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SURFACE ENRICHMENT OF Li ON LiF SINGLE CRYSTAL AFTER CLEAVING OR UNDER ELECTRON BOMBARDMENT

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The build-up of an excess metal layer on the surface of LiF(100), after cleaving or due to electron irradiation, is examined by monitoring the neutral atom and molecule emission during sputter depth profiling. At room temperature the Li enrichment on the surface saturates at an electron fluence of 2.5×10^{15} electrons/cm^2 at 500 eV energy. In addition, lesser enrichment of the crystal surface by Li after cleavage without electron irradiation was observed, which also reappears after removal by moderate sputtering by a 3 keV ion beam. Enrichment is attributed to the difference in the formation energies of cation and anion vacancies. The time constants for the build up of the metal layer at room temperature for the unirradiated but cleaved crystal and the cleaved crystal exposed to the saturation dose of electrons are 2 and 40 min, respectively.

1. Introduction

It has been known for some time that alkali-halides can be effeciently eroded in ultra-high vacuum (UHV) by electrons and photons [1]. Due to the negligible momentum transfer the sputtering (desorption) of alkali-halides under electron or photon bombardment cannot be explained by models of binary collision cascades. Electronic processes have been proposed to explain the desorption processes [1–4] and are generally referred to as desorption induced by electronic transitions (DIET). Briefly, the key steps of the proposed mechanism are as follows. An exciton is generated and then trapped at a halogen site. Then the lattice halogen ion, which was raised to an excited state, thermally relaxes to a molecular-like state with a neighboring halogen ion (self-trapped exciton). In this new system the excited electron can relax either by emission of luminescence and return to the normal lattice site, or by a nonradiative transition where the energy is released to the ions as kinetic energy directed along the ⟨110⟩ crystal direction leading to a replacement collision sequence along the chain of halogen ions. This last process leaves an

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F-center (a halogen vacancy occupied by an electron) at the origin and an H-center (a molecular halogen ion X_2^- occupying one lattice site) further away on the ⟨110⟩ crystal direction in the range of the replacement collision sequence. If the replacement collision sequence reaches the surface, directional emission of a halogen atom is caused at hyperthermal energies [1–4], otherwise thermal migration of the defect is needed to reach the surface and leads also to the emission of a halogen atom but at thermal energies [3]. As the replacement collision sequence and the diffusion of defects to the surface take place in the halogen sublattice only, this leads to an alkali-metal enrichment on the surface. With build-up, these excess metal atoms prevent further halogen emission or, if the temperature is high enough, the metal atoms may evaporate. This excess metal layer on the alkali-halide crystal surface is discussed in this paper.

2. Experimental

The experiments were performed under UHV conditions using the SALI technique (surface analysis by laser ionization) which has been described recently [5]. This method employs photoionization of sputtered/desorbed neutral atoms and molecules by intense untuned laser radiation followed by time-of-flight mass spectrometry. The samples are optical quality single crystals of LiF which have been cleaved in air before each experimental run exposing the (100) surface, but no further treatment such as sputter-cleaning has been applied. The system was equipped with a rapid sample introduction system, which introduces a freshly cleaved crystal in less than 5 min into the UHV environment. The sample stage could be heated from room temperature up to approximately 400 °C. The depth profile analysis was performed with a 3 keV Ar^+ beam with 1 μA DC current and a beam diameter of 50 μm provided from a duoplasmatron ion source. All the electron irradiation studies were performed with the electron gun set at 500 eV electron energy, giving a current of 3.5 μA at a beam diameter of 10 μm. Both the electron- and the ion gun axis are tilted 60° from the target normal. The electron- and the ion beam could be rastered electronically over the sample to maintain constant current density over the area of interest and to avoid crater-edge effects in the depth-profiling measurements by gating the laser pulse with the ion beam position. The raster area of the electron beam was 3.1 cm^2, and for the Ar^+ beam it was 0.06 cm^2.

The atoms and molecules sputtered by the Ar^+ beam were ionized by nonresonant multiphoton ionization (MPI) [6,7]. The photoions are accelerated into a high resolution ($m/\Delta m = 1500$), high transmission time-of-flight mass spectrometer of the reflecting type [8] and detected by a chevron microchannel plate assembly. Any secondary ions formed are electrostatically rejected [5]. Sample charging was largely reduced by placing a tungsten mesh tightly over the sample and keeping a low current density, by rastering the ion beam over the sample and by using a very low duty cycle (chopping the beam) for the analyzing ion beam, which had an additional advantage for high depth resolution. Under typical conditions, the time-averaged Ar^+ beam was 0.92 $\mu A/cm^2$. A fluence of 4.44×10^{15} ions/cm^2 was needed for a typical depth profile.

3. Results and discussion

A typical mass spectrum obtained by analysing a LiF(100) crystal with Ar^+ bombardment before electron irradiation is shown in fig. 1. The dominating feature in the mass spectrum is the Li peak with its isotope distribution (m/q 6, 7), which likely is formed primarily by nonresonant two-photon ionization of atomic Li. The fluorine atomic mass peak is missing due to the high ionization potential of 14.5 eV, which requires four 4.66 eV photons of the 266 nm laser radiation, and therefore a very high laser intensity for this fourth-order process, which our laser did not provide in this setup. The second outstanding

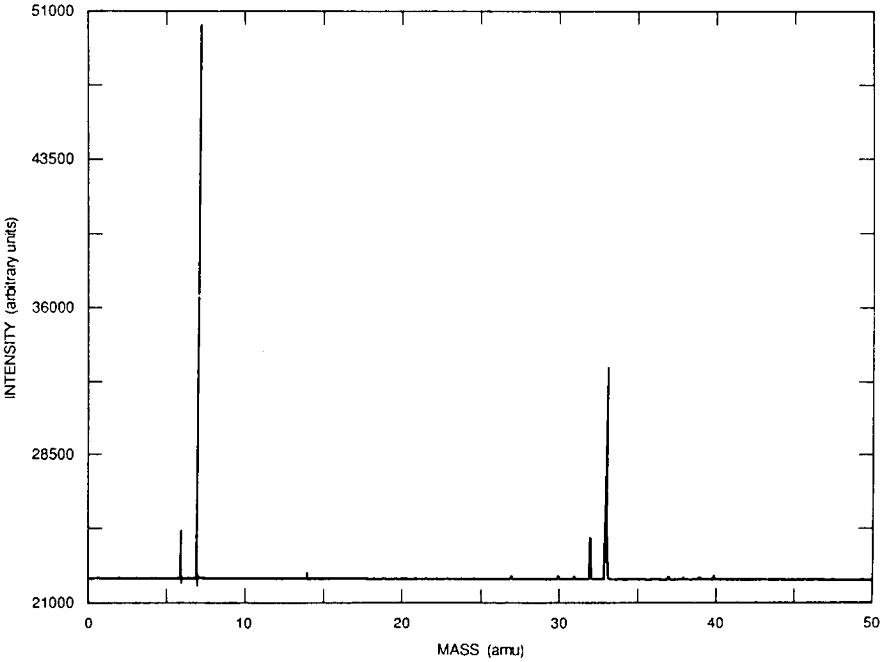

Fig. 1. Mass spectrum of single crystal LiF (100) under 3 keV Ar-ion bombardment and a laser wavelength of 266 nm.

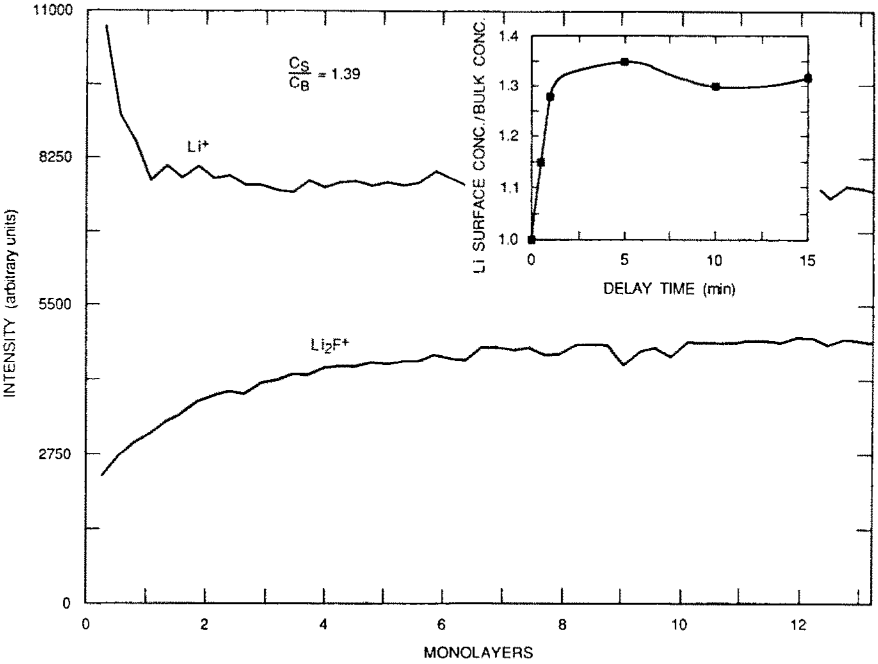

Fig. 2. Depth-profile of a freshly cleaved LiF crystal under 3 keV Ar^+ bombardment at room temperature. The insert shows the buildup of the Li surface enrichment over the time between successive Ar^+ bombardment depth profiles.

feature is the Li_2F^+ peaks (m/q 31, , 32, 33), which can be recognized by the Li isotope signature very easily and most likely result from two-photon absorption of $(LiF)_2$ to form the ion pairs Li_2F^+ and F^-. Direct photoionization of Li_2F as a source of Li_2F^+ is not very likely, because one would expect a much lower stability of the Li_2F molecule compared to the $(LiF)_2$ molecule and more energy is needed to break up the lattice. The absence of the LiF^+ photoion peaks can be explained by photodissociation to the ion pair state of Li^+ and F^- from sputtered LiF. There are also some minor peaks like Li_2^+ (m/q 12, 13, 14), Li_3F^+ (m/q 37, 38, 39, 40), Na^+ or LiO^+ (m/q 23) and $LiNa^+$ or Li_2O^+ (m/q 30). The $LiNa^+$ as well as the Li_2^+ peaks are probably resonantly enhanced. All masses seen in this mass spectrum are recorded simultaneously for each depth profile.

Fig. 2 shows a depth-profile recorded at room temperature of a freshly cleaved LiF crystal with no previous electron irradiation. Taking the sputter-yields for LiF under Ar^+ bombardment from Navinsek [9] and assuming a cosine angular dependence of the sputtering yield on the angle of incidence of the ion beam to the target normal, we can convert the sputter time into a depth scale. One can clearly notice the Li surface enrichment which is a factor of 1.35 ± 0.03 larger than the bulk steady-state signal and extends merely one monolayer. The steady-state signal was reached very soon and it was not necessary to exceed the investigation over more than 10 monolayers in depth for our experimental conditions. In contrast to the Li signal, the Li_2F signal increases from a lower than bulk value to the bulk value reflecting the expected fluorine depletion in the surface region. The fluorine depletion seems to reach deeper into the crystal than the Li enrichment, which is confined closer the surface. Although, monitoring the Li_2F signal is not a direct monitor of the fluorine depth-profile, it gives us some indication about the concentration profile.

We now have to consider if the effect of preferential sputtering [10] is operative and explains the results shown in fig. 2. Preferential sputtering would give the results shown in fig. 2, if we assume a higher sputter-yield of Li than of F sputtered from a LiF target. This would create an altered layer (in the range of the penetration depth of the Ar ions) with a lowered Li concentration at the surface. After a certain bombarding time, a steady-state situation will be attained and the composition of the sputtered flux will be equal the bulk concentration by conservation of mass. Preferential sputtering [10] is mainly caused by differences in the surface binding energies, beside a minor mass effect which would favour Li. But for Li and F the surface binding energies will be almost equal [11]. Thermal evaporation of Li would not contribute here to the sputter-yield of Li due to the negligibly low vapour pressure at room temperature (below 10^{-11} Torr [12], which gives an evaporation rate of less than 10^{-6} ML/s). The initial Li enrichment on the surface after cleavage disappears after removal of less than 10 monolayers by the ion beam. After approximately 2 min a Li surface enrichment equal to that obtained for the freshly cleaved crystal is attained again (insert of fig. 2). This measurement was done by taking consecutive depth profiles at the same spot and varying the time between two measurements, thus enabling us to monitor the migration velocity, by removing any Li enriched surface layer each time. The scatter of data points for higher delay times is attributed to the increased damage the probe beam generates.

Preferential sputtering of LiF has been claimed in other work, where a final enrichment of Li on the crystal surface of 1.34 compared to the freshly cleaved surface after 3 keV Ar^+ bombardment was reported [13]. But, Li enrichment on the crystal surface means preferential sputtering of fluorine by the Ar^+ beam [10]. In addition, the reported dose [13], which is needed for saturation of the non-stoichiometry of the crystal surface at 3 keV Ar^+ bombardment is 1.7×10^{17} ions/cm^2. That dose is almost two orders of magnitude higher than the dose we used for our depth profiles. Therefore the influence of the Ar^+ beam on the non-stoichiometry of the surface is expected to be rather small in the range of our investigations. This leads to the conclusion that fig. 2 shows a true enrichment of Li on the surface and is not a preferential sputtering artifact. That the enrichment shows a time dependence (insert of fig. 2) further rules out preferential sputtering.

When examining the temperature dependence of the Li surface enrichment of the freshly cleaved sample from room temperature up to 250 ° C with no previous electron irradiation, we observed a constant Li enrichment of 1.35 compared to the bulk signal. At 250 ° C the enrichment starts to decrease until around 400 ° C where we see no surface enrichment at all. This is ascribed to evaporation of Li metal and will be discussed below.

The dominance of one species on the surface of an ionic crystal as a result of different formation energies for cation and anion vacancies has been discussed in some length in literature [14,15]. The lower free energy of the cation vacancy compared to the anion vacancy leads to an excess of cation vacancies in the surface region (termed the Debye–Hückel layer) resulting in a negative space charge. The presence of a space charge is an inherent aspect of thermal equilibrium. As the overall neutrality of the crystal has to be maintained, the space charge is compensated by a positive charge on the surface (Li enrichment). The surface enrichment is expected to be very thin (merely one monolayer) compared to the space charge region, that extends to a depth called Debye length into the crystal.

When the LiF crystal is irradiated with electrons at room temperature, no desorption of any species is observed by the impinging electrons. But a considerable change in the surface composition takes place as seen in the depth profiles taken with an Ar^+ probe beam after electron irradiation. The electron irradiation leads to a maximum Li surface enrichement of 1.75 ± 0.04 compared to the bulk signal as seen in fig. 3. This is achieved by a minimum electron flux of 2.5×10^{15} electrons/cm^2 at 500 eV necessary for saturation of the surface enrichment. This Li surface enrichment seems to be self-inhibiting, as an increase of the electron flux even by orders of magnitudes does not lead to further increase of the Li enrichment on the surface. Furthermore, at room temperature it takes about 40 min after irradiating the LiF crystal with the saturation dose (that is 8.3×10^{12} electrons/cm$^2 \cdot$ s for 5 min) to establish the final enrichment of Li on the surface, shown in the inset of fig. 3. After the electron irradiation, consecutive depth-profiles were taken at various delay times, each on different spots within the area of electron bombardment, to monitor the formation of the Li enrichment (fig. 3).

The temperature dependence (fig. 4) of the Li metal layer on the surface under continuous 500 eV electron irradiation shows that the enrichment remains constant in the range from room temperature up to 250 ° C. At this temperature the evaporation rate of Li metal from the surface starts to exceed the generation of the Li metal layer due to migration of defects, until it is by far the fastest process and all excess metal on the surface evaporates essentially immediately above 400 ° C. The same situation applies for freshly cleaved crystals without electron bombardment as mentioned above, though

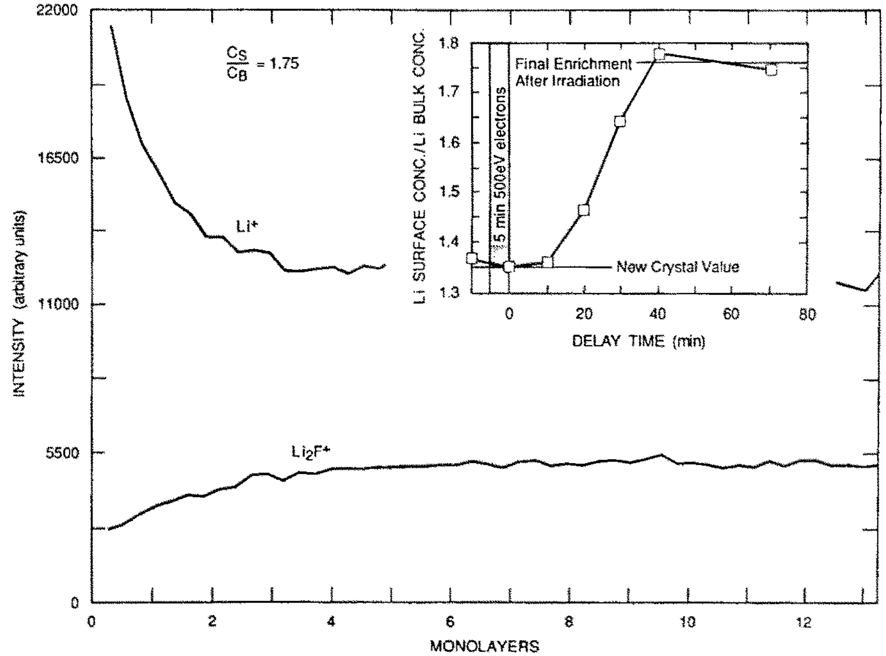

Fig. 3. Depth-profile of LiF at room temperature after a 500 eV electron fluence of 2.5×10^{15} electrons/cm^2 and 40 min delay after electron irradiation analyzed with a 3 keV Ar-ion beam. The insert shows the buildup of the Li surface enrichment after electron irradiation over time. Every Ar^+ depth profile was taken on a new spot of the homogeneously electron-irradiated crystal.

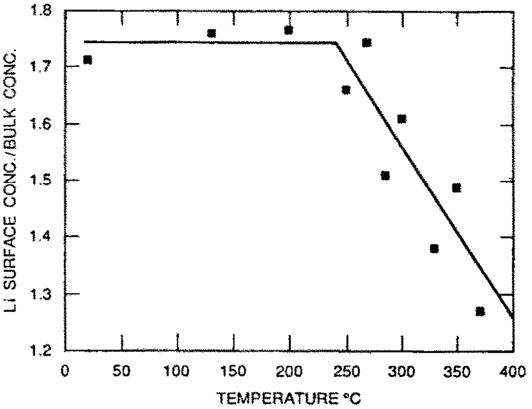

Fig. 4. Temperature dependence of the Li surface enrichment under continuous electron irradiation (7×10^{12} electrons/cm$^2 \cdot$s) at 500 eV analyzed with a 3 keV Ar-ion beam.

migration of Li towards the surface instead of migration of defects is the reason for the Li enrichment on the surface in that case. The Li metal evaporation rate increases from 1.2×10^{-2} ML/s at 250 °C to 11 ML/s at 400 °C according to the equilibrium vapor pressure [12] and assuming an evaporation coefficient of unity. The scatter of data points in fig. 4 at higher temperatures may be caused by the aggregation of the homogeneous Li overlayer on the crystal surface into three-dimensional islands above the melting point of the alkali-metal [16,17] and partly also by defects induced by the Ar^+ beam. Due to apparatus reasons the measurements of the temperature dependence were performed without a tungsten mesh over the sample, but the continuous electron irradiation prevented charging of the sample by the Ar^+ beam. Between each depth profile taken at different temperatures, sufficient time has passed to insure that the metal layer has reached its ultimate thickness. Also the electron fluence between two points was high enough to reach a steady-state situation.

The temperature dependence of the Li surface enrichment, and especially the onset for the decline of the enrichment found at 250 °C is in accord with recent laser-induced fluorescence measurements [18] of ground-state Li desorbed from LiF under 500 eV electron bombardment. The main contribution to the sputtered flux of alkali-metal atoms by ESD of alkali-halides are neutral ground-state atoms [18]. In that work [18] an onset of the Li ground-state desorption was found at a temperature of 250 °C, which coincides with the decrease of the Li surface layer described here (fig. 4). Above 400 °C metal evaporation is no longer the rate limiting process for the ESD, hence every excess surface Li atom can be expected to evaporate essentially immediately, which was also found by Haglund et al. [8]. The desorption yield will only be governed by the electron flux and not depend on the temperature above 400 °C [19].

4. Conclusions

The buildup of an excess metal layer on the surface of alkali-halides due to electron irradiation and also after cleavage with no electron irradiation has been confirmed by this experiment. The effects of the existence of an initial metal overlayer and the build up after electron irradiation were predicted by theory previously (refs. [14,15] and refs. [1–4], respectively) and also indicated by electron-based spectroscopies (e.g. refs. [16,17], and references therein) but never directly depth profiled until now.

The existence of a space charge on the surface of ionic crystals has been discussed to some length in numerous publications. The early work of Mott and Littleton [20] showed that the free energy to form a cation vacancy is less than that required to form an anion vacancy. Then there will be a tendency to form an excess of cation vacancies resulting in a region of negative space charge near the surface. This excess charge in the space charge region is compensated by a layer of positive charge lying on the surface, the result of an excess of cations. Not only the differences in the free energies of formation of the vacancies lead to a space charge on the surface, but also impurities, which accumulate near the surface have a strong influence on the sign and amount of the space charge [15]. We did not observe any accumulation of impurities on the surface in our experiment. Furthermore, the surface itself plays an important role as the energies for vacancy formation are different on the surface and in the bulk [21]. The number of surface sites, which are available as sources for defects depends on the orientation of the surface. This was shown in recent experiments with AgCl [22]. The cation enrichment on the surface was most pronounced for the (100) surface and for the (110) surface an anion enrichment was found. Oxygen on the surface could act as source for vacancies. Oxygen is present in small amounts on the freshly cleaved surfaces as can be seen in fig. 1 and might enhance the observed effect. After removal of ≈ 3 monolayers oxygen cannot be seen any more, although the surface enrichment reappears.

There is also the possibility, that the cleaving process introduces sufficient defects which could lead to a surface enrichment. Ref. [23] directly addresses the effects of fracture and cleavage of LiF. Cleaving results in long lasting electron and positive ion emission presumably from defects generated during the cleaving process. Spatial resolved measurements [23] showed that this particle emission originates only from the damaged part of the cleaved surface, that is the part of the surface which was hit by the blade and virtually no emission emerges from the undamaged surface. Emission will decrease with decreasing penetration of the blade and increasing load of the blade as discussed in detail in ref. [23]. In the usual cleaving practise to obtain a good surface one naturally is in the regime with low surface damage. Still we cannot rule out totally the possibility that the cleavage is at least partly the reason for the initial Li enrichment, but we think that our observance that the Li enrichment on the surface reappears in the same size after removal by the ion beam strongly favors the segregation.

In the case of electron bombardment the long time constant for the creation of the excess metal layer after electron bombardment supports the model that the migration of defects, and more specifically, the migration of F-centers is responsible to establish the metal overlayer on the surface. The replacement collision sequence will lead to halogen depletion well below the surface, to the depth of the electron range. Using the formalism given by ref. [24] we derive and electron range of 100 Å for 500 eV electrons directed under 60° from the sample normal onto the LiF crystal. The maximum of the deposited energy of the primary electrons is at 20 Å. The halogen depletion below the surface is caused by the fact that the F-center stays at the origin of the initial defect (seen with the time scale of a replacement sequence) and the halogen site at the surface at the end of the replacement chain is filled by the subsequent halogen atom in the replacement sequence immediately, thus not changing the stoichiometry of the surface directly. Also the migration of H-centers (an X_2^- molecule in one lattice site) to the surface will lead to the release only of a halogen atome without changing the surface stoichiometry. Only the thermal migration of F-centers (a halogen vacancy occupied with an electron) to the surface finally makes the Li enrichment possible. The importance of the F-center diffusion to the surface for the metal enrichment has been addressed recently by Loubriel et al. [25]. In addition, the fact that the halogen depletion reaches deeper into the crystal can also be seen from the depth profiles, because the Li_2F signal takes longer to reach the bulk value.

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