PHYSICAL REVIEW B VOLUME 39, NUMBER 17 15 JUNE 1989-I

Directional emission of nonthermal halogen atoms by electron bombardment of alkali halides

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(Received 28 December 1988)

We present the first experimental results on angle-resolved kinetic-energy distributions of halogen atoms desorbed from single crystals of alkali halides because of electron bombardment. We found that the ejection of nonthermal Br atoms from the (100) surface of KBr is strongly forward peaked along the normal. We suggest that this effect is caused by a thin damaged layer on the surface due to a strong nonstoichiometry of the erosion process itself.

Electron or photon bombardment of insulators is generally accompanied by the emission of charged and neutral particles from the surface. Inelastic processes responsible for this ejection have attracted much interest in recent years.[1,2] Alkali halides are frequently used as model materials because they have simple crystallographic and electronic structures, and because desorption processes in these materials are very efficient.[2,3] As a first step in conversion of energy deposited by the slowing-down projectile into the electronic system of the crystal, a Frenkel pair of defects is produced from the self-trapped exciton.[2] Although several models have been proposed over the last two decades,[4-7] even very recently details of the process have been matters for discussion.[8,9]

Further steps of the desorption mechanism in alkali halides (separation of defects and ejection of halogen from the surface) are subject to speculation, mainly due to a lack of reliable experimental data taken for well-defined single-crystal surfaces.

In this paper we present the first experimental results on angle-resolved energy distributions of halogen atoms desorbed from a (100) surface of a KBr single crystal subjected to electron bombardment. With the exception of some preliminary, unpublished data,[10,11] the only existing energy distributions of halogen atoms desorbed by electron bombardment were obtained for compressed powder polycrystals.[12] Our measurements provide simultaneous information on ejection angle and intensity ratio of nonthermal and thermal components of the energy spectrum of desorbed atoms. These measurements play an important role in identifying the final, precursor state for desorption of halogen from the surface and have significant implications for the interpretation of electron-desorption experiments.

The experiment was performed in an UHV chamber (base pressure 6×10^{-7} Pa) evacuated with combined ion getter and titanium sublimation pumps. A 200–700-eV electron beam with current densities of 5–10 μA/cm^2 was used for erosion of a (100) surface of a high-purity KBr single crystal (Harshaw Chemical Company). The sample was cleaved in air prior to experiment and cleaned by heating to 650 K in vacuum for several hours. Measurements were performed with target temperatures ranging from 300 up to 700 K. After a flight path of 41 cm, the emitted atoms were ionized in an electron-impact ionizer and mass selected in a quadrupole mass spectrometer. The time-of-flight distributions were measured with the correlation method.[12] The observation angle θ could be varied continuously from 0° to 90° against the normal to the (100) surface by rotating the target with respect to an axis of the mass spectrometer. Thus, the angular scan was made in a (010) plane of the crystal including the $\langle 100\rangle$, $\langle 110\rangle$, and $\langle 001\rangle$ crystallographic directions. The angle of incidence and the observation angle could be varied separately to within 0°–45°. Thus, we could compare the spectra taken at different observation angles but at the same angle of incidence. More details regarding the experimental setup will be given elsewhere.

The experimental time-of-flight spectra of Br atoms leaving a KBr target at several observation angles with

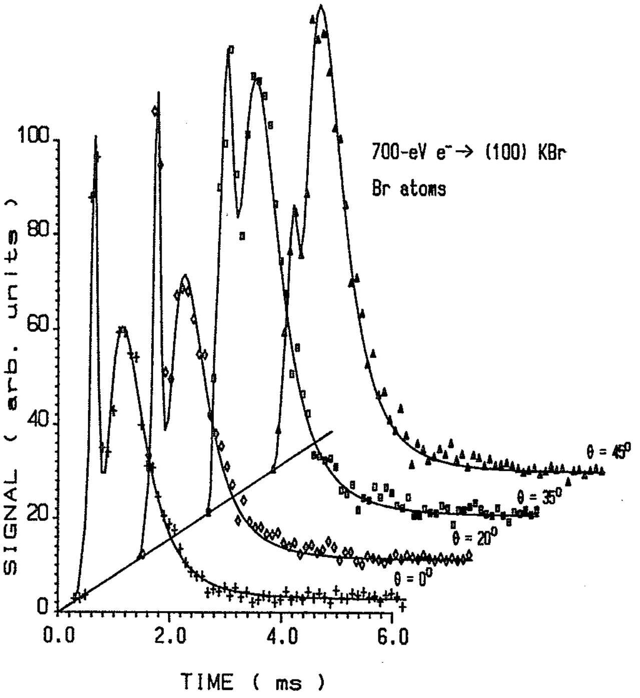

FIG. 1. Time-of-flight distributions of Br atoms leaving a (100) KBr target at various ejection angles θ. The spectra are normalized to their maximum values. The surface temperature was 120 °C.

respect to the ⟨001⟩ axis are displayed in Fig. 1. A double structure of the spectra taken up to 45° is clearly visible. The broad peak with a maximum at 1 ms corresponds to thermal particles, while the second narrow one with a maximum at 0.4 ms corresponds to faster, nonthermal particles. The high-energy side of the nonthermal peak shows a sharp cutoff below 0.2 ms (1.2 eV). As seen in Fig. 1, these fast particles are hardly present at observation angles above 45°. Thus the ejection of nonthermal Br atoms is strongly forward peaked along the normal to the (100) surface. Practically, only thermal atoms have been observed at angles larger than 50°. The ratio of nonthermal to thermal atoms, $S_{\mathrm{nth}}/S_{\mathrm{th}}$, as a function of the ejection angle is plotted in Fig. 2.

It was found experimentally that the shape of the $S_{\mathrm{nth}}/S_{\mathrm{th}}(\theta)$ dependence was not sensitive to variation of the angle of incidence within the investigated range. Thus it demonstrates a strong directional effect in the ejection process of sputtered particles. If we assume, following Ref. 13, that the evaporating thermal Br atoms have a standard cosine distribution, the distribution of nonthermal particles is equal to $[S_{\mathrm{nth}}/S_{\mathrm{th}}(\theta)]\cos\theta$, i.e., for the target temperature 120 °C is close to $\cos^{3.5}\theta$ around the normal. This is contrary to the common expectations,[1,2,7,8,14] which indicated that a ⟨110⟩ direction of the crystal (i.e., $\theta = 45°$) should be preferred in the ejection of nonthermal halogen atoms. In a final part of this paper we will offer an explanation for this unexpected behavior.

In order to exclude the influence of possible disturbing factors which would affect the ejection process, we have performed several additional measurements. We found that a change in the electron current density by a factor of 2 within the range available did not affect the $S_{\mathrm{nth}}/S_{\mathrm{th}}$ ratio for various observation angles. The dose of electron bombardment prior to the measurement had no effect either until a macroscopic crater, due to intense surface erosion, developed. Thus, for reproducible data we had to use a "diffuse," low-density electron beam.

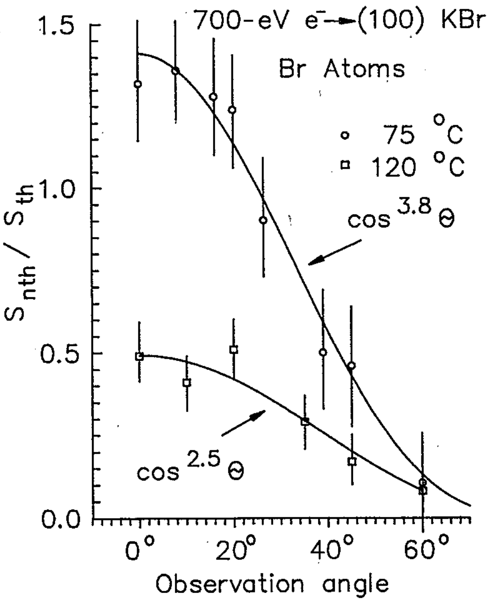

FIG. 2. Dependence on the observation angle θ of $S_{\mathrm{nth}}/S_{\mathrm{th}}$ for Br atoms originating from a (100) KBr target at 120 and 75 °C.

With increasing sample temperature, the thermal part of the spectrum grows as seen in Fig. 3. At 350 °C the number of nonthermal particles forms only a small fraction of all emitted Br atoms. We have found that the Maxwell-Boltzmann distribution described accurately the shape of the corresponding energy spectrum. The spectra for K atoms were Maxwellian at all temperatures. The dependence on the temperature of the target had already been studied for compressed powder samples[12] and our measurements for single crystals confirmed the previous findings.

The surface temperature, however, affects not only the magnitude of the $S_{\mathrm{nth}}/S_{\mathrm{th}}$ ratio but the shape of its angular dependence. As seen in Fig. 2, for a surface temperature of 120 °C this dependence is roughly $\cos^{2.5}\theta$, but for surface temperature lower than 75 °C it approaches $\cos^4\theta$.

It is widely accepted that the primary step in activation of the nuclear motion in electron-irradiated alkali halides relies upon formation of a Frenkel pair from a self-trapped exciton,[2] i.e., a halogen interstitial atom (*H* center) and an electron trapped in the complementary vacancy site of the *H* center (*F* center). The previous models[4,5] assumed the lowest self-trapped exciton state as the precursor of both *F*-*H* pairs and π-polarized luminescence. The experimental observation that the delay in *F*-

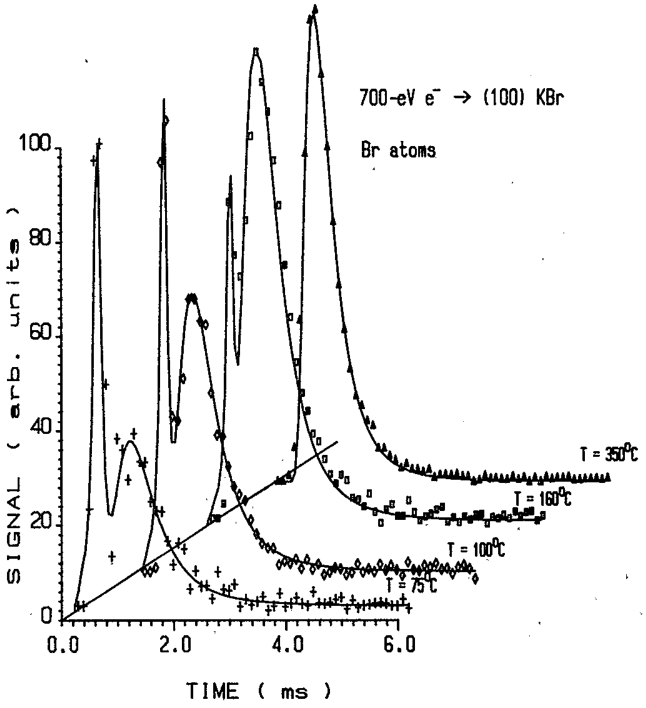

FIG. 3. Time-of-flight distributions of Br atoms leaving a (100) KBr target along the normal to its surface at various surface temperatures. The spectra are normalized in the same way as in Fig. 1. The corresponding count rates in the mass spectrometer were 500, 800, 3500, and 8300 counts/s for the target temperatures 75, 100, 160, and 350 °C, respectively.

center formation is much smaller than the lifetime of the π-luminescent state has ruled out this so-called "pooley-Hersch model." Thus, it has been suggested[6,7] that the F-H pairs evolve from a higher excited state of the self-trapped exciton. According to recent work by Williams *et al.*[8] energy stored in such higher electronic states can be released and channeled into unidirectional motion of the halogen atom along the $\langle 110 \rangle$ direction of the crystal, thus initiating so-called "focused replacement collision sequence." It was estimated that up to 1 eV kinetic energy can be retained by the accelerated H center and cause the ejection of nonthermal halogen atom, if this event occurs sufficiently close to the surface. A length of the replacement collision chain can be relatively large, since the calculated activation energy for the directional motion of the excited H center is only 75 meV.[8] Within the bulk of the crystal, the directional motion of the single energetic H center will quickly be partitioned among a number of vibrational modes, but the resulting interstitial halogen atom can migrate thermally to the surface (in particular at elevated temperatures) and evaporate contributing to the thermal part of the energy spectrum.[15]

Our measurements, however, indicate that the primary direction of the motion of energetic H centers ($\langle 110 \rangle$ direction) is not preserved in the ejection process. One possibility would involve the concept of a surface exciton. Although this concept still awaits theoretical treatment,[16] it cannot be excluded that the exciton self-trapped at the surface would have a symmetry axis different from the bulk one. It is unlikely, however, that for a dynamic situation in the nonstoichiometrically sputtered surface such an exciton would decay predominantly along the $\langle 100 \rangle$ direction. We propose that this effect is caused by the thin altered layer present at the bombarded surface due to the strong nonstoichiometry of the sputtering process itself. The excitonic mechanism activates the halogen sublattice only. Alkali-metal atoms, therefore, can be accumulated at the halogen-deficient surface depending on their evaporation rate at the given temperature.[3,12,15,17] It is very likely, therefore that under steady-state conditions, the energetic halogen atoms have to penetrate in the ejection process through the damaged, irregular surface overlayer.

An influence of the altered layer on angular distribution of ion sputtered species has been studied theoretically[18] and experimentally.[19–21] In general, it was found that atoms originating from deeper layers which must penetrate through the altered surface layer were preferentially ejected into a narrow cone around the surface normal. In particular Dumke *et al.*[22] found that less than a monolayer coverage of In on Ga substrate changed drastically the angular distribution of sputtered Ga atoms from $\cos^2\theta$ for a stoichiometric surface, to $\cos^4\theta$ for an In-covered one.

Interestingly, in our experiment a pronounced difference in angular distributions was observed between two groups of the same sputtered species. The first group of fast, nonthermal halogen atoms (a relatively large escape depth) showed the strong forward peaking. Naturally, the second group of thermal Br atoms evaporate from the very surface [they have a negligible escape depth, contrary to energetic (≥ 1 eV) H centers from the nonradiative decay of the self-trapped excitons], and thus they should obey the $\cos\theta$ angular distribution.

The thickness of the altered layer increases with lowering of the surface temperature, thus causing the angular distribution of nonthermal halogen atoms to be even more forward peaked. This was observed in our experiment. Indeed, as described above, lowering the surface temperature from 120 to 75 °C caused a change in the angular distribution of the nonthermal Br atoms from $\cos^{3.5}\theta$ to $\cos^5\theta$.

Our results and the proposed explanation concur well with the experimental work by Townsend *et al.*[13] In that work a strong central spot was always observed on the collector plate in front of the electron-bombarded surface of NaCl. The fact that this spot, but not the $\langle 110 \rangle$ one, dominated the pattern of ejected halogen atoms was never explained until now. As a result of our model, this central deposit is caused by strongly forward-peaked ejection of nonthermal halogen atoms due to the presence of the altered layer at the surface.

Very similar, forward-peaked angular distributions of desorbed particles were observed in laser-desorption experiments.[23–25] Recently Kelly and Dreyfus[24,25] used the concept of a Knudsen layer to explain those results. This is a regime in which gas-phase collisions occur due to the transient high gas density in front of the desorbing surface. The Knudsen-layer theory has been developed thus far only for thermally emitted particles, with the assumption that their inherent distribution is isotropic in the half-sphere normal to the surface. In our case, however, the inherent distribution is anisotropic (centered along the $\langle 110 \rangle$ direction of the crystal) and subsequently modified by collisions in the altered layer. Therefore, the Knudsen-layer concept in the present form is not fully applicable for description of our results. Nevertheless, the collision processes underlying the emission of atoms from deeper layers[18] are probably similar to those underlying Knudsen-layer theory.

We wish to thank Professor N. Itoh for fruitful discussions and for providing a single crystal of KBr. This work is part of the Central Program for Fundamental Research No. CPBP-01-09, supported by the Polish Ministry of National Education.

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[1] For a good collection of recent work, see (a) *Desorption Induced by Electronic Transitions, DIET 1*, edited by N. H. Tolk *et al.* (Springer-Verlag, Berlin, 1983); (b) *Desorption Induced by Electronic Transitions, DIET 2*, edited by W. Brenig and D. Mentzel (Springer-Verlag, Berlin, 1984).

[2] N. Itoh and K. Tanimura, Radiat. Eff. **98**, 269 (1986).

[3] M. Szymonski, J. Rutkowski, A. Poradzisz, Z. Postawa, and B. Jorgensen, in Ref. 1(b), p. 277.

[4] D. Pooley, Solid State Commun. **3**, 241 (1965).

[5] H. N. Hersch, Phys. Rev. **120**, 679 (1966).

[6] M. N. Kabler, in *Proceedings of the NATO ASI on Radiation Damage Process in Materials, Corsica,* edited by C. H. A. Dupuy (Noordhoff International, Leyden, 1975), p. 171.

[7] N. Itoh and M. Saidoh, J. Phys. (Paris) **34**, 101 (1973).

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

[9] N. Itoh, T. Eshita, and R. F. Williams, Phys. Rev. B **34**, 4230 (1986).

[10] G. L. Ostrom, Ph.D. thesis, Tennessee, 1974.

[11] A. E. de Vries (private communication).

[12] H. Overeijnder, M. Szymonski, A. Haring, and A. E. de Vries, Radiat. Eff. **36**, 63 (1978); **38**, 21 (1978).

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

[14] F. Agullo-Lopez and P. D. Townsend, Phys. Status Solidi B **97**, 575 (1980).

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

[16] Y. Al Jammal and P. D. Townsend, J. Phys. C **6**, 955 (1973).

[17] R. T. Williams, in *Proceedings of the Seventh International Workshop on Inelastic Ion Surface Collisions, Krakow,* edited by M. Szymonski and R. Pedrys (Gordon and Breach, London, 1989).

[18] P. Sigmund, A. Oliva, and G. Falcone, Nucl. Instrum. Methods **194**, 541 (1982).

[19] T. Okutani, M. Shikata, and R. Shimizu, Surf. Sci. **9**, L410 (1980).

[20] H. H. Andersen, V. Chernysh, B. Stenum, T. Sorensen, and H. J. Whitlow, Surf. Sci. **123**, 39 (1982).

[21] W. Huang, J. Onsgaard, and M. Szymonski, in *Proceedings of the NATO ASI on Erosion and Growth of Solids Stimulated by Atom and Ion Beams, Crete,* edited by G. Kiriakidis *et al.* (Matinus, Dordrecht, 1986).

[22] M. F. Dumke, A. Tombrello, R. A. Weller, R. M. Housley, and E. H. Cirlin, Surf. Sci. **124**, 407 (1983).

[23] A. Namiki, S. Cho, and K. Ichige, Jpn. J. Appl. Phys. **26**, 39 (1987).

[24] R. Kelly and R. W. Dreyfus, Surf. Sci. **198**, 263 (1988).

[25] R. Kelly and R. W. Dreyfus, Nucl. Instrum. Methods B **32**, 34 (1988).