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Hot-carrier transport processes in stimulated desorption of alkali halides

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Electron- and photon-stimulated desorption of epitaxial thin films and bulk single crystals of alkali halides has been investigated. It has been found that the widely accepted model based on self-trapped exiton decay and thermally activated defect diffusion cannot account for a number of experimental observations. In particular, it cannot explain the stability of the very thin alkali-halide films against the electron beam, and it fails to interpret correctly the yield dependence of the halogen atoms emitted with nonthermal energies on the film thickness and sample temperature. It is shown that for satisfactory interpretation of those data one has to take into account early stages of crystal excitation, i.e., hot carrier formation and transport processes occurring prior to self-trapped exciton phase. Consequently, a comprehensive description of the observed desorption features is presented. [S0163-1829(98)01943-2]

I. INTRODUCTION

When a keV electron hits a crystal it loses energy in a cascade of excitations[1] having a spatial extent of ∼1000 Å. Although most of the initial excitations are of a core-type, subsequent fast ($\sim 10^{-17}$ s) decay of these excitations and reabsorption of energy of their products causes that after a time of about 10^{-15} s nearly all primary energy is deposited in a form of valence-hole–conduction-electron pairs and the lattice vibrations.[2] The electrons and the holes created by the cascade are hot. They possess kinetic energies due to the fact that all states in the bands are equally populated by electron excitation. An average initial energy of the hot electron or hot hole may be taken as a half of the conduction of valence bandwidth, respectively. In case of alkali halides this amounts to 1–2 eV.[3] The evolution of moving charges in the polarizable lattice is often described in standard textbooks.[4] Nonstatic (e.g., moving) charges interact with the longitudinal-optical phonon field through the electric field of the polarization wave. Due to this coupling the kinetic energy of charged (quasi)particle is gradually transferred to the lattice by collisions with phonons. The energy released to (absorbed from) the alkali-halide lattice during a single optical phonon creation (absorption) event is 20–30 meV (Ref. 5) (depending on the compound). Typically a quasiparticle colliding with a phonon changes its energy by a small amount. However, due to comparable band momenta of the particle and the phonon, its velocity vector may undergo a considerable change in direction. As a result the motion of the hot quasiparticle in the alkali-halide lattice is Brownian-like. Furthermore, since we expect that the hot particle mean free path is much shorter than the size of an excitation volume, all electrons and holes should roughly be confined within the cascade. A dense electron-hole plasma formed this way ($\sim 10^{18}$ e-h pairs/cm^3) lasts until thermalization of the excitation products ($\sim 10^{-12}$ s). After that time electrons and holes become slow enough to cause the surrounding crystal to rearrange significantly and minimize the total system energy (self-trapping). There are a few possible lattice configurations around self-trapped electrons and self-trapped holes that have been discussed in detail by Williams *et al.*[6] Subsequently, the defects may decay or migrate in the crystal by the thermally activated hopping motion.

An extreme instability of alkali halides against ionizing radiation was discovered in the 1950s as a result of wide interest in radiation damage of materials. In the late 1960s it was discovered with the use of Auger electron spectroscopy (AES) that the alkali-halide surface subjected to electron bombardment was deficient in the halogen component.[7] Later measurements by Townsend *et al.*[8] and de Vries and co-workers[9] showed that the electron-stimulated desorption (ESD) of alkali halides occurs as a very efficient process leading to preferential emission of the halogen component. The excess alkali atoms either accumulate on the surface in a form of metallic islands or, if the sample temperature is high enough, evaporate from the crystal surface. Detailed measurements of the halogen atom-velocity spectra for rubidium and potassium halides indicated two components.[9,10] One is well described by a thermal, Maxwell-Boltzmann distribution characterized by the surface macroscopic temperature; the second is a hyperthermal component with a maximum around 0.3–0.4 eV. The intensity of the Maxwellian component is activated with the target temperature (Arrhenius-type dependence) while the intensity of the hyperthermal part decreases weakly with increasing temperature. Alkali atoms are emitted with thermal energies under all conditions but their time-of-flight spectra could be influenced by delayed emission from the surface at low temperatures.[11] It has been commonly believed that atomic emission from alkali halides results from evolution of the self-trapped excitons[9,12,13] and that the earlier stages of excitation are insignificant for the desorption processes. In the early model proposed by Townsend *et al.*[8] the nonthermal emission originates from the decay of the self-trapped exciton (STE) near the surface initiating the so-called ‘‘focused replacement cascade.’’ The thermal component was described by Szymonski[14] as due to the hopping motion of defects, F and H center pairs (the F center is formed by an electron trapped in a halogen vacancy, the H center is formed by an interstitial halogen atom), produced by internal decay of STE, carrying energy to the surface and either producing halogen adatoms on the surface (*H*) or neutralizing surface alkali ions (*F*). All these concepts assumed that the initial defect concentration was proportional to the primary deposited energy density.

It is expected, however, that hot quasiparticles, despite their very short lifetimes, can redistribute the primary excitation energy in the solid and provide an efficient transport of excitation energy from the bulk to the surface or to the interface. Elango[15] observed a loss of quantum efficiency in electron-excited intrinsic luminescence from impurity-doped NaCl, which they attributed to the hot hole diffusion transport of the excitation to impurities. Szymonski *et al.*[10] have measured the nonthermal emission of halogen atoms from alkali halides and argued that the emission process is preceded by the hot excitation diffusion. Nevertheless, the role of the hot excitation transport in radiation-induced processes in alkali halides is still controversial and not known in detail. In this paper we present a comprehensive review of our recent experimental data on electron- and photon-induced desorption of thin films and bulk alkali halides. A consistent description of these data is given in terms of a model taking into account both possible energy-transport processes: the transport by hot (nonequilibrium) carriers and by the thermally activated hopping motion of lattice defects.

II. EXPERIMENTAL TECHNIQUE

An UHV system consisting of two chambers was used in the experiment. The analysis chamber contained an electron gun, low-energy electron diffraction (LEED) diffractometer, a hemispherical energy analyzer, and a quadrupole mass spectrometer. The preparation chamber enabled substrate and sample preparation and it contained an ion gun, a quartz crystal microbalance, and an effusion cell for molecular-beam epitaxy. Magnetically coupled transfer allowed the sample to be moved between the two identical target manipulators in the two chambers. The base pressures were less than 3×10^{-10} torr in the analysis chamber pumped by a combined ion/titanium sublimation pump, and less than 3×10^{-9} torr in the preparation chamber, pumped by a turbomolecular unit. $A_{\mathrm{III}}B_{\mathrm{V}}$ semiconductors were used as substrates for thin-film epitaxial growth. These semiconductors have the cubic zinc-blende structure, and the variety of different component combinations allows finding a substrate that has a good lattice match with the given alkali-halide compound. Moreover, there exists a strong bond between the halogen ion and the A_{III} element of an $A_{\mathrm{III}}B_{\mathrm{V}}$ substrate that properly arranges the first monolayer of deposit.[16] In the present study a gallium arsenide substrate was chosen for sodium chloride (mismatch ~0.4%) and an indium antimonide substrate for potassium bromide (mismatch ~1.5%). The substrate was cleaned with repetitive sputtering of low-energy Ar ions (0.8 keV) and annealing (600 and 500 °C for GaAs and InSb, respectively). This procedure was used to generate the clean, $c(8\times2)$ reconstructed surface rich in gallium or indium, as indicated by comparing the AES spectra taken at grazing and 45° excitation. This was consistent with previous work on the structure of the reconstructed $A_{\mathrm{III}}B_{\mathrm{V}}$ surface.[17,18] The samples of thin epitaxial films were prepared by evaporation of the alkali-halide vapors from the effusion cell at a rate of 0.5–1 ML per second onto a clean substrate. ML stands here for a monolayer, understood as a single layer of atoms (thickness; 2.8 Å for NaCl, and 3.1 Å for KBr.) It was found that a deposition of the layer corresponding to 3 ML of KBr caused a complete quenching of substrate Auger peaks (appearing at 400–500 eV) observed at a low angle and the change of the LEED pattern from $c(8\times2)$ characteristic for the substrate to sharp (1×1) characteristic of an alkali-halide single crystal occurred below 4 ML, as illustrated in Figs. 1(a) and 1(b). Based on these measurements, together with the previous work by Saiki, Nakamura, and Koma,[19] it was assumed that the growth mode was a two-dimensional layer-by-layer type.

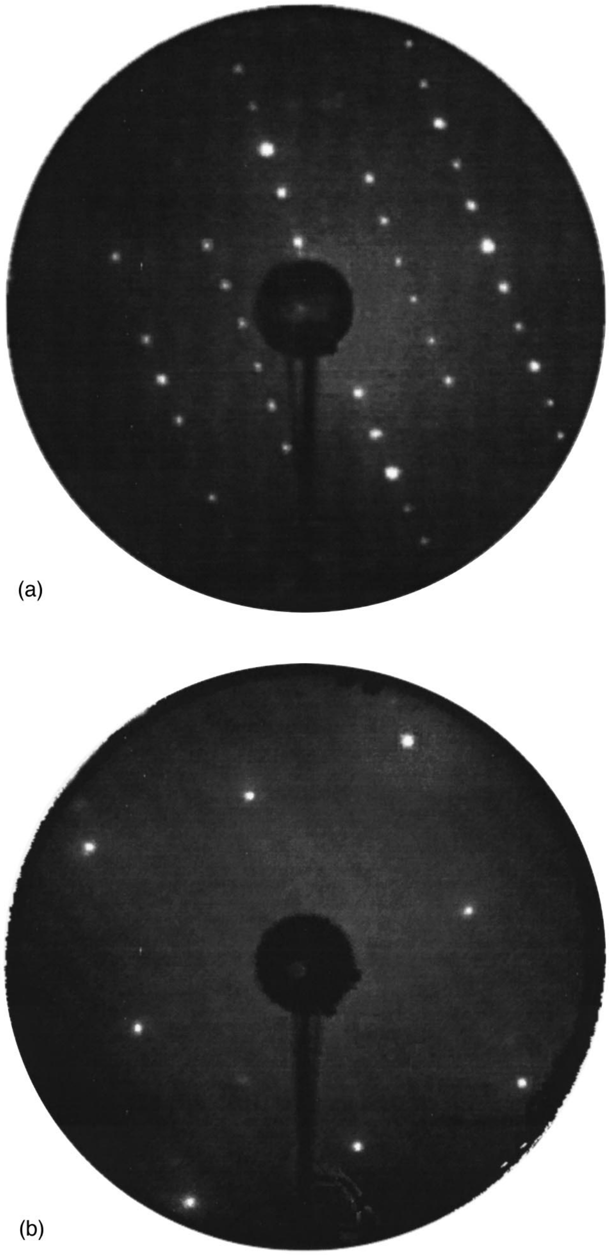

FIG. 1. The low-energy electron diffraction image of the substrate surface (100) InSb prepared for deposition of alkali-halide film (a), and for 4-ML-thick film of KBr on this substrate (b).

Alkali-halide epitaxial films were desorbed by a 2 keV electron beam focused into a 0.5 mm-diameter spot. A total desorption signal of halogen atoms was measured as well, as velocity distributions by means of time-of-flight[20] (TOF). Special care was taken to minimize erosion of the thin films. The electron beam was scanned over an area of ~30 mm^2, and the electron current was minimized to 0.5 μA. A film of given thickness was desorbed until no observable desorption signal was present (which took place at 20–30 Å as described further in the text). The total number of counts registered during this desorption allowed to calibrate our detection system in absolute units of the yield. Experimental conditions were chosen in such a way that the film thickness change due to desorption did not exceed 2% during a single experimental run (whenever constant film thickness was needed).

III. RESULTS, DISCUSSION, AND THEORETICAL CONSIDERATIONS

A. Thermal desorption yields and the thin-film stability against radiation

It has been well established that the thermal component of ESD is universal in alkali halides.[21] At elevated temperatures the majority of atoms emitted from the surface have thermal velocities. This is true for electron[9,22] as well as photon[23] and ion excitation.[24] Standard models describing the process leading to thermal emission start at the final stage of the excitation cascade evolution when the thermalized valence hole stops in the crystal bulk. Static charge causes a rearrangement of the surrounding lattice and trapping of the hole. Consequently, the hole is associated with a certain halogen in the lattice that becomes neutral. Opening an outer p shell of the lattice halogen by hole localization leads to V_k center formation.[6] A covalent bond is formed between the neutralized halogen and a neighboring halogen ion. They move closer together and a dihalide molecule is formed inside the crystal. The stable V_k may trap an electron forming a self-trapped exciton and finally decay into an F, H pair. A detailed description of the STE dynamics is given in Ref. 12. An essential process in ESD is the thermally activated hopping motion of STE decay products. The activation energies for H centers are particularly low and huge desorption yields can be expected in this process. At 400 °C for bulk crystalline NaCl bulk 14 molecules were recorded per single 0.8 keV electron.[25] A thermally activated hopping motion of the defects efficiently transports excitation energy to the surface. At lower sample temperatures an increased probability for the center's radiative recombination of F and H competes with desorption. Nevertheless, in an idealized crystal and at very low excitation density, F and H centers could have extremely long lifetimes and the number of molecules removed from the surface would be close to the number of electron-hole pairs generated in the crystal. Such a low excitation density case may be a model for our photon-stimulated desorption (PSD) experiment where fluxes of 10^{13} photons/mm^{-2} were applied.[23]

For a ~1 keV electron excitation the yield depends strongly on electron current. It is likely, therefore, that the main role in desorption quenching is played by the steady state F center density. For simplicity of the model we assume a constant diffusion length of defects (H centers) across the crystal. Such an assumption is justified since we do not have a large variation of primary deposited energy density in our films. The steady-state concentration of hopping H centers can be described by the following diffusion equation:

$$D_H \frac{d^2 n_H}{dx^2} - \frac{n_H}{\tau_H} + N(x) = 0, \tag{1}$$

where D_H is the diffusion coefficient, τ_H is the lifetime mainly due to F-H recombination, and n_H is a steady-state concentration of interstitials (H centers) as a function of depth (x). The source $N(x)$ is a combination of linear functions adopted from Al-Jammal, Pooley, and Townsend[26] and Bronshteyn and Protsenko[27]

The solution is found as

$$n_H(x) = A_{1,k} e^{x/\lambda_H} + A_{2,k} e^{-x/\lambda_H} + \tau_H N(x), \quad \lambda_H = \sqrt{D_H \tau_H}, \tag{2}$$

where index k stands for different regions of depth x in which the source $N(x)$ is linear, and $A_{i,k}$ are constants to be calculated from additional conditions.

When an H center arrives at the surface it produces a halogen atom weakly bound to the surface, which desorbs in a short time. Thus, the surface acts as a perfect trap for diffusing H centers. In the case of a thin film, an interstitial halogen atom cannot transfer to the substrate and the interface acts as a perfect reflector for diffusion. Accordingly, the following conditions should be taken at the film boundaries: at the surface,

$$D_H \frac{dn_H(0)}{dx} = \Delta_{s,H} n_H(0), \quad \Delta_{s,H} \rightarrow \infty,$$

and at the interface, at depth d,

$$D_H \frac{dn_H(d)}{dx} = -\Delta_{i,H} n_H(d), \quad \Delta_{i,H} \rightarrow 0,$$

where $\Delta_{s,H}$ and $\Delta_{i,H}$ are surface and interface recombination rates, respectively. The coefficients $A_{1,k}$ and $A_{2,k}$ are calculated from the boundary conditions and from the c^1 condition on a solution joining point (the first derivative continuous). The desorption intensity may be taken proportional to the interstitial concentration at the surface. Due to the fact that the hopping motion of interstitials is activated thermally we take, after Ref. 28,

$$\lambda_H = \lambda_0 e^{E_a/kT},$$

where T is the macroscopic target temperature, E_a is the activation energy for a jump to the neighboring interstitial site, and λ_0 is the high-temperature limit of diffusion length of H centers along the coordinate perpendicular to the surface. Additionally, in thin films we have to consider the influence of the interface on the initial energy deposition in the crystal. The substrate has a mass density approximately twice the density of the film (roughly the same holds for the stopping power for electrons[27]). Thus, we expect that the interface increases the amount of energy deposited by energetic electrons at its proximity. Assuming that the energy distributions of electrons at the interface plane are the same in the forward and the backward directions, we may account for this effect simply by mirroring the part of the profile of Al-Jammal, Pooley, and Townsend profile with respect to the interface plane with a certain weight g. This is equivalent

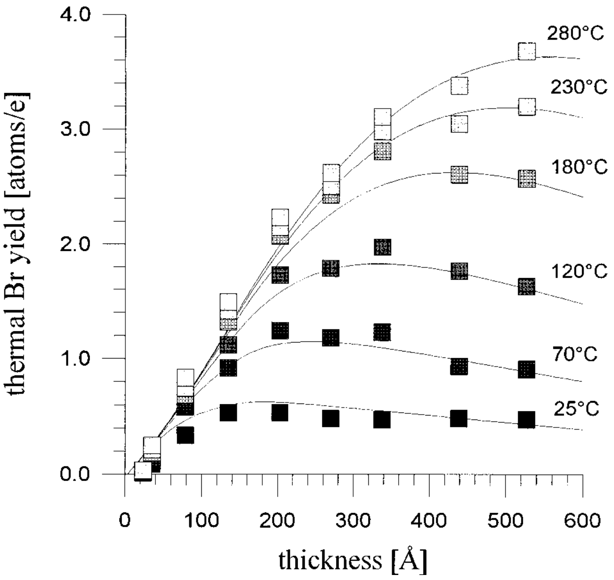

FIG. 2. The ''thermal'' component of Br desorption from KBr films as a function, the film thickness for few different temperatures. Solid lines were evaluated from the thermally activated defect (*H*-center) diffusion model.

to adding the factor $gN(2d-x)$ to the initial excitation source $N(x)$ (where g is the inelastic ''reflection'' coefficient at the interface). In Fig. 2 we can see a comparison of the measured halogen yields (points) and the solid curves calculated from our model. The activation energy found from the fit is 0.25 ± 0.02 eV in good agreement with previous results.[29] The diffusion length of our H centers changes from 30 to 700 Å with temperature increasing in the range 20–300 °C; these values certainly vary with different electron current densities.

The model fails, however, to explain the behavior of the desorption yield for a very thin films as seen in Figs. 3 and 4. The measurements show that there is no observable desorption for films thinner than 10 ML for NaCl and 8 ML for KBr. The diffusion model predicts a linear increase of the desorption yield from zero thickness (see Fig. 4, solid line). In principle, its artificial continuity (no atomic layers taken into consideration) could account for the absence of desorption from the initial 2–3 ML but certainly not from the 10 ML film. We shall argue that this thin-film stability is a manifestation of the hot excitation diffusion process and interface trapping. The electronic structure of the $A_{\mathrm{III}}B_{\mathrm{V}}$ semiconductor alkali-halide interface is represented by a diagram in Fig. 5. Conduction electrons and valence holes are likely to transfer from the alkali-halide film to the semiconductor substrate, but the opposite should not occur. Thus, we may expect that the interface acts as a trap for excitations at a very initial stage of their evolution. On the other hand, we assume that the surface acts as a reflector for hot holes. Once again we use the steady-state diffusion equation:

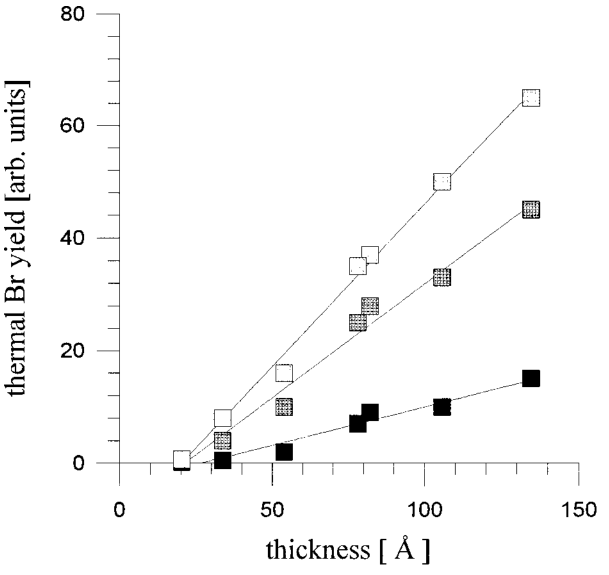

FIG. 3. The ''thermal'' component of Br desorption from KBr films as a function of the film thickness, thin films case. No desorption below 8 ML is observable. Lines were drawn to guide an eye.

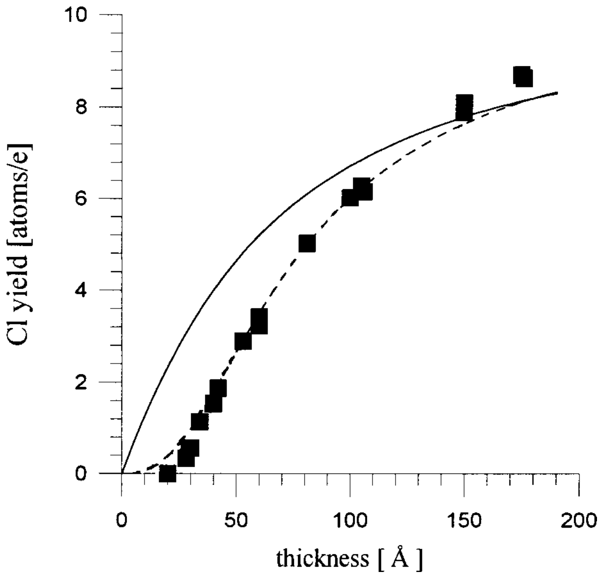

FIG. 4. The Cl desorption from NaCl films for a set of low thicknesses. No desorption is observable below 10 ML. The solid line is derived from continuous diffusion. The dashed line is from the model taking into account the interaction of hot holes with the interface.

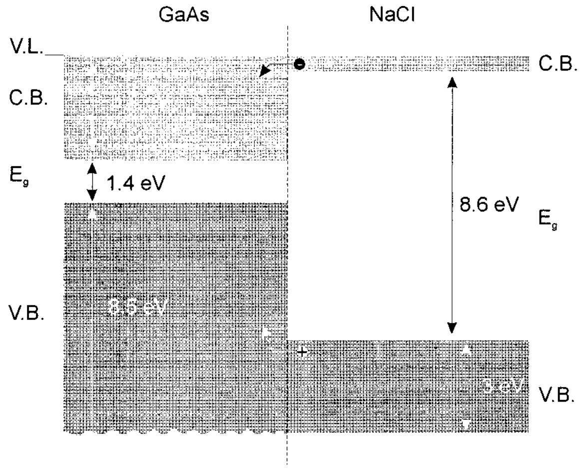

FIG. 5. The simplistic scheme of the valence–conduction-band electronic structure at the alkali halide–$A_{\mathrm{III}}B_{\mathrm{V}}$ semiconductor junction. (NaCl/GaAs).

$$D_h \frac{d^2 n_h}{dx^2} - \frac{n_h}{\tau_h} + N(x) = 0, \tag{3}$$

but with the boundary conditions reversed: a trap at the interface and a reflector at the surface. The lifetime τ_h is here associated with thermalization and self-trapping of the hole in the polar lattice of the crystal. We expect the excitations to disappear at the interface causing no desorption. In particular, when the film thickness is comparable with diffusion length of the hot hole ($\sqrt{D_h \tau_h}$) nearly all energy primarily deposited in the film is ''pumped out'' by the interface. We may improve our model of thermal desorption by taking the source to be $n_h(x)/\tau_h$ instead of $N(x)$. The curve evaluated from this improved model (dashed line in Fig. 4) reproduces our desorption data with much higher accuracy, including the case of a very thin film. The diffusion length of the hot hole giving the best agreement of the experiment for NaCl and the model may be assessed as 30 Å. We would like to stress that no apparent influence of the hot carrier diffusion could be observed for desorption of the thick (bulk) sample, since the change of a shape of the defect distribution caused by hot diffusion is insignificant in this case. In conclusion, we can say that our desorption data for very thin films reveal that the hot carrier diffusion takes place at early stages of the thermal-desorption process.

B. Nonthermal desorption vs the film thickness and primary electron energy

There were two attempts to explain the phenomenon of nonthermal desorption. The first, suggested by Szymonski *et al.*,[10] implied that the energy for crystal bond breaking and emission of a halogen atom is supplied to the surface by diffusion of hot electron-hole pairs. If a hole is localized on a surface halogen, the Coulombic bond disappears and the halogen atom could be ejected due to Pauli pressure of the surrounding electron cloud. In this case a creation of the hot electron-hole pair may take place inside the crystal and, subsequently, the pair could be transported to the surface via a hot carrier diffusion. The second concept, originally proposed by Townsend *et al.*[8] and recently modified by Chen, Cai, and Song[13] and Puchin *et al.*[30] implied that the nonthermal atoms are ejected as a result of the $(V_k + e)$ STE configuration decaying to F and H pair in a close vicinity of the surface. Calculations by Chen, Cai, and Song predicted that in this latter case the emission is expected from the third atomic layer of the crystal.[13] The authors, however, did not consider hot excitation diffusion. But such diffusion, to our opinion, must be included in order to understand phenomena such as the dependence shown in Fig. 6. The nonthermal desorption yield varies with the primary electron energy but it does not follow the stopping power of the electrons. Such behavior can be, however, explained by assuming that the diffusion of excitation changes the deposited energy density distribution prior to the desorption process.

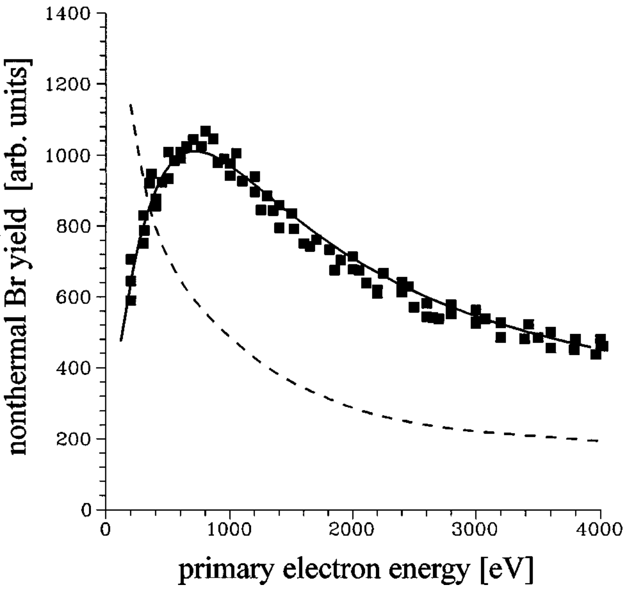

FIG. 6. The dependence of the ''nonthermal'' part of ESD of Br from KBr crystal on primary electron energy. Dashed line showes the primary deposited energy density at the surface. The theoretical dependence evaluated from the hot diffusion model is denoted by the solid line.

A systematic study of thin-film desorption provides further arguments for such a hot carrier-diffusion process. The dependence of nonthermal yield vs film thickness is plotted in Fig. 7. The onset of the yield is noticeable already at very low film thicknesses (<20 Å), then it rises smoothly and saturates at a thickness of about 200 Å. This behavior is almost independent of the sample temperature within the range 25–150 °C. For diffusion of the hot carriers we may write again

$$D_{ex} \frac{d^2 n_{ex}}{dx^2} - \frac{n_{ex}}{\tau_{ex}} + N(x) = 0, \tag{4}$$

where D_{ex} is the diffusion coefficient, τ_{ex} is the lifetime, and n_{ex} is the steady-state concentration of hot quasiparticles as a function of depth x.

If the source N is linear, the solution for thin films may be found in the form

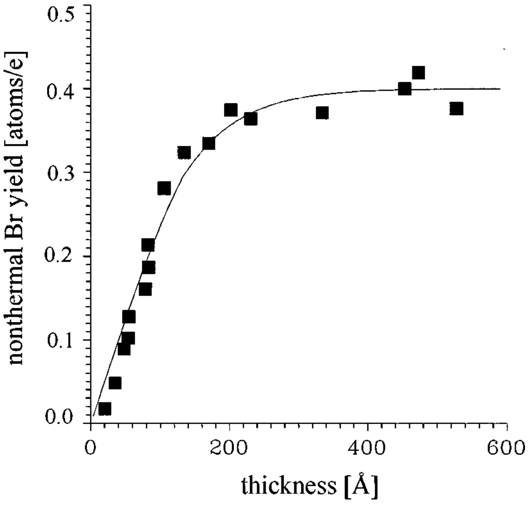

FIG. 7. The dependence of the ''nonthermal'' component of ESD from KBr films in absolute units (number of emitted atoms per one primary electron) vs the film thickness at room temperature. The solid line is evaluated from the hot diffusion model.

$$n_{\rm ex}(x)=B_{1,k}e^{x/\lambda_{\rm ex}}+B_{2,k}e^{-x/\lambda_{\rm ex}}+\tau_{\rm ex}N(x),\quad \lambda_{\rm ex}=\sqrt{D_{\rm ex}\tau_{\rm ex}}. \tag{5}$$

The coefficients $B_{1,k}$ and $B_{2,k}$ are calculated from the boundary and joining points conditions. It is assumed that the surface is a trap (as we observe desorption), thus

$$D_{\rm ex}\frac{dn_{\rm ex}(0)}{dx}=\Delta_{s,\rm ex}n_{\rm ex}(0),\quad \Delta_{s,\rm ex}\to\infty,$$

and the interface is a reflector for diffusing carriers (as we do not observe an ''interface'' pumping effect;

$$D_{\rm ex}\frac{dn_{\rm ex}(d)}{dx}=-\Delta_{i,\rm ex}n_{\rm ex}(d),\quad \Delta_{i,\rm ex}\to 0,$$

where $\Delta_{s,\rm ex}$ and $\Delta_{i,\rm ex}$ are surface and interface recombination rates. The desorption has to be proportional to the concentration of excitations at the surface. Comparing the curve from the model with experimental points, the diffusion length of excitation carriers is found to be 140 ± 15 Å. Similarly, for the primary electron-energy dependence (Fig. 6), we can evaluate the theoretical shape from the same model assuming infinite film thickness and allowing the source $N(x)$ in Eq. (5) to change according to the formula of Al-Jammal, Pooley, and Townsend.[26] A satisfactory fit (see solid line, Fig. 6) is obtained at diffusion length 130 Å. Thus, the assumption that ejection of nonthermal halogen atoms is preceded by diffusion of hot excitation carriers allows for the consistent description of the desorption yield behavior vs both the film thickness and the primary electron energy. Of course, the question arises, what is the nature of our diffusing quasiparticle. It cannot be a hole alone, since as we found in Sec. III A, its diffusion length is much shorter, and as shown by the results of our recent PSD measurements (see Sec. III D), we do not expect the nonthermal ejection to occur due to a hole arriving at the surface alone. However, in the electron-hole plasma created by electron impact in the crystal, we may find another candidate—a hot exciton. (It was found that in dense electron-hole plasmas the initial electric current is rapidly quenched due to the fact that a certain fraction of electron-hole pairs is converted into excitons.[31]) Such an exciton may have any momentum allowed by the band configuration. The hot excitons cannot decay radiatively until they become cool (the photon cannot take their momentum). Accordingly, they have to follow a random walk scheme, as already described for holes. The interaction of hot excitons with a longitudinal phonon field, which dominates in polar crystals, is weaker (comparing to charged quasiparticles) due to mutual screening of the electron and the hole. Thus, we expect much greater diffusion lengths for excitons than for holes. This implicates the hot exciton as a precursor state for the nonthermal ejection process.

In conclusion, we can state that the energy-transport process preceding surface ejection of the nonthermal halogen atoms is well described by the hot diffusion of free excitons.

C. Dependence of nonthermal desorption on temperature

As we have already mentioned, the intensity of the dynamic (nonthermal) halogen component decreases weakly with sample temperature. Previously, the present authors proposed that this behavior was due to a steady state concentration of defects created in the crystal by the electron beam.[20] However, further experiments have shown that the nonthermal component is not significantly dependent on the current density,[22] and on the concentration of impurities in the lattice.[32] In this section we demonstrate that this weak temperature dependence can be satisfactorily explained by the interaction of hot excitation carriers (excitons) with the polar lattice and that invoking of other concepts is not required.

Let us assume that the hot excitation of mean initial energy E diffuse in the polar crystal. The scattering rates due to interaction with the given mode (q) of the optical-phonon field may be expressed as follows[33]:

$$\frac{1}{\tau_{\rm em,abs}}=\frac{A}{q^2}\left(N_q+\tfrac{1}{2}\pm\tfrac{1}{2}\right), \tag{6}$$

where q is the wave vector associated with the optical mode, the parameter A may be treated as independent on q due to the flat dispersion relation for optical phonons, the sign ''+'' stands for emission and ''−'' for absorption of a phonon, and N_q is the population of the q optical mode.

An energy loss to the mode q is equal to

$$\frac{dE}{dt}=\hbar\omega_{\rm LO}\left(\frac{1}{\tau_{\rm abs}}-\frac{1}{\tau_{\rm em}}\right)=\frac{-A\hbar\omega_{\rm LO}}{q^2}. \tag{7}$$

Taking $\omega_{\rm LO}$ as constant (flat dispersion), we can easily integrate the energy loss (ΔE) over all phonon modes. The result does not depend on phonon population (or crystal temperature). In such a case the lifetime of the excitation does not depend on temperature either. However, the number of scatterings (n) suffered by our excitation is proportional to the sum of emission and absorption scattering rates over all phonon modes:

$$n\propto\sum_q\left(\frac{1}{\tau_{\rm abs}}+\frac{1}{\tau_{\rm em}}\right)\propto\sum_q(2N_q+1). \tag{8}$$

The mean free path is inversely proportional to the total scattering rate:

$$l\propto\frac{1}{\sum_q(2N_q+1)}.$$

Taking N_q from the Bose-Einstein relation:

$$N_q=\frac{1}{\exp[\hbar\omega_{\rm LO}/kT]-1},$$

with the optical-phonon energy from Ref. 5 and multiplying $\sqrt{n}$ and l we can obtain the diffusion length of hot excitations (λ) vs temperature:

$$\lambda\propto\frac{1}{\sqrt{2N_q+1}}. \tag{9}$$

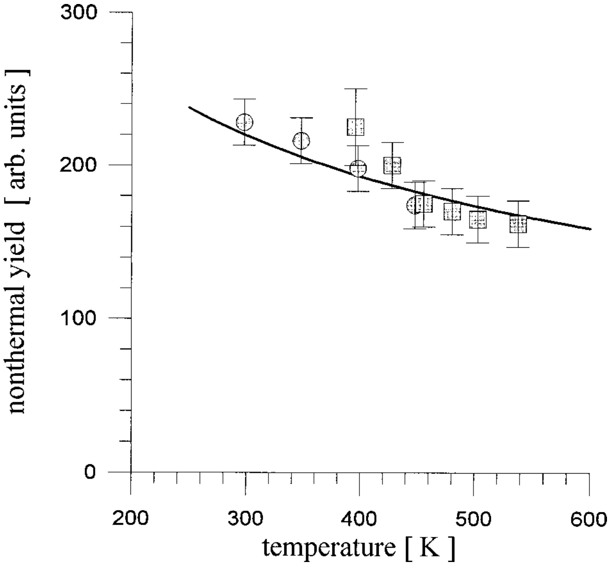

FIG. 8. The ''nonthermal'' component of ESD of KBr as a function of the sample temperature. Circles denote the data taken for 500 Å-thick film. Squares are for the data recorded for bulk crystal. Solid line is evaluated on the basis of the exciton-phonon interaction model.

This simple model enables us to calculate the instantaneous parameters of diffusion for excitation having certain kinetic energy (E). In fact, the energy of the excitation changes during time as far as we have to do with different initial kinetic energies. Fortunately, for one-phonon processes, all averaging, which is needed in order to take into account different possible initial excitation energies and excitation slowing, is done over the proportionality factor and the shape of the temperature dependence must survive intact as in Eq. (9).

The efficiency of the nonthermal desorption preceded by the diffusion of hot excitation carriers should be roughly proportional to the diffusion length of the carrier. In Fig. 8 the relative temperature dependences of the diffusion length as estimated from Eq. (9), and of the nonthermal yield are presented. It can be seen that the theoretical curve can be fitted quite satisfactorily to the experimental data.

D. Lack of the nonthermal component in photostimulated desorption

In contrast to ESD experiments the nonthermal component has not been found in our experiment on desorption of iodides stimulated by monochromatic vacuum UV radiation (see also Ref. 23). We argue that this is due to the very low excitation density created by the photon flux of $10^{15}/(\mathrm{s\ cm}^2)$ in such an experiment. Absorption of a single photon produces an isolated electron-hole pair, which, during its lifetime, decays without interaction with other excitations. At photon energies corresponding to fundamental exciton absorption the resulting primary excitons are static due to the fact that photon momentum is negligible in comparison to typical band momenta. In such a case the exciton is trapped immediately at the point of its creation and no excitation transport to the surface could take place. Moreover, even if the excitons are created directly at the surface they would not contribute to desorption, since only singlet excitons are created directly with light. However, dynamic ejection processes could be initiated by triplet excitons as shown by Tanimura and Troh.[34] Thus, the absence of the nonthermal part of desorption in PSD observed in our previous experiment is consistent with the concept of nonthermal desorption driven by diffusion of hot (nonequilibrium) excitons.

IV. CONCLUSIONS

Electron- and photon-stimulated desorption studies of epitaxial thin films and bulk single crystals of NaCl, KBr, KI, and RbI have shown that hot carrier formation and transport processes occurring prior to self-trapped exciton formation are of crucial importance for understanding and comprehensive description of the observed phenomena. In particular, the following conclusions could be drawn. (1) Thermal desorption component is properly described by thermally activated defect diffusion; (2) for thin alkali halide films with thicknesses less than 8–10 ML, interaction of hot holes with the interface quenches thermal desorption processes; (3) the ejection of nonthermal halogen atoms is preceded by the Brownian motion of hot excitations (most likely free excitons) in the ionic crystal; (4) the dependence of the nonthermal component on the temperature may be interpreted in terms of a hot exciton-phonon interaction; (5) the initial high excitation density (electron-hole plasma) is a necessary condition for nonthermal desorption (such conditions cannot be achieved by available UV photon sources).

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[1] W. Shockley, Solid-State Electron. **2**, 35 (1961).

[2] R. H. Bartram and A. Lempicki, Mater. Sci. Forum **239–241**, 241 (1997).

[3] R. T. Poole, J. G. Jenkin, J. Liesegang, and R. C. G. Leckey, Phys. Rev. B **11**, 5179 (1975); S. P. Kowalczyk, F. R. McFeely, L. Ley, R. A. Pollak, and D. A Shirley, *ibid.* **9**, 3573 (1974).

[4] See, for example, in C. Kittel, *Quantum Theory of Solids* (Wiley, New York, 1963), pp. 137–142.

[5] J. D. Dow and D. Redfield, Phys. Rev. B **5**, 594 (1972); T. Tomiki, T. Miyata, and H. Tsukamoto, J. Phys. Soc. Jpn. **35**, 495 (1973).

[6] R. T. Williams, K. S. Song, W. L. Faust, and C. H. Leung, Phys. Rev. B **33**, 7232 (1986).

[7] P. W. Palmberg and T. N. Rhodin, J. Phys. Chem. Solids **29**, 1917 (1968).

[8] P. D. Townsend, R. Browning, D. J. Garlant, J. C. Kelly, A. Mahjoobi, A. J. Michael, and M. Saidoh, Radiat. Eff. **30**, 55 (1976).

[9] H. Overeinder, M. Szymonski, A. Haring, and A. E. de Vries, Radiat. Eff. **36**, 63 (1978).

[10] M. Szymonski, J. Kolodziej, P. Czuba, P. Piatkowski, A. Poradzisz, N. H. Tolk, and J. Fine, Phys. Rev. Lett. **67**, 1906 (1991).

[11] Z. Postawa, R. Maboudin, M. el Maazawi, M. H. Erwin, M. C. Wood, and N. Winograd, J. Chem. Phys. **96**, 3298 (1992).

[12] R. T. Williams, Radiat. Eff. Defects Solids **109**, 175 (1989).

[13] L. F. Chen, Y. Cai, and K. S. Song, Nucl. Instrum. Methods Phys. Res. B **91**, 614 (1994).

[14] M. Szymonski, Radiat. Eff. **52**, 9 (1980).

[15] M. Elango, Radiat. Eff. Defects Solids **128**, 1 (1994).

[16] R. Klauser, M. Kubota, Y. Murata, M. Oshima, Y. Y. Maruo, T. Kawamura, and T. Miahara, Phys. Rev. B **40**, 3301 (1989).

[17] C. F. McConville, T. S. Jones, F. M. Leibsle, S. M. Driver, T. C. Q. Noakes, M. O. Schweizer, and N. V. Richardson, Phys. Rev. B **50**, 14 965 (1994).

[18] P. Drathen, W. Ranke, and K. Jacobi, Surf. Sci. **77**, L162 (1980).

[19] K. Saiki, Y. Nakamura, and A. Koma, Surf. Sci. **269/270**, 790 (1992).

[20] J. Kolodziej, P. Czuba, P. Piatkowski, A. Poradzisz, Z. Postawa, M. Szymonski, and J. Fine, Nucl. Instrum. Methods Phys. Res. B **65**, 507 (1992).

[21] J. Kolodziej, Z. Postawa, P. Czuba, P. Piatkowski, and M. Szymonski, Radiat. Eff. Defects Solids **128**, 47 (1994).

[22] J. Kolodziej, P. Czuba, P. Piatkowski, Z. Postawa, V. Kempter, and M. Szymonski, Vacuum **45**, 353 (1994).

[23] M. Szymonski, J. Kolodziej, P. Czuba, P. Korecki, P. Piatkowski, Z. Postawa, M. Piacentini, and N. Zema, Surf. Sci. **363**, 229 (1996).

[24] M. Szymonski, P. Czuba, T. Dohnalik, L. Jozefowski, A. Karawajczyk, J. Kolodziej, R. Lesniak, and Z. Postawa, Nucl. Instrum. Methods Phys. Res. B **48**, 543 (1990).

[25] M. Szymonski, J. Rutkowski, A. Poradzisz, Z. Postawa, in *Desorption Induced by Electronic Transitions DIET II*, edited by W. Brenig and D. Menzel, Springer Series in Surface Science Vol. 4 (Springer-Verlag, Berlin, 1985), p. 160.

[26] Y. Al-Jammal, D. Pooley, and P. D. Townsend, J. Phys. C **247**, 6 (1973).

[27] I. M. Bronshteyn and A. N. Protsenko, Radio Eng. Electron. Phys. **15**, 677 (1970).

[28] H. Overeinder, M. Szymonski, A. Haring, and A. E. de Vries, Radiat. Eff. **38**, 21 (1978).

[29] H. Hoche, J. P. Toennies, and R. Vollmer, Phys. Rev. Lett. **71**, 1208 (1993).

[30] V. E. Puchin, A. L. Shluger, K. Tanimura, and N. Itoh, Phys. Rev. B **47**, 6226 (1993).

[31] M. Combescott and R. Combescott, Phys. Rev. B **35**, 7986 (1987).

[32] Z. Postawa, J. Kolodziej, G. Baran, P. Czuba, P. Piatkowski, M. Szymonski, I. Plavina, and A. Popow, Nucl. Instrum. Methods Phys. Res. B **100**, 228 (1995).

[33] P. Vogl, in *Physics of Nonlinear Transport in Semiconductors*, Vol. 52 of *NATO Advanced Study Institute, Series B: Physics*, edited by D. K. Ferry (Plenum, New York, 1980), p. 83.

[34] K. Tanimura and N. Itoh, Nucl. Instrum. Methods Phys. Res. B **46**, 207 (1990).