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To cite this article: R M Montereali et al 2010 IOP Conf. Ser.: Mater. Sci. Eng. 15 012017

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Optical investigation of metallic lithium colloids and F-centres in ion-assisted LiF thin films

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Abstract. The advanced optical and electronic characterization of primary F-defects and metallic lithium colloids in lithium fluoride thin films produced by ion-assisted thermal deposition with Xe low-energy ions (< 200 eV) on transparent amorphous substrates is presented and discussed. The volume concentrations of defects and Li nano-clusters have been estimated by applying a best-fit procedure based on a comprehensive theoretical modelling to the spectro-photometric measurements. The appreciable presence of Li metal at the film surface was clearly demonstrated by X-ray photoelectron spectra. Advanced optical microscopy confirms the negligible formation of other types of more complex luminescent colour centres.

1. Introduction

Colour centres are produced in thermally evaporated lithium fluoride, LiF, thin films [1] by various kinds of ionising radiation, such as low-energy electrons [1] and ions [2] as well as photons, like gamma [3] and X-rays [4,5]. So far, most attention has been devoted to F_2 and F_3^+ laser-active electronic defects [1,2], due to their specific photoluminescence properties, which have found applications in miniaturised optical active devices [1] and novel imaging detectors [5].

When the colouring is performed by using low penetrating radiation, it is possible to prepare thin layers with high concentration of lattice defects located at the surface of the crystalline material [4]. Larger aggregates and macro-defects can be also created above a critical defect concentration and at irradiation temperatures where diffusion of single point defects is possible [6].

Quite recently clusters of colour centres in LiF crystals, generated by ion-beam irradiation, were studied [7], but the actual mechanism of formation of such "lithium colloids" is still an open question.

The simultaneous formation of stable primary F-centres and nanometric Li colloids was directly obtained in LiF films grown on transparent substrates by means of a versatile deposition technique consisting of low-energy ion-assisted thermal evaporation [8]. This novel method was proposed for the first time in 1998 for the preparation of LiF films containing electronic defects and Li clusters [9], but the specific characteristics of the materials, the complex physical processes involved in their production [10] and the great variations in the properties of the produced samples require further improvements in their investigation.

11th Europhysical Conference on Defects in Insulating Materials (EUROD	IM 2010)	IOP Publishing
IOP Conf. Series: Materials Science and Engineering 15 (2010) 012017	doi:10.1088/1757	-899X/15/1/012017

In this work we present some novel results concerning the advanced optical and electronic characterization of primary defects and lithium nano-clusters in LiF thin films prepared by ion-assisted thermal deposition in presence of Xe low-energy ions (< 200 eV) on transparent amorphous substrates.

2. Sample preparation

All the LiF films were grown by an evaporator plant (BAK 640, manufactured by Balzers) equipped with two different ion sources: a Kaufman ion source (Ion Tech.) and an end-Hall ion source (Commonwealth Scientific Corporation). The first one can produce mono-energetic ions ranging from 150 eV to 2 keV, while the second one produces ions in the energy range between 40 eV and 150 eV. In this last configuration the ions of the beam have a significant energy spread.

The vacuum chamber was evacuated by a cryopump at a back-pressure of ~ 3×10^{-6} Pa, whereas the working pressure during the deposition process was 10^{-2} Pa.

The LiF material was evaporated by a thermal Molybdenum crucible boat. LiF films were deposited on silica substrates at different ion energies. The substrate temperature, T_{sub} , during the growth, was chosen between 200 and 300°C, the deposition rate, *r*, was fixed between 0.5 and 1 nm/s, the thickness, *t*, monitored in situ by means of a quartz oscillator, was measured after the growth by a stylus profilometer, and it was varied between 700 nm and 3 μ m.

3. Sample characterization

3.1. Optical measurements

The specific optical properties of the selected ion-assisted LiF films were investigated by means of spectrophotometric transmittance and reflectance measurements. The spectra were measured by means of a Perkin-Elmer Lambda 19 spectrophotometer in the 300-850 nm spectral range. For reflectance measurements, a reference mirror calibrated with an NBS reflectance standard was utilized.

3.1.1. *Optical modelling*. The measured spectra were analysed by using a theoretical model that takes into account absorption contributions due to primary F colour centres, absorbing at about 248 nm, and nanometric lithium colloids, which are responsible for a very broad absorption band at about 440 nm [11].

The theoretical model deals with the effect of colour centres on the dielectric permittivity of the host material – LiF in this case – by means of harmonic-oscillator terms [12]. The effects of metallic Li nano-aggregates are introduced by recurring to a version of the Maxwell Garnett model [13,14] that includes particle shape [15] and size [16] corrections of the polarizability and dielectric permittivity of Li, respectively. The used Fermi velocity of bulk Li at room temperature (RT), needed to apply the above-mentioned size correction of the dielectric permittivity, was $v_F = 1.29 \times 10^6$ m/s [17]. Literature complex refractive indices of LiF and Li [18] were used for the calculations.

To get a better reproduction of the experimental spectra, the thin-film model has been further tweaked with the introduction of a parabolic-type variation of the refractive index along the film growth-axis that accounts for material inhomogeneity due to growth conditions [19,20].

3.2. Optical imaging

Imaging by means of transmission, fluorescence and reflection optical microscopy in conventional and confocal configurations has provided further insight into some distinctive features of these complex dielectric LiF-based microstructures incorporating metallic lithium colloids. A Nikon Eclipse 80i-C1 confocal laser scanning microscope equipped with with a mercury lamp and with a CW Argon ion laser Coherent INNOVA 90, operating at the wavelength of 457.9 nm in confocal mode, was used for optical imaging. In order to detect the fluorescent signal coming from the film, the pumping blue light was cut off by a suitable coloured glass filter.

3.3. XPS measurements

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The presence of Li metal in the ion-assisted LiF films was investigated by X-ray Photoelectron Spectroscopy (XPS) measurements performed on the Li 1s core level. X-ray photoemission spectra from the LiF films and from a LiF single crystal used as a reference were measured in an ultra-high-vacuum chamber at a 5×10^{-10} mbar base pressure and equipped with a Al K_a X-ray source (1486.6 eV) and a double-pass Cylindrical Mirror Analyzer operating at a total energy resolution better than 1.5eV.

4. Results and discussion

Figure 1 shows the optical transmission spectra of two LiF films obtained with different deposition parameters. The first one was assisted by Xe ions of energies at around 60 eV and its total thickness is about 800 nm. The other one has a total thickness of about 3 μ m and its growth was assisted by monoenergetic Xe ions at 150 eV. The ion fluxes on the sample surface are comparable. In both cases the substrate was heated between 200 and 300°C to reduce thermal stresses during the film growth.

The as-grown films appear of different colours at naked eyes, from light yellow to dark brown [9]. Generally, the colouring of irradiated LiF crystals results from the stable formation of aggregate colour centres, which give rise to well defined absorption bands in the visible spectral region [12], as the primary F center absorption is located in the near ultraviolet [21]. The yellowish colour is mainly related to the M absorption band at around 450nm [22], attributed to almost full overlapping absorption of F_2 an F_3^+ light-emitting defects. In the case of irradiated LiF thin films, the intensity of their absorption is generally limited by the film total thickness [1]. In figure 1, both the spectra of the ion-assisted LiF films show an intense, very broad absorption band in the spectral interval between 400 and 500 nm, ascribable to Li colloids [11].

The experimental spectra were best-fitted using the theoretical model described in 3.1.1. The fit parameters were: film thickness, F-centre band intensity χ_0 [12], nanoaggregate shape parameter β [15], volume fraction (filling factor) of the Li nanoaggregates, a size-correction adimensional parameter [16], and two parameters related to the parabolic inhomogeneity of the refractive index of the film [18].

The results, displayed in figures 2 and 3 for the thinner film deposited under 60 eV ion assistance, show a fairly good reproduction of the experimental spectra and correspond to best-fitting film thickness of (813 ± 2) nm, Li-nanoaggregate filling factor of (0.8 ± 0.1) %, and a shape parameter $\beta = (0.29 \pm 0.09)$, which corresponds, within the uncertainty, to spherical-shaped nanoparticles [8]. The model allows also calculating the extinction-coefficient dispersion spectrum of the film material over the examined spectral range, shown in Fig. 4 and featuring a peak at about 437 nm, very close to the wavelength of 444 nm that corresponds to the Li Frölich frequency, estimated to be equal to 4.25×10^{15} Hz by using bulk Li data at RT with no size correction [10]. This fact suggests that scattering phenomena of electrons with the Li particle shell should be not much relevant, thus the particle diameter should be comparable to or larger than the free mean path of conduction electrons in Li, estimated to be about 12 nm.

Confidence about the well known spectral features of the F-absorption band allowed us to estimate for these centres a concentration, N_F , of $(1.7\pm 0.1) \times 10^{20}$ cm⁻³. This number was deduced from the best-fit by applying the Smakula formula to the corresponding absorption band area and using an oscillator strength equal to 0.56 [21].

For the thicker LiF film deposited under 150 eV Xe ions assistance we obtained a concentration of F centres close to 10^{21} cm⁻³, which is comparable with the saturation concentration of F centre density in LiF as obtained in previous experiments carried out on ion-irradiated crystals [23]. Nevertheless the fitting of the spectra gave a slightly smaller colloid filling factor, of ~0.6%. The confidence level of this best-fit was lower due to the presence of fractures on the LiF film surface probably due to its higher thickness, whose effects influence the absolute values of the spectrophotometric measurements.



1.0 0.9 0.8 transmittance 0.7 0.6 0.5 experimental mode 0.4 uncoated substrate 0.3 300 400 500 600 700 800 wavelength (nm)

Figure 1. Spectral transmittance of two LiF films produced by ion-assisted thermal deposition in presence of Xe low-energy ions with different deposition parameters.



Figure 3. Spectral reflectance of the thinner LiF film (60 eV Xe ions). The spectral reflectance of the bare substrate is also shown for comparison.

Figure 2. Spectral transmittance of the thinner LiF film (60 eV Xe ions). The spectral transmittance of the bare substrate is also shown for comparison.



Figure 4. Calculated extinction coefficient of the thinner LiF film (60 eV Xe ions). The band peaked at $\lambda = 437$ nm is ascribed to Li nanoaggregates.

Figure 5 shows the XPS Li 1s core level spectrum from a LiF single crystal superimposed with the same core level measured on a 150 eV ion assisted LiF film. The two spectra have been normalized to the same height in order to enhance the shape differences . The film Li 1s core level spectrum shows a clear asymmetry on the low binding energy side together with a lower peak at about 6.5eV. According to the literature [24], the latter feature can be ascribed to the Li bulk plasmon hence indicating a metallic character of the LiF film. In this view, the asymmetry could be due to an additional metallic Li contribution to the spectral shape. The difference between the two spectra, weighted according to best-fit results (not shown), confirms the presence of such a feature. The additional component appears at about -1.2eV and the observed shift on the low binding energy side strongly supports the metallic character of this feature. These data point to the presence of metallic Li in the vicinity of the surface.





Figure 5. Li 1s core photoemission peak taken on a LiF single crystal (dots) superimposed to the Li 1s line measured on the 150 eV Xe ions assisted LiF film (line). Their difference is shown below.

Figure 6. Optical microscopy images of the 150 eV Xe ions LiF assisted film on silica in different operation mode (see text for details). Reference line=500µm.

As far as optical microscopy is concerned, although the spatial resolution is not sufficient to directly observe the Li nano-clusters, some morphological and optical features measured in the investigated samples further support the obtained results and their interpretation. In particular, in coloured LiF crystals [25] and thin films [26] containing visible-emitting F_2 an F_3^+ luminescent defects, confocal laser fluorescence microscopy is a very powerful and sensitive technique. In figure 6 the optical microscopy images of the 150 eV Xe ions LiF assisted film grown on silica are reported in different operation mode at low magnification. The images on the top and in the center are obtained in transmission mode under white light illumination, in bright field and dark field operation, respectively. The central stripe corresponds to the uncovered silica substrate, and the more absorbing film can be recognized also from some detached areas. No scattered light from the film covered areas is found in the image in the center. Finally, the bottom image, acquired in fluorescence mode under blue light illumination, allows to confirm the negligible, if any, contribution of a green-red luminescence signal emitted from F_2 an F_3^+ active defects.

5. Conclusions

Ion beam assistance during the deposition process is a powerful method to generate primary F colour centres and Li nano-clusters in the dielectric matrix of thermally evaporated LiF thin films. Their simultaneous stable formation was carefully investigated in the case of low-energy (<200 eV) heavy Xe ions, which appear very effective under some peculiar film growth conditions [10]. Although further experiments and complementary techniques are necessary for a better investigation, the advanced optical and electronic characterizations presented in this work allow obtaining more quantitative information about the nature of point defects in these complex and intriguing systems.

11th Europhysical Conference on Defects in Insulating Materials (EURODIM 2010)IOP PublishingIOP Conf. Series: Materials Science and Engineering 15 (2010) 012017doi:10.1088/1757-899X/15/1/012017

Further improvements are expected from advanced optical microscopies, such as the scanning near-field optical [27] and confocal ones.

Acknowledgements

The authors are indebted with S. Alessandrini, J. Lancock, T. Marolo, F. Menchini, F. Somma and A. Rufoloni for their skillful support. The authors would like to dedicate this work to Prof. Henri W. den Hartog, brilliant scientist and dear friend, who spent his scientific work and life to studying colloids in salts and to encouraging a quest for knowledge and to keep for fighting. This work was partially funded by the Italian Ministry of University and Scientific Research MIUR with the project "*Tecnologie per Sistemi di Visualizzazione di Immagini*" (Technologies for Image Visualization Systems)-TECVIM.

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