# Spatial distribution of defects in LiF induced by low-energy electron bombardment: Evidence for rapid hot-hole diffusion

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We report measurements of concentrations and spatial distributions of defects, defect clusters, and surface metal arising from low-energy electron bombardment of LiF crystals. The method employed to monitor defect concentration as a function of depth uses optical transmission spectroscopy in conjunction with depth-profile techniques. Investigations at $-90\,°C$ indicate that the observed spatial distribution of defects can be explained best by long-range diffusion of hot holes.

It is well known that low-energy electron and photon bombardment of alkali halides produce $F$ and $H$ centers in the crystals by generation of holes in the valence band.[1,2] The migration of an $H$ center to the surface of the crystal leads to the desorption of a halogen atom, since halogen atoms are only bound to the surface by weak van der Waals forces. This gives a thermal contribution to the energy spectrum of desorbing halogen atoms.[3] Szymonsky et al.[4] observed the angularly dependent desorption of energetic, nonthermal halogen atoms, which the authors hypothesize to be related to the formation of surface hot holes, i.e., holes in the valence band that localize directly on the surface at a halogen ion position. A hot hole is a hole in the valence band, which is formed *below* the top of the valence band. Thermoluminescence studies on silver doped NaCl indicated hot-hole diffusion with a self-trapping limited diffusion length of 720 Å for low-impurity contents.[5] Green et al.[6] speculated that their experimental desorption results could be explained by considering that significant hot-hole diffusion is occurring. So far, however, no direct evidence for the existence and importance of hot-hole diffusion in alkali halides has been given. Our new results provide strong evidence that hot-hole diffusion is essential for the interpretation of experimentally observed desorption yields of halogen and alkali atoms.

It is widely believed that the migration of an $F$ center to the surface of an alkali halide results in the neutralization of an alkali ion with subsequent surface metallization, although this process is not yet well understood in detail.[7,8] Optical absorption spectroscopy and other experimental methods have provided strong evidence that the bombardment of alkali halides with electrons leads under certain experimental conditions to the formation of alkali islands on the surface of the crystals.[9,10] The migration of $F$ centers in the crystal can also lead to the production of small $F$-center clusters (such as $F_2$, $F_3$ centers), or even large clusters consisting of several hundred $F$ centers. The latter show metallic behavior and are actually small alkali inclusions (colloids) in the crystal.[11]

Up to now it was only known the $F$ centers are formed in the bulk and metal clusters—depending on temperature and radiation dose—on the surface or in the bulk of

electron bombarded alkali halide crystals.[9,10,12] A detailed mapping of the spatial distribution of various defects formed by bombardment with ionizing radiation has not yet been done according to our knowledge. We present first experimental results of $F$, $F_2$, and metallic Li cluster concentrations as a function of depth after electron bombardment at $-90\,°C$. Knowledge of the initial spatial distribution of the primary defects is of major interest and importance. To first order, one might assume that the defect distribution is identical to the energy deposition profile which is usually approximated by a triangular shape[13] (see Fig. 2, thin line). However, the depth profile can be altered due to temperature-dependent $F$-center diffusion. Without rapid diffusion of $F$-center predecessors such as hot holes and of $F$-centers themselves, one would expect a distribution of defects very similar to the initial energy-loss profiles shown in the paper of Jammal et al.[13] If the average diffusion length of $F$ centers or of $F$-center predecessors, however, is of the order of the penetration depth of the electrons, it is necessary to take it into account for determining the final spatial distribution of stable defects.

Experiments were performed in a stainless-steel UHV chamber with a base pressure of less than $1 \times 10^{-9}$ Torr during electron bombardment. In our experiment, LiF $\langle 100 \rangle$ surfaces were bombarded with electrons of 2000 eV at $-90\,°C$. Electron current densities were typically 700 $\mu A/cm^2$. The angle of incidence of the electron beam and the low-energy ion beam was about $45\,°C$ with respect to the target normal (see Fig. 1). A low-energy ion gun provided current densities of $N_2^+$ ions of approximately 3 $\mu A/cm^2$ at 4.5 keV. Electron and ion currents were measured with electrically biased samples. For our transmission optical absorption experiments, incident light from a deuterium lamp was directed along the surface normal. The transmitted light was detected with a spectrometer/PMT system. Temperatures were measured with a thermocouple, which was thermally connected to the surface of the crystal and to the target holder.

Absorption measurements carried out during low-energy electron bombardment showed the formation of $F$ centers, and $F_2$ centers (Fig. 2). The formation of a broad band centered around 5500 Å was also observed,
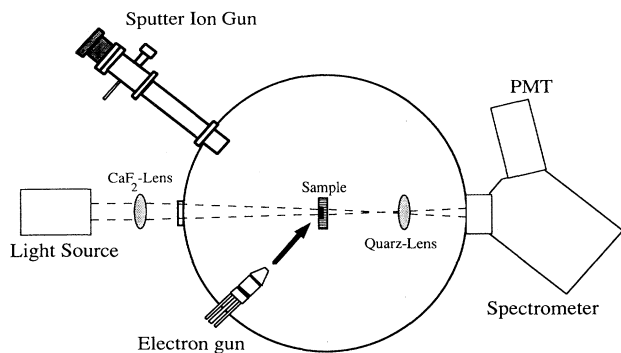
FIG. 1. Schematic representation of the experimental setup.

which is believed to be due to a metallic phase.[14] Below we will see that the depth profile measurements provide strong evidence that the metallic phase is near the surface and not in the bulk of the irradiated LiF crystals. Another strong evidence that the metallic phase is on the surface is the known low mobility of $F$ centers at room temperature and below. Since colloids (metallic clusters in the crystal) are large $F$-center clusters which have rearranged to a metallic phase, a high mobility of $F$ centers is required for the formation of colloids.[11,15] In contrast, the mobility of alkali atoms on the surface of insulators is most likely considerably higher and it is consequently possible to form large alkali clusters on the surface of the bombarded crystals at temperatures where $F$-center mobilities are negligible.[16]

The concentration of $F$ centers and $F$-center-type defects can be computed using Smakula's formula[17] which relates $F_n$-center concentrations to the zero moment of the absorption band. The oscillator strength for the transition from the ground to excited state equals approxi-
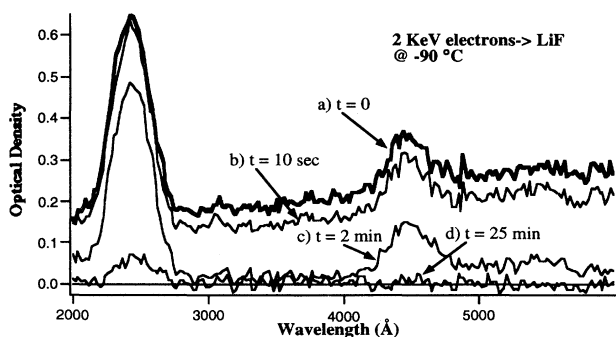


FIG. 2. Optical densities of LiF plotted as a function of wavelength at $-90\,°C$. The topmost spectrum (thick line, $t=0$) was recorded immediately following 30 sec of 2-keV electron bombardment. Prominent features in the spectrum include the $F$ band (2500 Å), the $F_2$ band (4500 Å), and a broad metallic band which extends over the entire spectrum. Subsequent spectra obtained after intervals of ion bombardment on the same spot clearly shows a decrease of the optical density and consequently of defects in the crystal (thin lines $b-d$). Note, that the broad metallic band is gone after about 2 min of low-energy ion bombardment (line $c$), whereas the height of the $F$- and $F_2$-center bands stayed constant.

mately 1.0 in the case of the $F$ centers, whereas it typically equals 0.2 to 0.3 for $F_2$ centers.[18,12] One can also use Smakula's formula to compute the number of metal atoms in metallic clusters. Doyle showed that the absorption of light per electron is the same irrespective of whether the electron is in an anion vacancy ($F$ center), or in the conduction band of the metallic particles.[19] However, for very large clusters [i.e., larger than a few hundred Å (Ref. 11)], the cross section for scattering is larger than the cross section for absorption of light and the use of Smakula's formula breaks down.

In our experiments, the spatial distribution of defects following electron bombardment in the crystal was measured using an ion gun in conjunction with optical transmission spectroscopy. The experiments were carried out by monitoring the total defect concentration as the ion gun sputtered away the surface area, layer by layer (Fig. 2). The difference in optical densities before and after a sputtering event is a measure of the defect concentration in the corresponding layer which was sputtered away. This applies under the assumption that the *effective* number of defects created by the ion bombardment is small compared to the number of defects created by the initial electron bombardment. The projected range of the N atoms or ions is of the order of 80 Å,[20] which indicates that certainly not all defects produced by the ion impact are formed on the surface. However, the resulting bulk defect densities are negligible compared to the defect densities produced by the electron bombardment. Ion bombardment did not result in the formation of a detectable amount of defects, as measured by optical methods, under our experimental conditions (Fig. 2). This observation and the fact that we measured large differences in defect concentrations as a function of depth (see Fig. 4), justifies our assumption that the difference of optical densities between two scans (one before and one after a sputtering process) corresponds to the number of defects of the sputtered layers *prior* to ion bombardment.

The sputtering time is directly related to the depth we are probing during the ion bombardment. The depth is computed by assuming a sputter yield of four.[21] Neidhart *et al.* measured the sputter yield for 500-eV Ar+ ions on LiF using a quartz crystal microbalance. Unfortunately no values are available for 4.5-keV $N_2^+$ or 2.25-keV $N^+$ ions on LiF. However, the computed penetration depths for 2-keV electron bombardment are of the same order as those measured by Bronshteyn and Protsenko[22] for 1–4 keV electrons on LiF.

Charging due to ion bombardment did not influence our results under our experimental conditions, since employing different ion bombardment times (i.e., different number of sputtered layers per sputter event) gave practically the same results. We believe that we were in a steady-state situation for ion bombarding times used in our experiments.

A definitive test for the relevance of rapid diffusion of $F$-center predecessors can be made only at low temperatures (as low as $-90\,°C$) where the $F$ centers are effectively frozen in place. The fact that under our experimental conditions the concentration of $F_2$ centers corresponds to statistically distributed immobile $F$ centers in-

dicates that the $F$-center mobility is not enhanced significantly near the surface. We computed the amount of $F_2$ centers by assuming that all $F$ centers are distributed statistically in the irradiated volume and that the $F$ centers are completely immobile. The results of this simple model are consistent with our observed data. Further evidence is provided by the fact that the relative amount of metal on the surface increases only slightly between $-90$ and $0\,°C$. $F$-center diffusion may consequently be disregarded for temperatures as low as $-90\,°C$. Following the procedure outlined above, the data taken at $-90\,°C$ in Fig. 4 clearly show that there is substantial metal located very close to the surface as indicated by the broad metallic band at depth "zero." Due to the uncertainty in the sputter yield it is difficult to say if the metal is spread a few layers into the crystal. One would expect to observe this because of the three-dimensional structure of the metal clusters. As soon as the metal is sputtered away, the $F$-, and $F_2$-center concentration starts increasing as a function of depth in the crystal. After about $100\,\text{Å}$ these concentrations reach a maximum and then decrease again. The total number of $F$ centers in the bulk of the LiF crystals produced by 2-keV electron bombardment for about 30 sec was about $10^{15}$ per $\text{cm}^2$. The number of metal atoms on the surface is of the order of at least $4\times10^{15}$ alkali atoms per $\text{cm}^2$ if it is assumed that the clusters are small enough such that scattering of light is not of importance. If most of the light is scattered rather than adsorbed by the (relatively) large alkali clusters, then at least 20% of all produced defects are in form of alkali atoms on the surface, which would correspond to a hot-hole diffusion length of approximately $200\,\text{Å}$. This rough estimate assumes that the average clusters size is about $200\,\text{Å}$ and that there are about $10^9$ nucleation sites per $\text{cm}^2$ on the surface.[16] This indicates that roughly 2 orders of magnitude more defects are produced on the surface than may be accounted for by the surface energy-loss function of the bombarding electrons (see Fig. 3, thick line). The calculations plotted in Fig. 3 show the calculated distribution of defects (i.e., $F$ centers or metal atoms) after 2-keV electron bombardment at $-90°C$, where $F$-center diffusion is negligible. For a hot-hole diffusion length of $0.0\,\text{Å}$, the final distribution of defects would correspond to the initial triangular-shaped energy-loss profile. In that case one expects that only a small fraction ($<1\%$) of all defects are localized on the surface, which we have shown experimentally is clearly not the case as shown in Fig. 4. For a hot-hole diffusion length of $200\,\text{Å}$ the number of holes on the surface accounts for about 25% of all defects. In the calculations it is assumed that all hot holes which arrive at the surface are trapped on the surface. The calculations show that the region immediately below the surface is clearly depleted, an observation which is clearly shown also in our experimental data (Fig. 4). We presently do not understand why hot holes are trapped specifically at the surface. The interaction of the holes with electrons trapped at the surface[23] might be one possible explanation.

It is worth noting that in Fig. 3 the defect production efficiency has been assumed to be the same in the bulk and at the surface of the crystal. The defect production
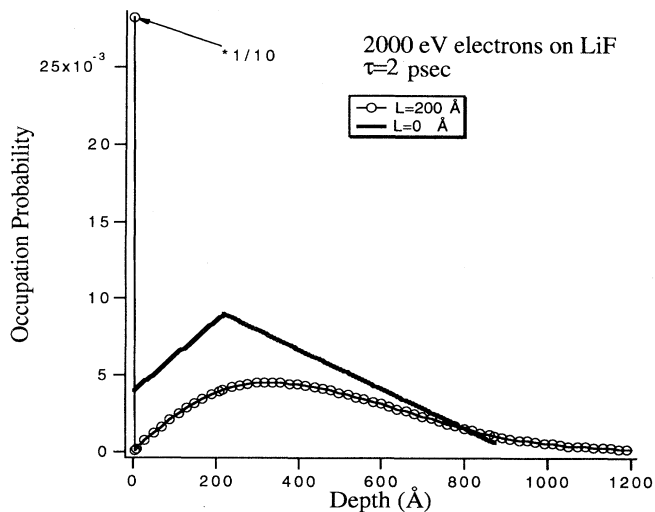


FIG. 3. Calculated spatial defect profiles plotted for hot-hole diffusion lengths of 0 (thick line) and $200\,\text{Å}$ (circles) each with an electron energy of 2 keV. Under the assumptions that the hot hole diffusion length is $200\,\text{Å}$ and that the surface is 100% absorbing for hot holes, the surface is left with a high percentage of alkali metal content arising from hot holes.

efficiency in the bulk is roughly of the order of 0.3 at $-90\,°C$ in the case of KCL (type-III configuration).[2,24] The surface-defect production efficiency can consequently be at most a factor of 3 larger, which is negligible compared to the 2 orders of magnitude larger defect concentrations observed on the surface. The fact that the experimental data show a maximum of the $F$-center concentration at about $100\,\text{Å}$ rather than at $300\,\text{Å}$ (calculated data, Fig. 3) can be explained by considering that the
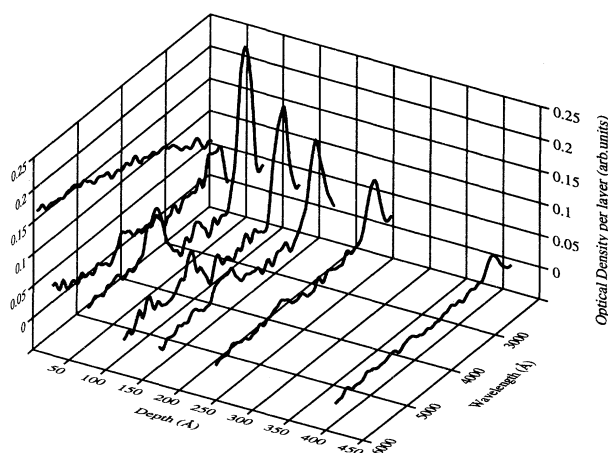


FIG. 4. Optical density per lattice site is plotted as a function of depth and wavelength after 2-keV electron bombardment at $-90\,°C$. This plot is obtained from subtracting adjacent spectra plotted in Fig. 2. One clearly sees that there is a significant metal concentration on the surface of the crystal, whereas the $F$-center-type defects are in the bulk of the LiF crystal. The region close to the surface is clearly depleted.

sputtering rate is not very well known and that the experimental uncertainty of our $F$-center concentration is roughly 20%.

It is clear at this point that very mobile defects other than $F$ centers are responsible for the high concentration of defects on the surface. The diffusion of self-trapped holes, free thermalized excitons, or self-trapped excitons can hardly account for the observed spatial defect distribution since their lifetime is typically of the order of a few tens of psec in type-III crystals such as, for example, LiF or KBr.[2,25] Only in the cases of low defect (electron) concentrations or high densities of electron trapping impurities, self-trapped holes are stable long enough to diffuse significant distances. This is, however, clearly not the case under our experimental conditions, and the self-trapped holes are converted efficiently into $F$-$H$ center pairs by electron capture in less than a few hundred psec.[2] Unfortunately, no exact lifetimes are known in the case of LiF (according to our knowledge). A considerably longer lifetime of excitons in LiF (i.e., of the order of a few hundred nsec or more at $-90\,°\text{C}$) could account equally well for the observed defect distribution. However, another evidence for hot hole rather than self-trapped hole or exciton diffusion is the fact that the relative amount of metal on the surface increases only slightly between $-90$ and $0\,°\text{C}$, whereas it increases significantly for temperatures around and above room temperature. Hot-hole diffusion, in contrast to an $F$-center, self-trapped hole, and exciton diffusion, is known to be independent of temperature. Consequently, our data are best described by the assumption that long-range hot-hole diffusion determines the final defect distribution in LiF.

Depth-profile measurements with optical transmission spectra provide significant insights into the interaction of low-energy electrons with ionic crystals at or close to crystal surfaces. Our data show the surprising result that at temperatures as low as $-90\,°\text{C}$, large quantities of alkali clusters are formed on the surface of the alkali halides. These data can be explained best by the assumption that hot-hole diffusion plays a major role in determining electron-bombardment-induced defect distribution in LiF and that the surface acts as an efficient trap for hot holes. However, further investigations are necessary to determine whether exciton diffusion plays an important role in the case of LiF. Investigations of the spatial distribution of defects in alkali halides with known exciton mobility and lifetime have the capability to differentiate between hot-hole and exciton contributions. More investigations with different alkali halide crystals are necessary (and planned) to resolve this problem.

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