Electron-stimulated desorption of lithium from LiF and the influence of metal islands on the surface

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Our experiments focus on the metal overlayer on LiF created by bombardment with low energy electrons. At higher temperatures the metal atoms did not form a continuous film but three-dimensional islands. This was derived from measurements of the activation energy for desorption that varies as a function of island size (Kelvin model). We also found that island sizes rise with current density. These results were obtained using electron stimulated desorption and thermal desorption techniques.

1. Introduction

Studies on the interaction of low-energy electrons with alkali halides [1–3] have shown, that dissociation of the crystal takes place followed by emission of halogen and alkali atoms. This process is well known as electron induced sputtering of alkali–halides and is part of the field of electron stimulated desorption. Although the underlying mechanism is generally agreed on [4], some questions concerning the details of the process are still open.

If the energy deposited by the incoming electron suffices to overcome the bandgap, an electron of the valence band may be excited into the conduction band, thus forming an electron–hole pair, which may lead to production of a F–H-center pair via a self-trapped exciton. A F-center is an electron on a halogen (X^-) vacancy and a H-center is comparable to a X_2^--molecule on an anion lattice site. While H-centers are mobile and will diffuse already at temperatures as low as 30 K [5], F-center diffusion is limited to temperatures above a few hundred K and may lead to the formation of F-center aggregates in the bulk [6]. If a H-center reaches the surface it will decay and emit a neutral halogen atom. Whereas H-centers are responsible for halogen emission, F-centers cause alkali de-

sorption [7]. F-centers formed at the surface or having diffused to the surface will decay in neutralizing a surface alkali atom. An alkali overlayer is observed at the surface [8–11]. At low temperatures this metal overlayer inhibits desorption. If the vapor pressure of the alkali metal is sufficiently high, alkali atoms in the electronic ground-state evaporate from the crystal. This is the dominant emission mechanism for alkali atoms. Emission of excited alkali atoms and ions constitute only a minor contribution to the total flux and have a different mechanism of formation [3]. In this paper we reveal details of the evaporation process of the alkali metal overlayer using electron stimulated desorption (ESD) and thermal desorption (TD).

2. Experimental

Single crystal (100) surfaces of LiF at different target temperatures (300–800 K) were irradiated with 100 and 400 eV electrons with currents up to 100 µA. We chose a primary electron energy as low as possible to minimize penetration depth in order to focus on surface effects. In ESD-measurements we were able to perform our measurements with 100 eV, in TD-measurements the beam en-

ergy had to be increased to 400 eV to obtain sufficient signal. The irradiated area had dimensions of approximately 2 by 4 mm. The angle of incidence of the electron beam was 45° with respect to the crystal normal. We have measured desorption of neutral lithium atoms with a quadrupole mass analyzer viewing the surface perpendicularly. The pulses from the secondary electron multiplier were processed digitally in pulse counting mode with a dwell time of 1 s. The UHV system maintained a base pressure of less than 3×10^{-10} mbar during the measurements. The crystals were heated at a rate of 8.6 K/min and 1.5 K/s for ESD and TD measurements, respectively. The temperature was measured with a thermocouple connected to a small metal clamp in thermal equilibrium with the surface to insure sufficient heat transport. The crystals have been cleaved in air and cleaned in the vacuum system by prolonged heating at 450°C, which has been proven to give satisfactory surface cleanness [12]. The detection efficiency for the quadrupole in our setup was 10^{-5} counts per desorbing atom. We estimate a desorption efficiency of 0.1 atoms per incoming electron with an energy of 100 eV [13]. This value is in reasonable agreement with previous estimates [14–16].

3. Results

In the first set of experiments (figs. 1 and 2) we measured the desorption yield of Lithium atoms during electron irradiation (ESD). Fig. 1 shows the temperature dependence of the Li desorption from a LiF crystal surface under continuous electron irradiation. Four temperature ranges can be distinguished: (i) At low temperatures the vapor pressure of the alkali metal was negligible and no alkali evaporation took place. No ESD of ground-state Li atoms was observed below 150°C at all irradiating energies. (ii) As the temperature was increased, alkali atoms could evaporate from the surface and an exponential increase in the yield was observed. The desorption flux was limited only by the evaporation rate in this range. (iii) As soon as the evaporation rate exceeded the Li metal formation rate at the surface, a constant
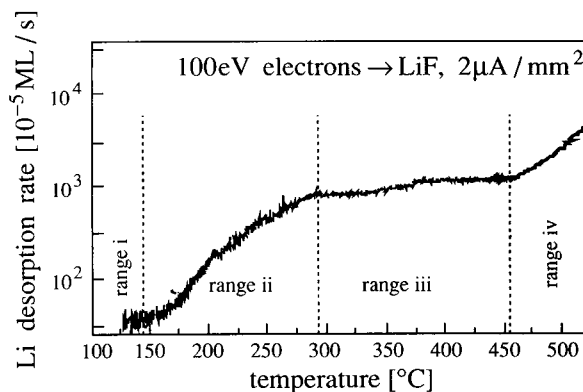

Fig. 1. The ESD yield of Li⁰ as function of crystal temperature during 100 eV, 2 μA/mm² electron bombardment of LiF. Four temperature ranges can be distinguished: (i) No desorption below 150°C due to negligible vapor pressure of the Li layer on the surface. (ii) Exponential increase limited by the evaporation rate of Li. (iii) Desorption rate independent of temperature, limited only by irradiation intensity. (iv) Evaporation of the LiF crystal adds significantly to the desorption yield.

yield was observed even with increasing temperature (plateau). (iv) At temperatures above 450°C the evaporation of the crystal added significantly to desorption. Separate measurements for an unirradiated surface verified this point.

Fig. 2 (ESD) shows the temperature dependence of the Lithium yield for three different current densities in an Arrhenius-plot for ranges (ii) and (iii). For the process governing the behavior in range (ii) activation energies Q were deduced, which range from 0.8 to 1.6 eV. The height of the plateau was proportional to the current density. The onset of range (iii) was shifted to higher temperature with higher current density, because a higher temperature is needed to make the evaporation rate exceed the formation rate of Li metal on the surface. The correlation between current density and activation energy is evident. The results were the same for both heating or cooling the sample. For a low current density and a correspondingly low activation energy we observed a sudden jump of signal around 300°C as a reproducible effect.

In the second set of experiments thermal desorption spectra (TD) [17–19] were recorded (figs. 3 and 4). We irradiated the crystal at tempera-
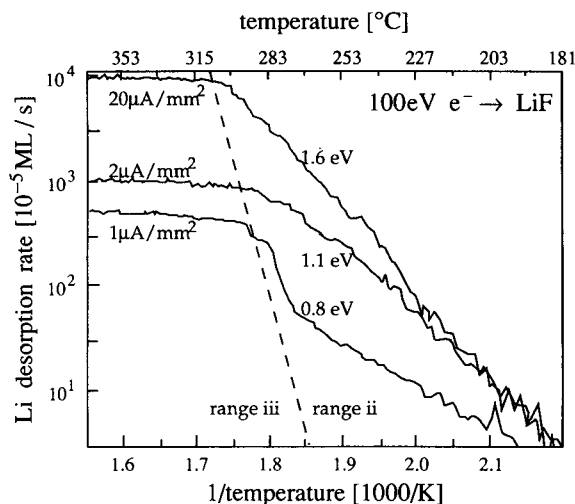
Fig. 2. Arrhenius-plot of ranges (ii) and (iii) during 100 eV electron irradiation for three different current densities (ESD). The activation energies smaller than 1.6 eV (bulk lithium metal) are due to the formation of lithium metal islands on the surface of LiF.

Fig. 4. Arrhenius-plot of three TD measurements. The metal layer was formed by 10 min 400 eV electron irradiation at 150°C for different current densities. As we are close to saturation, the desorption yield depends only slightly on the current density: the calibrated countrate is valid only for the uppermost curve, the others are shifted down by one mark each. It can be seen that the extracted activation energy for desorption is smaller than the value expected for bulk lithium (1.6 eV) and rises with current density.

tures, where no or low desorption occurs and metal accumulates on the surface (100°C and 150°C, corresponding to range (i) or (ii) in fig. 1, respectively). After irradiation the crystal was heated while measuring the desorption of Li atoms. The metal islands evaporated at temperatures cor-
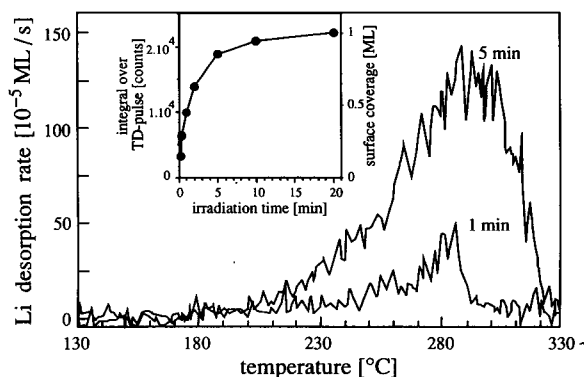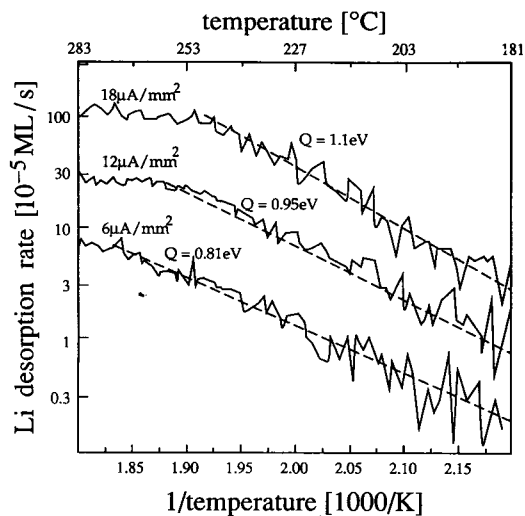

Fig. 3. TD spectra of a lithium metal overlayer on the crystal surface, which was caused by previous irradiation at 100°C with 400 eV, 6 μA/mm^2 electrons. While heating, the metal forms islands which subsequently evaporate. Shown are measurements with irradiation of 1 and 5 min, respectively. The inset shows the integral over the desorption pulse, which approaches saturation for an irradiation time of 20 min with 400 eV, 18 μA/mm^2 electrons.

responding to range (ii) as shown in fig. 3. The integral over the desorption pulse gives the total number of metal atoms evaporating from the surface. The total number of desorbed Li atoms grew with irradiation time until saturation was reached for an irradiation time of 20 min with 400 eV, 18 μA/mm^2 electrons (see inset of fig. 3).

With increasing electron current density we observed an increase in the activation energy for desorption (fig. 4), very similar to the effect shown in fig. 2. For an irradiation of 10 min at 150°C and 400 eV electron energy the activation energy rose from 0.8 eV to 1.1 eV while tripling the current density. As we were close to saturation, the desorption yield rose only slightly with current density.

4. Discussion

The activation energies (figs. 2 and 4) found in range (ii) can be explained by the formation of

metal islands on the surface and their subsequent evaporation. The agglomeration of alkali metal to three-dimensional islands on alkali–halide surfaces under electron irradiation has already been observed with AES [8] and EELS [9–11]. The size of the islands determines the vapor pressure $p(r)$ of the metal and can be calculated on the basis of the Kelvin model [19,20]. For a given temperature $p(r)$ is proportional to $e^{A/r}$ where r represents the radius of curvature on the island surface and A is a constant. Consequently, small islands evaporate faster than larger ones at a given temperature. This relation can also be expressed in terms of the activation energy for desorption of a surface atom, giving larger activation energies for desorption from larger islands. The activation energy for desorption from an infinite lithium surface represents the upper bound at 1.6 eV [21].

We determined an average activation energy Q by heating the crystal and measuring the desorption of Li atoms. Due to evaporation, islands reduce in size and thus the desorption energy from their surface decreases [20]. Small islands vanish already at lower temperatures so that larger islands remain on the crystal surface. Therefore the contribution of large islands to the average activation energy increases and balances the fast evaporation of the small islands, resulting in a constant Q for a reasonable temperature range. The average activation energy Q for desorption describes a certain island size distribution, e.g., a smaller average island size results in a smaller Q [19].

Both ESD and TD measurements demonstrated average activation energies Q smaller than the value for an infinite surface (figs. 2 and 4). As a main point of our paper we conclude from this, that electron irradiation generates a metal enrichment on the surface of LiF in form of islands of a certain size distribution.

It is known that electron irradiation causes small metal islands on an alkali–halide surface to condense to larger ones with increasing irradiation dose, since electron irradiation may change the condensation coefficient of the islands and the number of nucleation sites on the surface [22,23]. In our case the size distribution of the islands is shifted to larger radii with current density at con-

stant irradiation time. For the lowest current density the lowest activation energy and therefore the smallest average island size is found.

In ESD measurements (fig. 2) the surface is enriched with alkali metal in a dynamic equilibrium determined by defect creation in the bulk and evaporation from the surface. In the ESD measurements with an activation energy of 0.8 eV, the step observed around 300°C is not well understood. It might be attributed to a sudden evaporation of small islands above a certain temperature.

One might think that TD measurements (figs. 3 and 4) are influenced by diffusion of F-centers from the bulk to the surface, as the lithium metal due to the dissociation of the crystal by irradiation damage is not only stored at the surface but also in the bulk in form of F-centers and their aggregates [6]. There are some similarities between F-center aggregates in the bulk and metal islands on the surface. In both cases metallization creates an energetically favorable state. Furthermore, the binding energies of both species amount to about 1 eV [5,19]. The following arguments show, that lithium originates predominantly from the surface of the crystal in our TD measurements: (i) Several minutes have passed between irradiation and heating of the crystal. Furthermore, F-centers are sufficiently mobile at our irradiation temperature of 100°C [6]. Therefore, F-centers will either have diffused to the surface (forming Li metal) or will have formed F-center aggregates. (ii) In a previous paper we showed that the disintegration of F-center aggregates contributes less than 5% to the total desorption yield [13].

For irradiation at low temperatures (negligible evaporation of Li) the metal enrichment on the surface approached a saturation value (inset of fig. 3). This behavior was also observed previously [9,25]. The lithium overlayer is assumed to be homogeneous for temperatures below the melting point of lithium and forms three-dimensional islands above [9]. The metal enrichment on the surface reaches a maximum value of approximately one monolayer after irradiation at room temperature [24]. One monolayer of metal will not prevent incident electrons from penetrating below the surface and from creating F–H-center pairs in

the bulk. It does, however, conserve the H-centers in the crystal, because they cannot decay at the surface by emitting a halogen atom. Because of the high mobility of the H-centers, they consequently recombine with F-centers, thus inhibiting further alkali enrichment of the surface.

It follows from the above discussion, that a homogeneous monolayer forms under electron irradiation before heating the crystal in a TD measurement. As soon as the temperature exceeds the melting point of lithium (180°C for bulk metal, somewhat lower for a surface layer), the metal aggregates to islands. Our measurements demonstrated an increase of activation energy with current density (fig. 4), implying an increase in the average island size. In all three spectra of fig. 4 the alkali enrichment on the surface was close to saturation, so that the current density constitutes the only difference between the measurements. Actually, the electron fluence was varied in the experiment, as the bombardment time was identical in all three cases. A higher fluence will increase the number of defects on the surface. We assume the existence of a mechanism that favors larger islands under these conditions, resulting in a larger average island size on the surface. Consequently, in TD measurements the average activation energy Q for desorption rises with current density, in analogy to the behavior found in ESD measurements.

5. Conclusions

We have performed temperature dependent measurements of the neutral Li atom desorption yield. We found that the evaporation of Li metal from the surface is the rate limiting quantity for desorption at low temperatures. Furthermore, the formation and evaporation of alkali metal islands on the surface has to be included in the current model of ESD from alkali–halides. The island size depends on electron current density, which was found in both ESD and TD measurements. After a suitable calibration these techniques may represent methods to study the average size of alkali metal islands on alkali halide surfaces.

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