

F-COLOUR CENTERS AND LITHIUM NANO-CLUSTERS IN ION-BEAM ASSISTED LiF THIN FILMS

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Various kinds of ionising radiation can be utilised to produce primary F centres (anion vacancies occupied by electrons) and aggregate defects in lithium fluoride (LiF) thin films. The creation of large aggregates of F centres and intrinsic metallic nanometre sized clusters (nano-aggregates) above a critical defect concentration and at irradiation temperatures where the diffusion of single point defects is not negligible has also been reported in LiF crystals. In this work, we present results concerning the stable formation of primary electronic defects (F centres) and lithium nano aggregates in lithium fluoride thin films grown by Xe ion-assisted thermal evaporation. The optical properties of the as grown LiF films are reported as a function of the deposition parameters (ion energy, density of the ion-beam current). The mechanism of the simultaneous formation of F colour centres and lithium nano-clusters is tentatively explained in the framework of low energy knock-on collisions and the thermal spike theory.

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1. Introduction

The stable formation of defects and nano-clusters in lithium fluoride by high energy ion bombardment has been widely reported in the literature [1-3]. In contrast, only a few articles have been published on the effect of low energy (<200 eV) ion bombardment on defect and nano-cluster formation. Ion beam assistance during the deposition process is one of the methods to generate colour centres and nano-clusters in lithium fluoride thin films [2].

In this work, we present a model to describe the physical processes that underlie the formation of primary defects (F colour centres, anion vacancies occupied by electrons) [3] and lithium nano-clusters (Li colloids) [4], during the low energy assistance by Xe ions of thermal evaporated LiF thin films. The model is a combination of the physics on which the program SRIM (The Stopping and Range of Ions in Matter) [5] is based, and the cylindrical spike thermal model [6,7].

The influence of the deposition conditions – such as ion-beam energy and the current density of Xe ions – on the F centres and nano-cluster formation of as-grown LiF films is investigated through optical photometric measurements in the ultraviolet-visible spectral range.

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2. Model of colour centres and nano-cluster formation

Fig. 1 represents the different processes involved in the ion beam assisted deposition of lithium fluoride thin films. Energetic Xe ions hit the growing film, and each ion colliding with various atoms in the target generates a collision cascade of the recoils. Vacancy production, replacement collisions and interstitial atoms are calculated by SRIM, as well as the portion of energy transferred to the target atoms by phonons and by the ion-atom and atom-atom collisions.

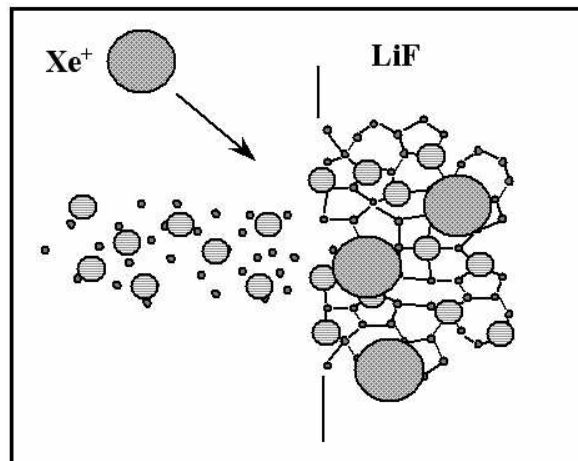


Fig. 1. Xe-ion bombardment during lithium fluoride growth.

A simulation of Xe-ion irradiation of LiF by SRIM in the energy range 30-200 eV shows that, for the most part, the ion energy is actually transferred to the target by phonons (Fig. 2a). Nevertheless, part of the energy is also dissipated to displace fluorine and lithium atoms from their equilibrium positions. In particular, F atoms are displaced at lower energies with respect to Li atoms (Fig. 2b). Because the F centre in LiF is a fluorine atom vacancy, from the results of SRIM simulations one can infer that a primary colour centre is created for each fluorine atom displaced from its equilibrium position.

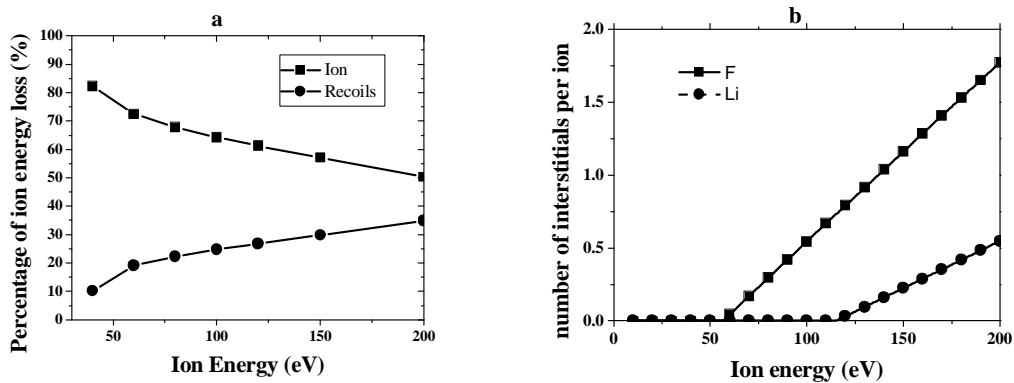


Fig. 2. a: percentage of the ion energy transferred to the target as phonons from the incident Xe ions and Li and F recoils, as calculated by SRIM program. b: the number of Li and F interstitials with the Xe-ion energy, as calculated by the SRIM program.

Depending on the thermal properties of the target, the portion of the ion energy transferred by phonons can generate a thermal spike that would be high enough to induce a permanent

rearrangement of the atoms. The collision process described by SRIM suggests that a cylindrical symmetry of the temperature spike can be considered. The temperature $T(r,t)$ at distance r from the axis of the cylinder at the time t is [7]:

$$T(r,t) = \frac{E_{ph}}{4\pi\rho D} e^{-\frac{r^2}{4Dt}} \quad (1)$$

where c and D are the specific heat and diffusion coefficient of LiF, respectively, ρ is the mass density and E_{ph} is the ion energy transferred to the LiF as phonons. F centres in LiF are stable at room temperature, but at higher temperatures their mobility is large enough for them to recombine with the hole centres [8]. Then, the local thermal spike could be considered responsible for the *destruction* of colour centres if the temperature value within a cylinder of radius r_F (distance from the cylinder axis and the interstitial fluorine atom, see Fig. 3a) at time t_{coll} (the time until the incoming ion comes to rest, see Fig. 3b) is higher than the temperature T_{fus} (the melting temperature of LiF, 1143 °C) where the fluorine mobility is significant.

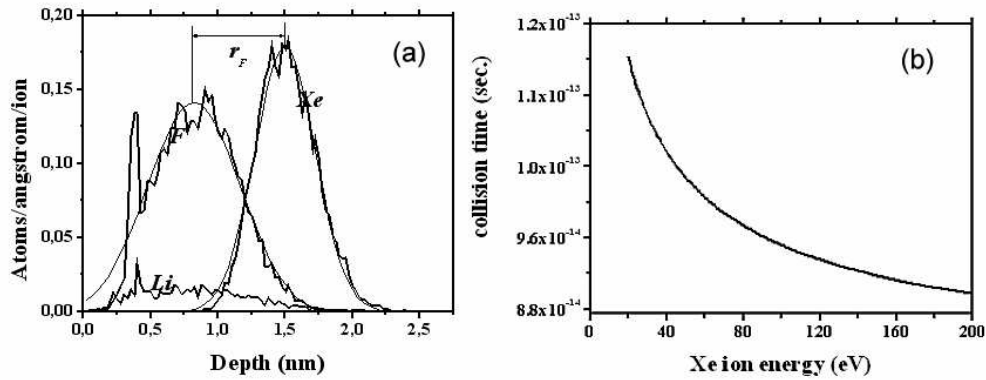


Fig. 3. (a) distance r_f between the Xe ion and the displaced fluorine atom, as simulated by SRIM; (b) collision time as a function of the Xe ion energy.

The collision time t_{coll} was calculated by the relation:

$$t_{coll} = \frac{\sqrt{2ME_{ion}}}{\frac{dE}{dx}} \quad (2)$$

where M and E_{ion} are the ion mass and energy, respectively, and dE/dx is the stopping power of Xe ions in LiF. In the range of ion energy from 20 to 200 eV, t_{coll} varies from 9×10^{-14} s to 1.5×10^{-13} s.

Considering the competitive mechanisms of the formation and destruction of the colour centres, their density can be calculated as:

$$n_{tot}(E_b) = \frac{n_{Xe}(E_b)n_F(E_b) - n_{Xe}(E_b)n_F(E_b)T_{coll}(t_{coll}(E_b), r_F(E_b))}{r_{LiF}} \cdot L_{Xe}(E_b) \quad (3)$$

where

- $n_{Xe}(E_b)$: is the flux of Xe ions ($\text{cm}^{-2} \text{s}^{-1}$) hitting the growing film, as calculated from the measurements reported in Figs. 4a and 4b;
- $n_F(E_b)$: is the number of interstitial fluorine atoms generated by the Xe ions (see Fig. 2b);
- $T_{coll}(E_b)$: is 1 if $T(r_F, t_{coll}) > T_{fus}$ (recombination of a fluorine atom with a vacancy), otherwise it is 0 (creation of a colour centre);
- $L_{Xe}(E_b)$: is the ion range, i.e. the depth at which the ion comes to rest.
- r_{LiF} : is the growth rate of the lithium fluoride thin film.
- E_b : is the energy of the Xe ions.

3. Experimental details

In order to verify the suitability of the suggested physical mechanism for the defect formation in ion assisted LiF thin films, a set of samples was produced and the F colour centres and the Li nano-cluster densities were estimated.

The samples were grown by an evaporator plant equipped with an end-Hall ion source (Advanced Energy, model MARK I) that produces ions in the energy range 30 - 150 eV. The ions of the beam produced by a gridless ion source have a significant energy spread [9] that depends on the anode voltage and cathode current, V_a and I_{cath} , respectively.

The vacuum chamber was evacuated by a cryopump at a back-pressure $\sim 3 \times 10^{-6}$ Pa, whereas the working pressure during the deposition process was $\sim 10^{-2}$ Pa. The layout and the details of the deposition plant are reported in previous publications [10, 11].

The LiF material was evaporated by a thermal crucible boat onto silica substrates. The anode voltage values used for ion-assisted deposition (IAD) are reported in the second column of Table 1. For all samples, the other deposition parameters were: cathode current $I_{cath} = 0.4$ A, film thickness $t_{LiF} = 700$ nm, substrate temperature $T_{sub} = 150$ °C, growth rate $r_{LiF} = 0.5$ nm·s⁻¹.

Table 1. Comparison between the estimated densities of F centres and Li nano-clusters and those calculated by the interstitial and thermal spike model. In column 2, the anode voltages of the ion source are listed for the different samples.

Sample	V_a (V)	Estimated density of F centres (cm ⁻³)	Simulated density of F centres (cm ⁻³)	Estimated Li nano-cluster density (cm ⁻³)	Simulated Li nano-cluster density (cm ⁻³)
# 1	30	0	0	0	0
# 2	60	$(1.6 \pm 0.2) \times 10^{18}$	1.7×10^{18}	0	0
# 3	110	$(1.7 \pm 0.1) \times 10^{20}$	1.1×10^{20}	1.0×10^{19}	1.3×10^{20}
# 4	130	$(3.7 \pm 0.9) \times 10^{17}$	9.7×10^{19}	1.4×10^{20}	7.8×10^{20}

The density of the Xe ion beam current was measured by a Faraday cup, varying the retarding potential (see Fig. 4a). The energy distributions of Xe ions were obtained directly by the derivative of the retarding potential curves, (see Fig. 4b). For convenience, the maximum probe currents are normalized to unity.

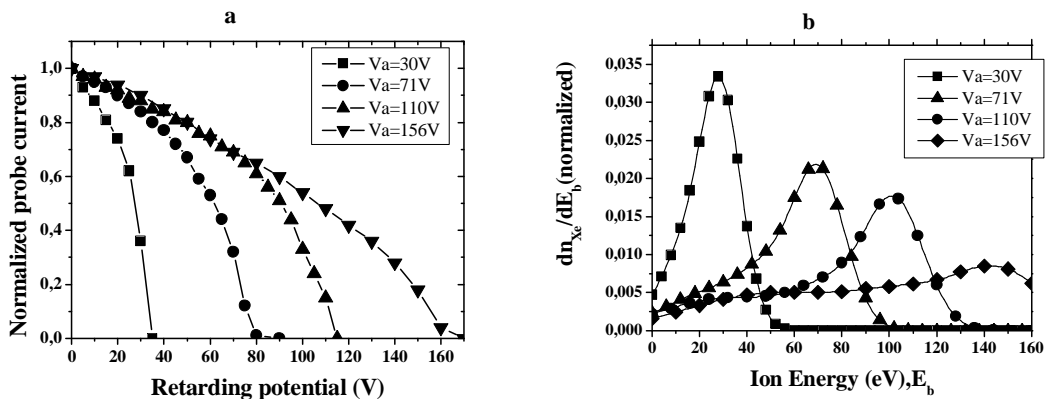


Fig. 4. a, The normalized probe current versus the retarding potential of the gridless ion source; b, the energy distribution of the Xe ion generated by a gridless ion source.

The optical reflectance and transmittance spectra were measured at normal incidence with a Perkin Elmer Lambda-19 spectrophotometer, in the UV-visible spectral range.

4. Results and discussion

A theoretical model was developed and used to estimate the real and imaginary parts of the refractive index and other physical parameters of the deposited films. In our model, embedded colour centres and Li nano-particles add dielectric-susceptibility terms to the permittivity of the LiF matrix. As far as the colour centres are concerned, a dipole-field interaction model [12,13] was used to evaluate their contributions to the whole permittivity. The contribution due to the colloids was included, extending the quasi-static approximation of the Mie theory [14] by means of Maxwell Garnett's effective-medium relation [15]. Particle size and shape effects were also taken into account, through appropriate adjustable parameters [16,17]. The best fitting of the ion-assisted LiF film transmission and reflectance spectra allowed us to estimate the wavelength of the band peaks ascribed to the defect centres induced by the ion-assisted growth and the *filling factor* f of the lithium colloids, i.e., the volume fraction occupied by the metallic aggregates. In Table 2, the F centre band, the filling factor and the mean nano-cluster radius, $r_{cluster}$, are reported for all the samples. Further details about the method for obtaining the best fit of the transmittance and reflectance measurements, taking into account the parameters of Table 2, are reported elsewhere [12].

Table 2. F colour centre absorption band peak positions, filling factors and mean nano-cluster radii, as estimated by optical transmittance and reflectance measurements for LiF samples.

Sample	F band (nm)	Filling factor Li/LiF (%)	Mean nano-cluster radius (nm)
# 1	-	0	0
# 2	247	0	0
# 3	247	0.8 ± 0.1	0.5
# 4	243	0.0502 ± 0.0020	0.4

As mentioned above, the ions of the beam produced by a gridless ion source have a wide dispersion in energy. Consequently, because of the dependence of the ion energy on the physical mechanism for colour centre formation, the integral of equation 3 gives the density of the colour centres, as reported in the third column of Table 1. For different values of V_a , the behaviour of the density of colour centres vs. the dispersion of the Xe energy (equation 3) and the integral of the relation (3) are respectively reported in Figs. 5a and 5b.

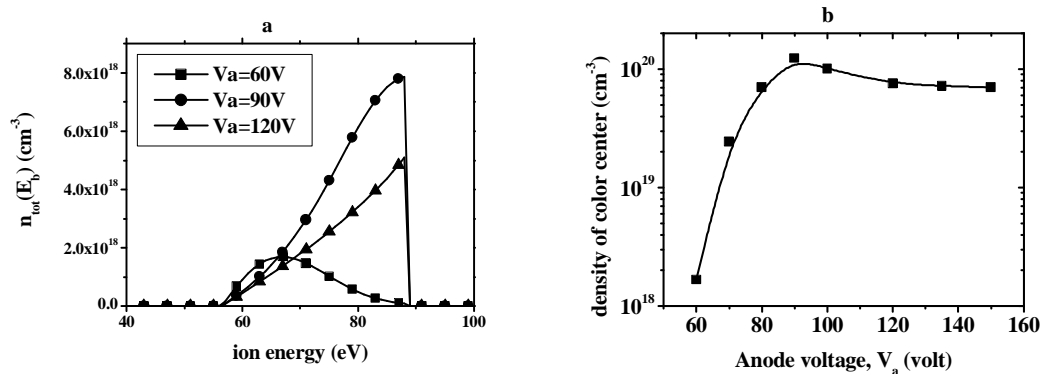


Fig. 5 a. Density of colour centres vs. the dispersion energy of the ion beam at different anode voltages (V_a), as calculated with equation (3); b: Density of colour centres with different V_a , as calculated with the integral

$$\text{of equation (3)} \int_0^{V_a} n_{tot}(E_b) dE_b$$

As far as the nano-cluster formation is concerned, by comparing the formation energies of Li-Li and Li-F bonds, 159 and 1024 kJ/mol, respectively, it could be inferred that during the

rearrangement induced by the thermal spike, the probability of formation of lithium metallic colloids is greater than that of LiF. The density of Li nano-cluster is calculated considering that for each Xe ion a colloid is formed if there exists a sphere with radius r_{fus} in which, after time t_{coll} (ion at rest), the temperature is higher than T_{fus} . Here, r_{fus} is defined as the distance at which the curve $T(r, t_{coll})$ intercepts the line T_{fus} (see Fig. 6). Table 1 reports the results for this calculation.

The quantitative agreement between the concentration of the colour centres and Li nano-cluster particles, estimated by photometric spectral measurements and those calculated by the interstitial-thermal spike model, is satisfactory even if some basic approximations were made in the calculation. For instance, the term D which is related to the thermal conductivity C , the specific heat c and the mass density ρ by the equation $D = C/(c\rho)$ depends upon the temperature. However, for simplicity, it is considered constant in equation (1). A further approximation has been performed concerning T_{fus} , which has been assumed to be equal to the melting temperature of LiF. Nevertheless, the comparison between primary F centres and the Li nano-cluster concentration, as estimated and simulated in Table 1, clearly indicates the same qualitative behaviour as a function of the Xe ion energy. Moreover, at the highest energy, the decrease in the F centre density is still accompanied by a further increase in the number of Li nano-clusters, as expected from the general behaviour of alkali halides [3] once the primary defect concentration has reached a saturation value higher than 10^{20} cm^{-3} .

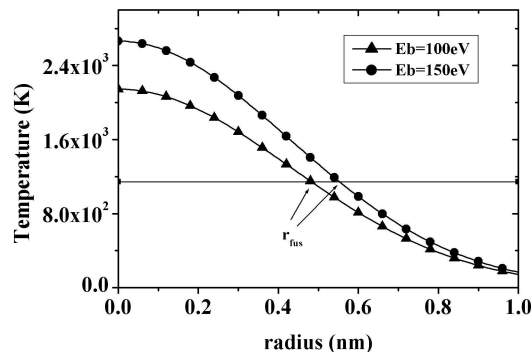


Fig. 6. Temperature vs. the distance from the cylinder axis at time t_{coll} , at two different values of the Xe ion energy. The radius of the Li nano-cluster r_{fus} , is indicated, i.e. the intercept between the temperature distribution and T_{fus} (the melting temperature of LiF, 1143 °C).

5. Conclusions

The stable formation of F colour centres and Li nano-clusters (metallic colloids) in LiF thin films obtained by bombarding the growing films with heavy ions (Xe) is described. The concentrations were estimated from the measured optical spectra by a theoretical model that takes into account the absorption bands of the colour centres and metallic nano-clusters in optical measurements. The estimation was performed on a set of differently grown samples that were deposited by thermal evaporation and Xe ion-beam assistance, and by varying the anode voltage of the ion source (30-130 V). The concentration of colour centres and colloids changes with the anode voltage, up to a value $\approx 10^{20} \text{ cm}^{-3}$. Similar concentrations were found by modelling the formation of the colour centres and nano-clusters in terms of the fluorine atoms displaced by the colliding Xe ions (colour centres) and by supposing that the major part of the ion energy is transferred to the target by phonons (thermal spike).

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