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OBSERVED BY SCANNING FORCE MICROSCOPY**

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Heavy-ion induced modification of lithium fluoride observed by scanning force microscopy

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Abstract. To study ion-induced damages in single crystals of lithium fluoride with scanning force microscopy (SFM), samples were irradiated with several heavy-ion species of a kinetic energy of 11.4 MeV per nucleon at the linear accelerator UNILAC of GSI. As concluded from a previous analysis of ion tracks in LiF by optical absorption spectroscopy and small-angle x-ray scattering, single point defects occur in a track halo with a radius of about 15-30 nm, whereas defect aggregates are formed in a track core region possessing a radius of only about 1-2 nm. These aggregates can be attacked by chemical etching if the energy loss along the ion trajectory surpasses a critical value of about 1 keV/Å. SFM images of etched as well as unetched sample surfaces revealed new damage characteristics: Etched ion track profiles directed parallel to the ion trajectories exhibit a sequence of single etch pits with an average distance of about 140 nm. After exposure to heavy-ion irradiation at normal incidence, the unetched LiF surface is covered with round hillocks with a mean diameter of 55 (8) nm and heights in the order of 3 nm.

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1 Introduction

The irradiation of alkali halides with energetic electrons, photons (i.e. x-rays and gammas), or heavy ions creates damages of the crystal lattice via the excitation of the electron subsystem. These processes have been studied by numerous groups (see, e.g., refs. [1-8]). The main defects are *F*-centers (an electron at an anion vacancy) and *V*-centers (a covalent molecular halogen anion at a regular anion site). At a high dose, complex microdefects such as *F*-center clusters (nF) and alkali colloids, diatomic halogen molecules and their aggregates, and vacancy clusters can be formed. Such processes depend strongly on the dose, dose rate, and temperature during irradiation.

The present work deals with the characterization of heavy-ion induced changes in single crystals of lithium fluoride. The objective of the study is to complement the techniques of optical absorption spectroscopy, small-angle x-ray scattering, and track etching by applying scanning force microscopy (SFM) to etched as well as unetched ion tracks in LiF. Since the early nineties, SFM has been used to image ion tracks in various materials (e.g. mica, polymers, high- T_C superconductors, and others) [9-12]. Furthermore, SFM was applied to different ionic crystals such as alkali halides (e.g. LiF [13-15], NaCl [14-18], NaF [19], KI [20], and KCl [14, 15]) and alkaline-earth halides (e.g. CaF₂ [14, 15, 21, 22] and BaF₂ [14]), with particular emphasis on atomic resolution and the visualization of microscopic defects.

2 Review of complementary work on LiF

In order to mark the frame of the present study, we briefly review recent results achieved by optical spectroscopy, small-angle x-ray scattering [23], and chemical etching [24]. Using optical absorption spectroscopy, the concentration of *F*- and *F*₂-centers was determined as a function of the ion fluence. For high fluences, the density of *F*-centers saturates due to an overlapping of single tracks. Assuming that the *F*-centers occur within a cylindrical volume along the ion trajectory, radii of this region in the order of 10 and 30 nm were deduced for Zn and Pb ions, respectively [23].

A damage zone with a much smaller radius was obtained when analyzing ion tracks by small-angle x-ray scattering. This technique probes the density difference between ion tracks and the undamaged surroundings [25]. Typically 10^{10} ion tracks serve as scattering centers producing a strongly anisotropic pattern on a position-sensitive area detector. From the intensity of the scattering pattern, a mean radius can be deduced, describing the tracks as cylindrical damaged zones with a Gaussian radial density variation. For Kr and U ions, radii in the order of 1-2 nm were found. They are more than one order of magnitude smaller than those of the outer zone (track halo) in which *F*-centers are created. We conclude that the small radii mark narrow track cores characterized by the formation of large defect aggregates or of Li colloids.

The assumption of colloid formation draws further support from the observation that ion tracks can be etched. In LiF, single tracks of fission fragments can be revealed by chemical etching as first reported by Young [26]. Since a suitable etchant attacks the ion-induced damage at a higher rate than the unperturbed surroundings, the latent track is gouged out forming an etch pit on the crystal surface. More recently, this effect was reinvestigated in more detail, showing that track etching is only successful when the linear energy transfer of the ions surpasses a critical threshold of about 1 keV/Å [24, 27].

3 Results and discussion of scanning force microscopy

3.1 Sample irradiation with heavy ions and chemical etching

Thin platelets ($10 \times 10 \times 0.5 \text{ mm}^3$) were cleaved off from a single-crystal block of high-purity lithium fluoride grown in an argon atmosphere. They were irradiated under normal incidence (the surface coinciding with a cleavage plane of the cubic LiF lattice) with Pb and Au ions of a specific energy of 11.4 MeV per nucleon at the Universal Linear Accelerator (UNILAC) of GSI (Darmstadt, Germany). We applied fluences between $5 \cdot 10^6$ and 10^{11} ions/cm². After irradiation, some of the crystals were etched in a solution of concentrated hydrofluoric acid (50 vol%) and glacial acetic acid (50 vol%) saturated with ferric fluoride, as recommended in ref. [26]. The etching was performed at room temperature and without agitation, using 1 to 10 s for SFM studies and 10 to 20 min for scanning electron microscopy (SEM).

3.2 *Imaging with the scanning electron microscope*

In nonirradiated surface regions, etched LiF crystals showed only etch pits of dislocations with a typical density of several 10^5 cm^{-2} . In irradiated areas, the number of etch pits corresponded to the ion fluence. Similar to dislocations, each single ion track developed to an etch pit of pyramidal shape owing to the cubic symmetry of the LiF lattice. The etched surface of a sample irradiated with $5 \cdot 10^6 \text{ Pb ions/cm}^2$ is shown in a scanning electron micrograph in Fig. 1.

The region where the ions came to rest after having totally lost their kinetic energy can be made visible by cleavage of the LiF crystal parallel to the ion trajectories and subsequent etching. The scanning electron micrograph of Fig. 2 shows a cross section of the crystal with about $82 \text{ }\mu\text{m}$ long striated structures of etched Pb tracks. Their length represents the full range of the ions in the crystal and agrees within about 20% with the ion range calculated by means of the computer code TRIM [28]. The bright zone close to the crystal surface is attributed to damage of the surface layer caused by the cleaving process. The rhombic features between the ion tracks are etch pits originating from natural dislocations. They exhibit a slightly distorted geometry possibly due to the superposition of the ion-induced damage.

3.3 *Observation by scanning force microscopy*

Scanning force microscopy was applied to ion-irradiated LiF samples prior to and after track etching. The microscope, developed in our laboratory, was operated with a bar-shaped Si_3N_4 cantilever. The loading forces applied were in the range between 10 and 100 nN. The detection method is based on a reflected laser beam registered on a four-segmented photodiode. Topographic and lateral force images are acquired simultaneously by monitoring the vertical bending and the lateral torsion of the cantilever.

Fig. 3 compares the topographic and the lateral force images of Pb ion tracks which were etched for 10 s. While the topographic image visualizes only the shape of the outer border line of the etch pits (Fig. 3a), the lateral force images provide additional information on their internal

spatial structure (Figs. 3b and c). In some cases, the walls of the etch pits are not planar but consist of finely spaced terraces (Fig. 3c).

A topographic SFM image of etched track profiles directed parallel to the ion trajectories (similar to the SEM image of Fig. 2) is presented in Fig. 4. Micrographs registered with higher magnification reveal that the etched ion tracks exhibit a sequence of single etch pits, adjacent pits having an average distance of about 140 nm. This finding is illustrated in Fig. 5.

Furthermore, the surface of a LiF sample only partly irradiated with $5 \cdot 10^{10}$ Au ions/cm² was studied with SFM in order to visualize the ion-induced modifications without previous etching. The result is displayed in Figs. 6a-d. The micrographs a and b represent the simultaneously recorded topographic and lateral force images of an unirradiated surface area. Ignoring commonly occurring surface defects, this area appears completely structureless. Fig. 6c is a topographic image of an irradiated zone. The surface is covered with round hillocks, the brightness being a measure of the vertical height.

A lateral force image represents a convolution of friction and of the partial derivative (i.e. the slope) of the surface topography with respect to the lateral coordinate along the fast-scanning direction [29-31]. When the force sensor scans over a hillock, the slope reverses its sign, indicated by a change in brightness. Accordingly, the lateral force micrograph of Fig. 6d, which was recorded by scanning from top to bottom, exhibits the hillocks even more clearly. By changing their brightness from dark to light, the spots reveal their topographic nature.

The statistical evaluation of a subgroup of 60 hillocks comprising the most pronounced hillocks visible in Fig. 6d resulted in a mean diameter of $d=55(8)$ nm. The error is one standard deviation. The evaluation of the complete ensemble of hillocks would probably provide a somewhat smaller value. The hillocks have heights in the order of 3 nm. At a dose of $5 \cdot 10^{10}$ ions/cm², about 1100 ions were expected to impinge on the surface area displayed in Fig. 6d. If each ion would create a hillock with $d=55$ nm, the hillocks would cover about 70% of the surface. Less than 1% of the area would be covered by the overlapping zones of double-hits. We conclude that almost each of the hillocks was caused by a single-ion impact, but that the coverage has just reached the limit where a mutual overlapping of ion tracks becomes significant.

Similar circular hillocks were imaged with SFM on the surface of LiNbO_3 single crystals irradiated with ^{112}Sn ions of a kinetic energy of 1015 MeV [32]. The authors found a mean diameter of 100 nm and a maximum height of about 1.5 nm.

4 Conclusions

Using high-resolution microscopy of ion-induced radiation damage in lithium fluoride crystals, we aim to acquire information complementary to results yielded with methods such as optical absorption spectroscopy and small-angle x-ray scattering. The present work contains our first results on etched as well as unetched samples achieved by means of scanning force microscopy. Lateral force images provided information on the shape of etch pits, in some cases visualizing finely spaced terraces of the inner walls. After cleavage of a LiF crystal parallel to the ion trajectories and subsequent etching, SFM micrographs revealed a sequence of single etch pits along the tracks with an average distance of about 140 nm. A more detailed inspection of the damage trails, including a careful evaluation of the mean etch pit size and distance of adjacent pits, should contribute to an improved knowledge of the nature, size, and morphology of the defect aggregates.

Simultaneously recorded topographic and lateral force images of a LiF surface irradiated with $5 \cdot 10^{10}$ Au ions/cm² show a dense coverage with circular hillocks, each hillock probably being created by a single-ion impact. Future SFM studies will concentrate on a quantitative characterization of the hillocks as a function of ion fluence with special emphasis on the aspect of ion-induced swelling.

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Figure captions

Fig. 1. Scanning electron micrograph of a LiF surface after etching. The sample was irradiated with $5 \cdot 10^6$ Pb ions/cm² of 11.4 MeV/u. The etching process (20 min) resulted in pyramidally shaped etch pits.

Fig. 2. Scanning electron micrograph of the cross section of etched tracks (10^{10} Pb ions/cm²) in LiF (etching time 20 min).

Fig. 3. Etch pits of Au-ion tracks in LiF, imaged by scanning force microscopy:

a) Topographic image (850 x 850 nm²).

b) Lateral force image recorded simultaneously with image 3a (850 x 850 nm²).

c) Lateral force micrograph of a surface section different from 3b. The walls of the etch pits indicate narrow parallel terraces (690 x 730 nm²).

Fig. 4. Topographic SFM image (11 x 9 μm²) of etched ion tracks in LiF visualizing the region where the ions came to rest. Prior to etching, the crystal was cleaved parallel to the ion trajectories.

Fig. 5. Topographic SFM image (3 x 3 μm²) of a cleavage plane in LiF, similar to Fig. 4 but with a higher magnification.

Fig. 6. SFM images (1.5 x 1.5 μm²) of irradiated (5×10^{10} Au ions/cm²) and unirradiated areas. The images a and c show the topography, whereas b and d represent a lateral force mapping.

Fig. 1

Fig. 2

a *b* *c* *Fig. 3*

Fig. 4

Fig. 5

a *b* *c* *d* *Fig. 6*

1
2
3

4
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