VUV light induced surface interaction and accelerated diffusion of carbon, silicon and oxygen contamination elements in LiF crystals

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Abstract

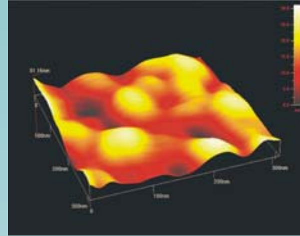
Irradiation of LiF crystals at 157nm accelerates the penetration of C, O, N, Si and other elements within the crystal bulk. The concentration of the elements in the irradiated areas was larger in comparison to the non-irradiated ones. A thin interface film quickly grows and diffuses ~ 100nm inside the crystal, which penetrates five times deeper than in the non-irradiated areas. The accelerated diffusion has its origin to a force acting perpendicular to the crystal surface. The force is generated by the laser's electric field gradient in the direction of beam propagation due to the radiation absorption in the interface. New bonding is forming between the crystal ionic sites and the film's elements. AFM surface imaging reveals initially the presence of inhomogeneous nano/micro-islands, which further agglomerate to form larger homogeneous structures. A theoretical diffusion model in the presence of a laser field is in agreement with the experimental results.

Experimental

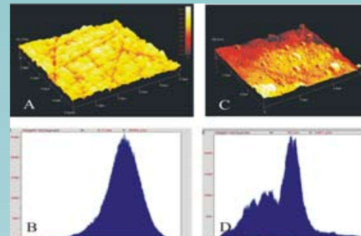
❖High optical quality LiF crystals, were used as a protective window in the exposure apparatus using the F_2 molecular laser (0.5-4cm apart from CaF_2 projection optics). Parts of the outgassed products were collected on the surface of the LiF crystal.
❖ The **absorption spectra** of the LiF crystal at room temperature, before and after exposure were recorded from 120-220nm with a VUV absorption spectrometer.
❖**ATR spectroscopy** was employed to investigate the bonding between the contaminants in both the irradiated and non-irradiated areas of LiF crystals.
❖**XPS measurements** were performed on the PHI-TFA XPS spectrometer (Physical Electronics Inc).
❖**AFM imaging** of the surface of both non-irradiated and irradiated areas was performed using a ¨Quesant-Qscope250¨. All AFM images were recorded in intermittent contact mode.

Results and discussion

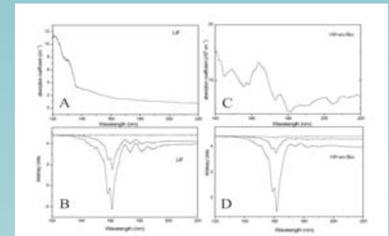
AFM surface imaging and VUV absorption spectroscopy



AFM image of surface interface. The elongated structures correspond to discrete configurations 500nm long, 150nm wide.

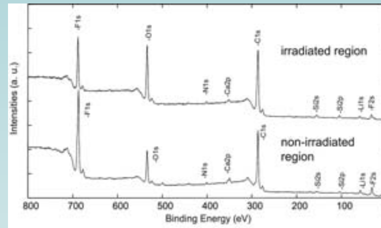


a) AFM surface image of a non- irradiated part of LiF crystal. b) Surface roughness histogram (z-axis) of Fig a. The average surface roughness of the non-irradiated area is ~7nm. c)AFM surface image of the irradiated part of LiF crystal. d)Surface roughness histogram (z-axis) of Fig c. Surface roughness distribution of contaminants on LiF crystal indicated four main groups of agglomerations with heights of 50, 120, 220 & 320nm.



a) Absorption coefficient of non-irradiated areas of LiF (5mm thick). b) VUV transmission spectrum of non-irradiated areas of LiF (5 mm thick). c) Absorption coefficient of the irradiated areas of LiF. d) VUV transmission spectrum of irradiated areas of LiF (film thickness ~100 nm).

XPS spectroscopy



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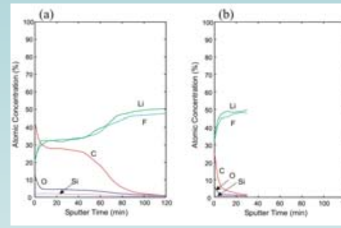
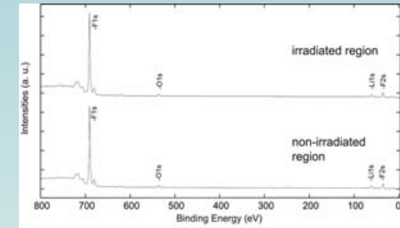


XPS depth profiles of relative elemental distributions for (a) the irradiated (b) the non-irradiated parts of the LiF crystal. The sputtering rate was measured to be ~1nm/min measured on reference sample of Cr.



XPS survey spectra obtained after depth profiling in the bulk of the non-irradiated and irradiated parts of the LiF crystal.

Before Etching (d=0nm)			After Etching (d=100nm)		
Atomic %	Non Irradiated	Irradiated	Atomic %	Non irradiated	Irradiated
C 1s	40.3	55	C 1s	1.1	0.7
Li 1s	26.4	12.4	Li 1s	53	51.5
F 1s	20.9	11.2	F 1s	44	46.1
O 1s	10.1	18	O 1s	1.5	1.7
Si 2p	0.8	1.8			
N 1s	0.8	0.8			
Ca 2p	0.7	0.5			

XPS analysis of the surface of irradiated /non-irradiated part of LiF crystal prior and after ion etching. 1) on the surface and 2) 100nm deep inside the LiF crystal bulk respectively.

Diffusion dynamics of contaminants in LiF bulk

$$\vec{E}(x,y,z)=E_x(x,y,z)\exp(ikz)\vec{i}+E_y(x,y,z)\exp(ikz)\vec{j}$$

$$E_{x,y}(x,y,z)=E_{x,y}(x,y)\exp(-\alpha(z)z)$$

$$\sigma_{ik}=\sigma^{(0)}{}_{ik}+\frac{(2\varepsilon_0-a_1)}{8\pi}E_iE_k-\frac{(\varepsilon_0+a_2)}{8\pi}E^2\delta_{ik}$$

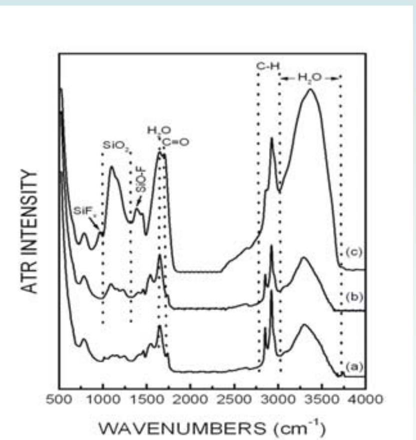
$$F_k=F^{(0)}{}_k+\frac{a_1+2a_2}{8\pi}[\alpha(z)+\frac{\partial\alpha(z)}{\partial z}z]E^2(x,y)\exp(-2\alpha z)$$

$$C(z)_{NR}=C(0)\exp(\frac{-F^0{}_k z}{KT})$$

$$C(z)_R=C(0)\exp(\frac{-(F^{(0)}{}_k+\frac{a_1+2a_2}{8\pi}[\alpha(z)+\frac{\partial\alpha(z)}{\partial z}z]E^2(x,y)\exp(-2\alpha z))}{KT})=C(z)_{NR}\exp(\frac{[\alpha(z)+\frac{\partial\alpha(z)}{\partial z}z]\Gamma\exp(-2\alpha z)}{KT})$$

where $$\Gamma=\frac{a_1+2a_2}{8\pi}E^2(x,y)$$

ATR spectroscopy



ATR spectra of LiF crystal for (a) the non- irradiated opposite side of the film, (b) the non- irradiated area of the film's side, and (c) the irradiated area of the film's side.

Conclusions

❖Enhanced diffusion and adsorption of C, O, N and Si surface contaminants on LiF crystals was observed on the 157 nm laser-irradiated part of a LiF crystal.

❖ Infrared ATR spectroscopy showed that contamination elements are found in forms of amorphous SiO_2, H_2O, carbonyl compounds and hydrocarbons. In the irradiated area of the film, the nature of the organic compounds is altered and the relative intensity of water and amorphous $_{SiO2}$ is enhanced as compared to the non irradiated area of the LiF crystal..

❖The penetration of surface elements deep in the crystal, was based on the forced ejection by the gradient of the laser intensity in the direction of the beam, due to the absorption of the laser beam in the interface layer.