F -center absorption band. The light induces the F -center diffusion and aggregation. A resulting F -center microscopic distribution can be maintained at elevated temperatures (100–250 °C) for a long time provided that the crystal is kept in darkness. Similar findings, although for a different crystal, have been reported by Kubo *et al.* [5] who observed emission of Na atoms from NaCl crystal pre-irradiated with electrons and then exposed to the light within the NaCl F -absorption band. According to Puchin *et al.* [6] the F center in the ground state cannot cause atomic emission because of the energy deficit of about 2 eV. Although the excited F cen-

ter may have sufficient energy to facilitate the emission the probability for such a process is rather low. Alkali atom desorption is then likely to occur preferentially at low-coordinated surface sites. It is expected that the diffusing F^* center is either reflected back to the bulk at the flat (100) surface [4] or, when it hits a surface step, it is trapped there. At the step the F^* center neutralizes an alkali ion and initiates its emission—in effect a pair of vacancies (anionic and cationic) is created at the surface edge. This is consistent with our NC-AFM results that, during irradiation, the ripening of pits, rather than the formation of new features, is seen. Depending on the surface state different fractions of the diffusing F^* centers are reflected back to the bulk where they can deexcite and stabilize. In such a case, within the distance of the F^* -center diffusion length from the surface, the concentration of stable F centers is controlled by the surface topography. Consequently, in a steady state, the H -center diffusion takes place in a space containing a number of traps which is dependent on the surface topography. As a result of F -center and H -center annihilation the Br desorption signal should vary with the electron dose “sensing” the inverse F -center concentration at surface proximity.

In order to demonstrate the above described role of the immobile, ground state F centers in desorption the following analysis of our experimental data has been performed. First, the K and Br signals have been normalized using signal values for large doses where oscillations are not present and where, without a doubt, equal numbers of both crystal constituents are emitted [3]. Second, the difference between Br and K signals has been obtained. Since angular distributions are the same (cosinlike) for both Br and K desorbed atoms, this function, plotted in Fig. 1d, reflects the instantaneous nonstoichiometry of desorption, or number of F centers being accumulated in the crystal at a given time. Third, this difference function has been integrated over time and, as a result, the total number of immobile F centers stored in the crystal has been obtained. As seen in Figs. 1b and 1c stored F -center density is in striking anticorrelation with the desorbed halogen atom flux. This evidences that the desorption efficiency is indeed controlled by the process of annihilation of the H center and the immobile F center.

Taking into account the number of counts recorded upon desorption of a single monolayer we can estimate the amount of stable F centers accumulated in the crystal—it varies in the range 0.5×10^{13} – 2×10^{13} cm $^{-2}$. Although we have expressed the amount of stable F centers stored in the crystal in surface density units, we do not argue that they are accumulated in the strict surface layer. In particular, recent NC-AFM images of electron-bombarded (100)KBr, taken with atomic resolution, indicate that F centers are not present in the above concentration in the top surface layer [16] and, moreover, the stored F -center density is anticorrelated with the surface edge density, so these defects do not accumulate at terrace edges.

Apart from the F - H annihilation a few other reactions may, in principle, occur in the crystal bulk: aggregation of $F^{(*)}$ centers into X centers [15] and reactions of the H center with the F^* or X . However, transient F^* concentration (resulting from the primary excitation cascade) is of the order 10^{18} cm^{-3} [2] while the stored F concentration is estimated as $\sim 10^{19} \text{ cm}^{-3}$. Therefore, it is expected that the stored F -center concentration is a dominant factor controlling the ESD efficiency. On the other hand, the total number of stored F centers (of the order of 10^{13} cm^{-2}) is small if compared with the number of K atoms in the monoatomic layer of (100)KBr ($0.459 \times 10^{15} \text{ cm}^{-2}$). Thus both K and Br signals are observed to be almost in phase—the variation of the total number of stored F centers does not superimpose significant changes on the K atom desorption flux apart from the very beginning of irradiation where the steady-state concentration of F centers is rapidly building up from zero.

Finally, we reiterate that efficient desorption of alkali atoms from alkali halide crystals and the time scales of this process provide strong evidence that electron irradiation leads to the production of the excited (mobile) F^* centers. Whether the excited F^* center is a primary product of the exciton/electron-hole pair decay or the ground state F center is excited in a secondary process is an open question. (For example, the F center could be excited in the electron-hole plasma created by a single incident electron as discussed by Puchin *et al.* [6] in a sequence of events: trapping a hole by the F center resulting in an anion vacancy and trapping an electron by the vacancy into an excited F^* -center state.)

In conclusion, the following scenario is proposed to describe defect-mediated desorption processes in alkali halides. The electron bombardment of the crystal leads to production of mobile F^* and H centers. These defects diffuse through the crystal independently. If the H center reaches the surface the halogen atom is immediately emitted. However, the F^* center cannot initiate desorption unless it is trapped at the terrace edge. Thus, at the surface, a large fraction of F^* centers is reflected back to the bulk where they deexcite and stabilize. The steady-state concentration of immobile F centers is built after a certain dose of irradiation. This concentration in the surface proximity is controlled by the surface recombination/reflection rate for diffusing F^* , which depends on the surface step

density. Since the desorption occurs in a layer-by-layer mode, oscillating step density and accordingly modulated balance between the H - F annihilation and the desorption leads to observed oscillatory behavior of desorbed atom fluxes. The damping of the oscillations is explained by the fact that the desorption process does not occur in a perfect layer-by-layer mode, but the next layer is damaged before the previous one has been completely removed [7,8]. After a few periods of oscillations, holes in the surface are distributed across several layers and the modulation of the surface step density is lost.

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