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Quantitative determination of desorption time delays for ion bombarded $\{1\,0\,0\}$ alkali halide single crystals

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Abstract

The time-of-flight (TOF) spectra of neutral alkali atoms which desorb from the $\{1\,0\,0\}$ surface plane of RbI and KI single crystals have been obtained using multiphoton resonance ionization (MPRI) in tandem with our experimental method for detection of energy and angle resolved neutral (EARN) atoms. The desorption events were initiated by a 400 ns pulse of 5 keV noble gas ions (He^+ and Ar^+) impinging along the $\langle 1\,0\,0\rangle$ crystallographic direction. The relative contributions of the collisional and electronic channels of desorption have been determined for various target temperatures with both incident projectiles. In all cases the obtained results are accurately described by the Maxwell-Boltzmann distribution above 160°C. However, at lower target temperatures desorption time delays become apparent and have been quantitatively determined as a function of projectile mass and the target temperature. The delays increase with decreasing target temperature and appear not to be sensitive to the mass of the incident projectile. The obtained delays are discussed with respect to a recently proposed model in which the emission of neutral alkali atoms results from the recombination of a surface alkali ion with an adjacent excited F center. Furthermore, based on the observed experimental trends in the relative intensity of the thermal and ballistic channels, electronic processes are suggested to be primarily responsible for the production of lattice defects while the eventual ballistic formation of F and H centers appears at best a secondary process in the observed desorption trends.

1. Introduction

Alkali halides have been widely used to study the electronic processes which lead to desorption. This widespread use is predominately the result of the simple electronic and crystallographic structures of these materials. Various projectiles have been used to stimulate desorption from these substrates. The desorption induced by electron and photon irradiation of these systems is clearly dominated by perturbation of the electronic subsystem of the target and the subsequent production of lattice defects [1]. Surprisingly, it has also been observed that during ion bombardment most of the neutral particles are emitted with very low thermal energies which are characteristic of desorption induced by electronic transitions [2-4]. Because the electronic and ballistic channels of desorption coexist for ion bombarded alkali halides these materials offer a unique opportunity for fundamental mechanistic study. The mechanistic details of the desorption processes which result from keV ion bombardment of alkali halides are not fully understood although it is clear that both electronic and nuclear processes contribute to the overall desorption yield. Several experimental observations pertaining to ion irradiation of alkali halides have been recently reviewed [5].

As a keV ion impinges on a solid surface energy loss occurs through elastic collisions with species of the solid as well as through excitation of the targets electronic system. Desorption occurs from the ballistic channel via the elastic processes of the collision cascade. The more complex electronically induced desorption channel begins with an inelastic energy transfer into the electronic subsystem of the substrate lattice. This transfer produces valence holes which typically localize on the sub-picosecond time scale [6]. The halide upon which the hole localizes will no longer have a closed shell rare gas electronic configuration. As a result the halide displays partial open shell covalent character and interacts with

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a neighboring halide ion to form a negatively charged molecular halogen ion in the lattice. The self-trapped hole then can interact with an electron to form a self-trapped exciton (STE). The STE has a short lifetime and decays either radiatively by emitting polarized light or non-radiatively through formation of electrons occupying lattice vacancies (F centers) and interstitial halogens (H centers). Alkali ions resident on the surface can interact with an F center and be neutralized. This interaction could occur as the result of diffusing ground state F centers as proposed by Green [7] and/or by interaction with an excited state F center at the surface as recently proposed by Puchin et al. [8, 9]. Because of only a small physisorbtive interaction with the surface, the neutral alkali atom can evaporate into the gas phase, assuming the vapor pressure of the metal is sufficient to induce desorption.

The energy distributions of ground state alkali atoms can be described by the three-dimensional Maxwell–Boltzmann distribution assuming the neutralization step is not delayed. In other words if the formation of neutralized alkali atoms is very fast with respect to ion impact then the equilibrium conditions described by the Maxwell–Boltzmann distribution are applicable. However, under certain conditions of irradiation this is not the case and a delay component becomes evident in the TOF distributions [2–4, 10]. As a result the experimental data cannot be described by only the Maxwell-Boltzmann equation but should also include considerations for the supply of defects to the surface [7] and/or the time for alkali neutralization once defects are present at the surface [9].

In this paper we have measured the time-of-flight distributions of ejected alkali atoms which result from ion bombardment in an attempt to gain insight into the fundamental processes which are responsible for the observed desorption phenomenon. The relative contributions of the collisional and thermal processes have been obtained for 5 keV Ar^+ and He^+ bombardment of RbI and KI single crystals in order to better understand the processes which lead to the partition of deposited energy between the ballistic and electronic desorption channels. The desorption time delays have also been quantitatively determined under various experimental conditions. These findings suggest that low energy particles emitted subsequent to ion bombardment of these materials and the low energy particles ejecting from electron irradiated alkali halides experience very similar interactions previous to desorption. The desorption delays can be possibly understood based on the relative inelastic interaction of the different projectiles with the electronic subsystem of the target, the depth of energy deposition, the mobility of neutralizing defects in the alkali halide lattice of interest, and/or the probability of tunneling through various potential barriers leading to neutralization.

2. Experimental

The experimental apparatus will be described only briefly as it has previously been extensively detailed [11]. An ultrahigh-vacuum (UHV) chamber (2×10^{-9} Torr pressure) is equipped with a low energy electron diffraction (LEED) unit, retarding grid electron optics for Auger analysis, a Kelvin probe for evaluation of changes in surface work function, and an energy and mass filtered ion gun capable of operating in either pulsed or continuous mode for either experiment or cleaning, respectively. To initiate the experiment a 400 ns pulse of 5 KeV noble gas ions is focussed onto a well defined 2 mm spot of the single crystal surface (dose < 10^{12} ions/cm^2) which was cleaved in air and then heated for several hours in vacuum at 575 K. A variable delay tunable dye laser pulse is focussed into a narrow ribbon which selectively ionizes ejected neutral atoms, thus defining the translational energy by the corresponding velocity time-of-flight (TOF). For resonant ionization of Rb, a two photon scheme was used where the first absorption is to the $^2P^0_{3/2}$ atomic level at 322.9 nm and transfer to the continuum involves a 645.8 nm photon. In the case of K atoms the same scheme is used with the first transition through the $^2P^0_{3/2}$ level at 321.9 nm and the transfer to the continuum from this intermediate at 643.8 nm. The ionized neutrals then enter a series of ion optics and eventually impinge upon a position sensitive microchannel plate (MCP) backed with a phosphor screen biased to extract the amplified ion signal exciting the rear of the MCP. The resulting image is monitored by a video camera and sent to a video processing unit which is interfaced to a personal computer and eventually deconvoluted into a time resolved photon map through software developed in our laboratory. Each complete set of temperature-dependant data was collected via a sequence whereby the sample temperature was cycled both up and down between 295 and 475 K.

3. Experimental results and discussion

Displayed in Fig. 1 are the TOF distributions of alkali atoms emitted at a polar angle of 45° in a ⟨110⟩ azimuthal plane within a solid angle of approximately 0.25 steradians for 5 keV He^+ bombardment of RbI at various temperatures. As is evident the spectra are composed of two peaks. The narrow high energy peak can be attributed to the particles emitted via the relatively high energy ballistic processes of the collision cascade. The high energy component was fit with the following:

$$\frac{dS_c}{dE} \propto \frac{1}{t^4\left(\frac{ML^2}{t^2} + E_b\right)^{\alpha}}, \qquad (1)$$

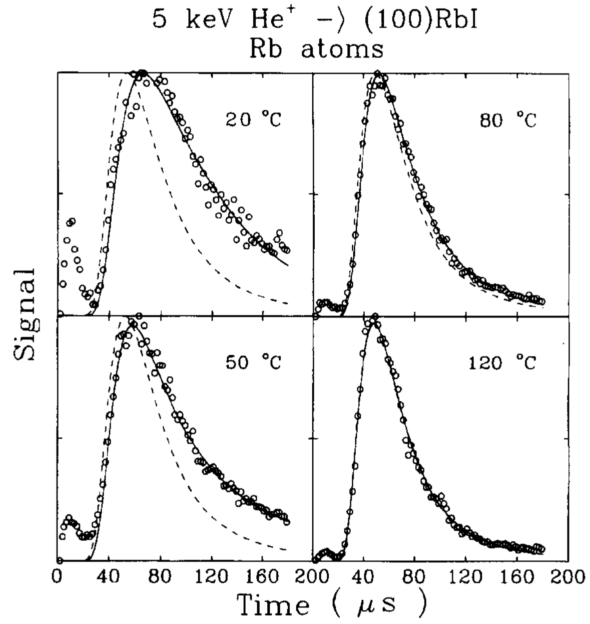

Fig. 1. The TOF spectra measured for 5 keV He^+ bombardment of RbI {001} at four temperatures. The open circles are the experimental points while the dashed line describes the Maxwell–Boltzmann distribution at the given temperature. The solid line is the obtained fit using Eq. (3).

which is a particle density–time representation of the well established Thompson formula [12, 13] where S_c is the collisional yield of particles measured along a flight path L at time t with mass M. The constant E_b is the surface binding energy of the described particle and α is a fitting parameter. The value of α obtained by fitting is consistently less than the value predicted by linear collision cascade theory. However, this is not surprising since this theory was derived for amorphous materials and our experiments were performed on single crystals. Contrary to the high energy peak, the broad peak at long TOF is temperature dependant. At high temperature (> 160°C) this low energy component can be described by the following formula:

$$\frac{\mathrm{d}\Phi(t)}{\mathrm{d}t} \propto t^{-4} \exp\left(\frac{-ML^2}{2kTt^2}\right), \tag{2}$$

which is the density–time representation of the three-dimensional Maxwell–Boltzmann distribution. $\Phi(t)$ is the time dependence of the thermal yield of particles for an equilibrated system at temperature T and k is the Boltzmann constant. For temperatures larger than 160°C the value for the temperature obtained from the fit agree within 5% of the target temperature measured during the experiment. Deviations from this simple description become evident as the sample temperature is decreased and have been previously observed experimentally on different systems [2–4].

To understand the deviations observed during electron bombardment of LiF, Green and coworkers assumed that neutral alkalis are emitted when a surface alkali ion is neutralized by recombination with a bulk created F center which has diffused to the surface [7]. This group evaluated the diffusion time via a mathematical model which yielded time delays in the millisecond time regime for electron irradiation. In this account of the events which surround alkali evaporation the observed deviations or time delays are determined predominately by the time of diffusion for F centers to reach the surface although additional processes such as diffusion of H centers and F–H center recombination could also be important. The mathematical relation between the time delays and the temperature are complicated but in general the delays increase with decreasing temperatures. Recently another theoretical model has been proposed by Puchin and coworkers to describe the microsecond time delays observed from electron irradiated NaCl [8]. This account is based on ab initio quantum calculations. These calculations suggest that the delay in emission of neutral alkali atoms is because a significant barrier to neutralization exists. They have shown that a surface Na ion which is adjacent to a ground state F center at the surface is severely energetically hindered with respect to neutralization [8]. However, their calculations suggest that this barrier is much less when the F center is in an excited state [9]. Therefore, they have proposed that desorption occurs when a Na ion recombines with an excited F center which has been created by a non-radiative decay of a surface exciton. The delays in this model can be attributed to the rate of penetration through the potential barrier and/or the rate of excited F center production at the surface.

In order to quantitatively estimate the time delays for desorption, our TOF spectra were described by the following two term exponential [2, 3, 7]:

$$\frac{\mathrm{d}F(t)}{\mathrm{d}t} \propto \int_0^t \mathrm{d}t' \frac{\mathrm{d}\Phi(t-t')}{\mathrm{d}t'} \sum_{i=1,2} c_i \exp\left(\frac{-t'}{\tau_i}\right), \tag{3}$$

where c_i is a constant and τ_i is the desorption time delay. Shown in Table 1 are the experimentally obtained time delays. In general two delay components are required to properly fit the measured spectra. The significance of this is not completely clear at this moment. It is possible, according to the predictions of Puchin, that the time delays depend on the quantum state of the neutralizing F center. Following this logic it is conceivable that two distinct excited states of the F center are involved in the neutralization process. On the other hand, it is also possible that the functional form used to obtain the time delays is not complete and modification of the mathematical model is necessary. However, even in the later case the presently used model could be expected to supply the proper order of the time delays. The longest time

Table 1
Displayed are the values for the relative yields of the collisional and thermal channels of desorption as well as the values of the time delays and their relative contributions versus temperature. A dash indicates that a value is beyond the accuracy of our measurement and could not be determined

T (°C)	S_{col}/S_{tot} (%)	τ_1 (μs)	τ_2 (μs)	S_{τ_1}/S_{tot} (%)	S_{τ_2}/S_{tot} (%)
5 keV $He^+ \rightarrow$ KI(1 0 0)					
23	3	6	145	31	66
50	1	1	63	16	83
80	< 1	0.3	18	61	39
100	< 1	< 0.1	7	84	16
120	< 1	< 0.1	—	> 99	< 1
160	< 1	< 0.1	—	> 99	< 1
5 keV $Ar^+ \rightarrow$ KI(1 0 0)					
23	94	1	130	2	4
50	58	2.5	59	15	27
80	49	1.5	55	38	13
100	47	< 0.1	25	39	14
120	39	< 0.1	14	44	17
160	21	< 0.1	—	79	< 1
5 keV $He^+ \rightarrow$ RbI(1 0 0)					
23	10	4	94	29	61
50	6	2.4	74	55	39
80	3	1.8	30	85	12
100	2	1.7	14	86	12
120	< 1	1.1	—	> 99	< 1
160	< 1	< 0.1	—	> 99	< 1
5 keV $Ar^+ \rightarrow$ RbI(1 0 0)					
80	89	2.1	26	8	3
100	82	1.2	—	18	< 1
120	70	< 0.1	—	30	< 1
160	50	< 0.1	—	50	< 1

delay observed in our experiment is about 150 μs. Much longer time delays have been reported in high dose experiments by Betz et al. [10]. These delays have been attributed to the formation of large complexes of alkali atoms at the surface. Because of the low ion dose used in our experiments ($< 10^{12}$ ions/cm^2) the surface should remain stoichiometric and the formation of such complexes is improbable. Further verification that our experiments have been performed in the low dose regime lies in the fact that the relative contributions of the thermal component to the overall yield is opposite to the trend in the calculated vapor pressures of the samples. The magnitude of the observed delays appears not to depend on the penetration depth of the projectile which strongly suggests that short range events, as in Puchins model, are primarily responsible for the observed delays.

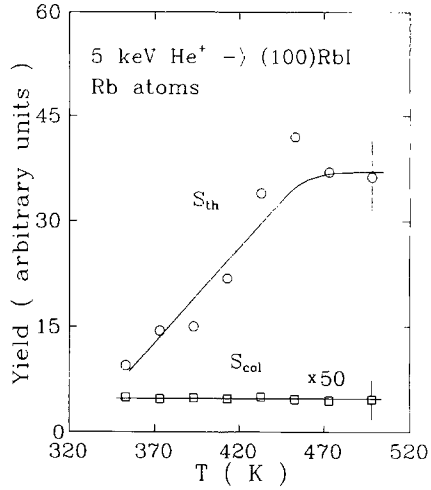

Fig. 2. The temperature dependence of the thermal channel (circles) and the collisional channel (squares) of desorption for 5 keV He^+ irradiation of RbI (1 0 0) . The line is drawn only as a visual aid.

Another quantity of use in understanding the competition between defect-induced desorption and ejection resulting from intersection of the collision cascade with the surface plane is the relative contributions of the collisional and thermal channels. Shown in Fig. 2 are the temperature dependencies of neutral alkali atom flux for the collisional and thermal channels of desorption resulting from the 5 keV He^+ ion bombardment of RbI. The ratios presented in Fig. 2 are obtained by integrating the fitted areas of both the collisional and the thermal peaks. In all cases the collisional component remains constant with temperature and has wide varying contributions to the overall yield as a function of both the target composition and the projectile conditions. For 5 keV Ar^+ bombardment the collisional component becomes substantially smaller, as shown in Table 1, with decreasing alkali mass. The experimentally determined thermal to collisional ratios approximate the trends in the relative contributions of the inelastic and elastic energy transfer as derived from the Winterbon tables [14]. The high energy component also decreases significantly for 5 keV He^+ bombardment relative to Ar^+ irradiation. This can be related to the decreasing probability of elastic interactions with increases in the projectile velocity as well as the decreased ionic radii of the projectile. Furthermore, the thermal contribution is less for the interaction of 5 keV He^+ with RbI relative to the same irradiation of the collisionally less active KI lattice. This suggests that electronic processes are primarily responsible for the production of lattice defects and that the eventual ballistically initiated formation of F and H centers is at best a secondary process in the observed desorption trends.

4. Conclusion

The emission of neutral alkali atoms from ion irradiated alkali halide surfaces has been investigated as a function of the projectile, surface temperature, and substrate. The resulting TOF distributions are described by a modified version of the collision cascade formula. The high energy collisional component is shown to be independent of temperature in all systems examined. The low energy region can be described by the Maxwell–Boltzmann distribution at high temperatures. However, increasing deviation from this distribution occurs with decreased temperature. These time delays have been quantitatively determined and shown to be relatively independent on the depth of deposited energy. This suggests that short range events such as those in the recently proposed model of Puchin are primarily responsible for the observed delays in alkali atom emission. The discussed trends in the ratio of collisional to thermal desorption suggests that the previously categorized processes, which are active in electron and photon irradiation of alkali halide targets, are primarily responsible for the production of lattice defects during ion bombardment.

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