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High resolution and high efficiency coloration of lithium fluoride by soft X-rays irradiation

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Abstract

The efficient coloration of LiF material, in the form of bulk and films, by EUV and soft X-rays emitted by a laser-plasma source is demonstrated. The short penetration depth of soft-X-rays is exploited to obtain high spatial resolution luminescent patterns while the high dynamic range of proportionality between X-ray dose and coloration is exploited for using LiF as image detector in micro-radiography and soft X-ray microscopy applications.

1-Introduction

As well known ionizing radiation like UV, EUV (Extreme Ultra-Violet), X-rays, electron beams, etc., can generate color centers (CCs) in alkali halide crystals [1]. In particular, in lithium-fluoride (LiF) several types of point defects can re-emit visible light when excited by blue light and, after being generated, they remain stable for a very long time (centuries) even at room temperature [2]. For this reason LiF, in the form of bulk and films, is interesting for many applications like optical memories [2], miniaturized optical devices like broad-band optical emitters [3] and active waveguides [4], microcavities [5] and point light sources [6,7]. The increasing demand for low-dimensionality photonic devices imposes the utilization of advanced lithographic systems for producing structures with submicrometric spatial resolution. On this regard, the emerging technologies presently investigated in the field of EUV lithography allow to push the spatial resolution to values below 100 nm [8,9]. An essential aspect for low-dimensionality is the use of low penetrating radiation like EUV or low energy electron beams.

In the present work we show how the EUV radiation produced by a laser plasma source can efficiently create high resolution luminescent patterns at a much higher rate compared with electron beam treatment on large areas and how this combined use of laser plasma sources and LiF films as sensitive radiation detectors can improve the performances of soft X-ray microscopy and micro-radiography.

2-Coloration of LiF by EUV

The photon energy of EUV radiation ($20 < h\nu < 200$ eV) and soft X-rays ($0.2 < h\nu < 8$ keV) is sufficient to generate CCs in alkali halide crystals and in particular in LiF [1]. The irradiated areas of the crystal, where CCs are generated, become non-transparent to some specific wavelengths, mainly in the blue region, where the F_3^+ and F_2 CCs possess almost overlapping broad absorption bands. They emit a strong luminescence in the green-red region when optically excited by blue light. The penetration depth of EUV radiation in LiF is so short that the colored layer of the crystal can be as thin as 20-100 nm, as shown in figure 1. The CCs formation process can involve non-linear mechanisms so that the CCs density increases when the EUV (or soft X-rays) energy deposition rate is larger. For this reason laser plasma sources, characterized by a high peak brightness, are extremely suitable to be used for the LiF material coloration.

Due to their high peak power and to the short penetration depth of EUV in the material, the dose deposition rate ,P, can be as high as some gigawatts per cubic centimeter. In our case we used a laser plasma source pumped by a large volume excimer laser having a pulse energy ranging between 1 and 7 J and a pulse duration ranging between 10 and 120 ns [10]. The efficiency of the laser plasma is as high as 20% in the EUV [10] so that at 10 cm from the source the dose rate in LiF is as high as 3 GW/cm³ and with just 1000 shots we could reach in the LiF samples a dose of some tens kJ/cm³; after the irradiation, a CCs density in the order of 10¹⁹ cm⁻³ is reached in the the irradiated LiF samples and a strong luminescence is observed.

According with the literature, when using hard X-rays the F-type CCs results to scale approximately as the root-square of the X-ray dose (D) and with the logarithm of the dose rate (P), as shown in figure 2 for a NaCl crystal; in this case the experimental data are taken from page 221 of [1].

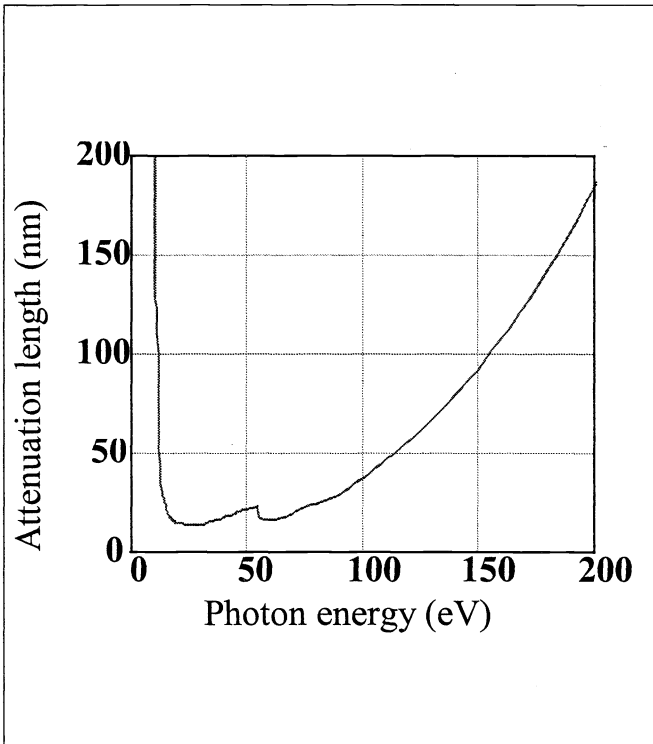


Fig. 1: Penetration depth of EUV radiation in a LiF crystal.

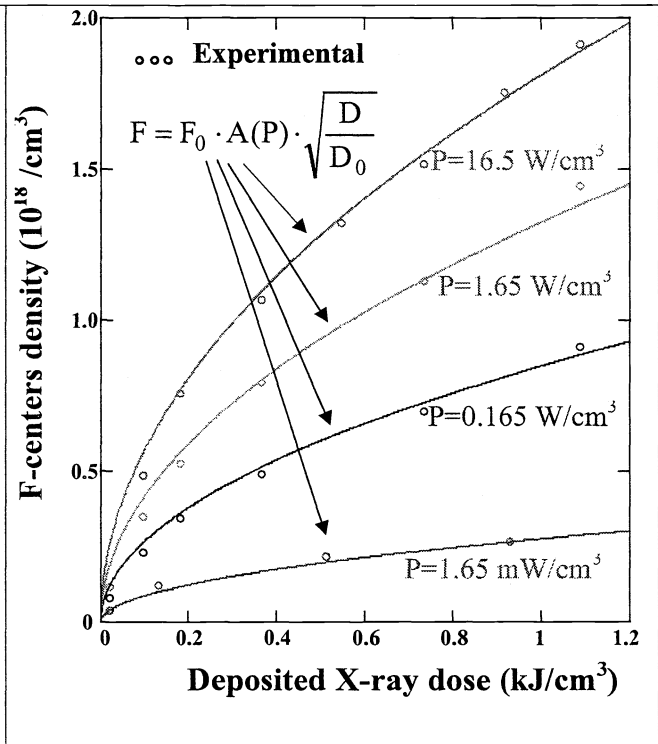


Fig.2: F-type CCs density vs X-ray dose deposited in a NaCl crystal: exper. results (circles) and best fit with an empirical function (solid lines).

The empirical best-fit function for the debris density in figure 2 is $F = F_0 \cdot A(P) \cdot \sqrt{\frac{D}{D_0}}$, where D is the deposited EUV dose, P is the dose rate, $D_0 = 1 \text{ J/cm}^3$ is the unity dose, $A(P) = 1 + 2 \cdot \log(1 + P/P_s)$, $P_s = 10 \text{ mW/cm}^3$ is the threshold dose-rate for non-linear effects and $F_0 = 7.7 \cdot 10^{15} \text{ centers/cm}^3$ is the centers density due to a unity dose at $P \ll P_s$. From our preliminary experiments on LiF crystals, it seems that exactly the same function is also followed by the F-type CCs in LiF when irradiated with EUV.

3-Luminescent patterns formation

Since the EUV penetration depth is very short, the LiF crystal can be substituted by a LiF film obtained as a layer deposited on different kind of thermal substrates by evaporation. In this way, smooth surfaces can be obtained and the active CCs formation efficiency is found (for the F₂ and F₃⁺ CCs) to be one

order of magnitude larger than for a LiF crystal as shown in fig. 3, where photoluminescence spectra of CCs, pumped by the 458 nm line of our Ar laser are reported [11]. The reason for this result lies in the different structure of the film (polycrystalline) compared with the bulk crystal (monocrystalline).

Under the above mentioned experimental conditions for the EUV irradiation (1000 shots at 10 cm from the plasma source, absorbed EUV dose $\sim 30 \text{ kJ/cm}^3$) we irradiated a LiF crystal with a copper mesh placed in contact over the crystal [12]. In this way, colored patterns are obtained on the LiF surface since the areas under the mesh structure are not colored while those which received directly the EUV radiation presents a strong luminescence (when excited by blue light), as shown in fig. 4. The resolution in the luminescent patterns is less than $1 \mu\text{m}$, limited mainly by diffraction effects as explained in [12].

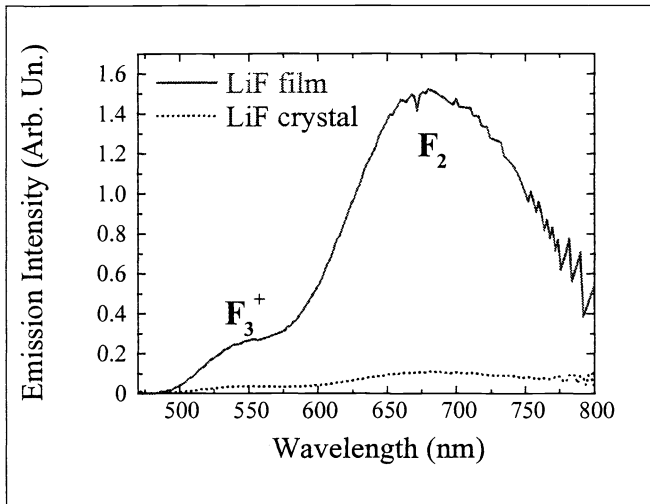


Fig. 3: Comparison between the photoluminescent spectra re-emitted by a LiF crystal and by a $6 \mu\text{m}$ thick LiF film after being irradiated by EUV in the same conditions (120 mJ/cm^2). (Room temperature; excitation by argon laser at $\lambda=458 \text{ nm}$)

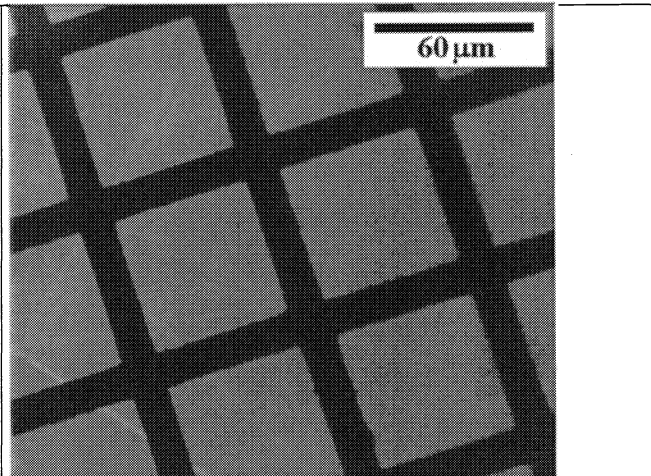


Fig. 4: Image of a LiF crystal irradiated by EUV observed by an optical microscope in fluorescence mode (through a yellow filter, objective 40X) while excited by an argon laser at $\lambda=458 \text{ nm}$. Clearly visible is the luminescent zones of the crystal, as well as the shadow of the mesh placed over the sample during the EUV exposure.

Another technique for the generation of luminescent patterns consists on writing the patterns by e-beams [2], but salts like LiF are insulators and hence charge-space effects appear and low e-beam current values must be used; the main advantage of the use of EUV radiation is that large areas (some square centimeters) can be treated at sub-micron resolution with exposure-times orders of magnitude lower than for e-beam direct writing: in our case by operating the laser at 10 Hz it is possible to reach the proper exposure of the LiF plate ($\sim 100 \text{ mJ/cm}^2$) over some centimeters area in less than two minutes.

Considering the above described properties of LiF, this material can be used as soft X-ray imaging detector. Compared with photographic films, typically used for μ -radiography of small animals, or with PMMA (PolyMethylMethAcrylate) photoresist, typically used as detector for soft X-ray contact microscopy [10, 13, 14, 15], the LiF film allows a much smaller resolution (the CCs size is less than 1 nm) and a much wider contrast dynamic range, respectively. This second characteristic of LiF films is due to the quadratic response of the CCs density vs X-ray dose shown in figure 2. Consequently, images of 10-12 bits can be obtained and no development is needed after the exposure to X-rays, while by using PMMA the dynamic range is limited by the development process so that the final dynamic in the images is just 5-6 bits [10,14]. The problem of the contrast dynamic is much smaller when photographic films are used but, in this case, the

emulsion grains size limits the resolution to few microns. For comparison between LiF and PMMA, in figure 5 we show the micro-radiography of a polypropylene phantom: the much larger dynamic of LiF is evident allowing a clear imaging of both regions exposed at a low X-ray intensity (the regions where the phantom is thicker) as well as regions exposed to a large X-ray intensity (where the phantom thickness is zero). On the phantom image on PMMA, the low dose regions can't be distinguished each other nor at optical analysis neither at AFM analysis, as shown in the expanded details of figure 5.

6- Conclusions and acknowledgments

We have demonstrated that laser-plasma sources can efficiently generate color centers in LiF and that high resolution luminescent patterns can be obtained. The application of LiF films as image detectors seems to be very promising for microradiography and soft X-ray contact microscopy. Authors thank Dr. A. Reale and his group of L'Aquila University (Italy) for their support in the experiments and Dr. A. Lai of ENEA C.R. Frascati for important discussions and for her contribution.

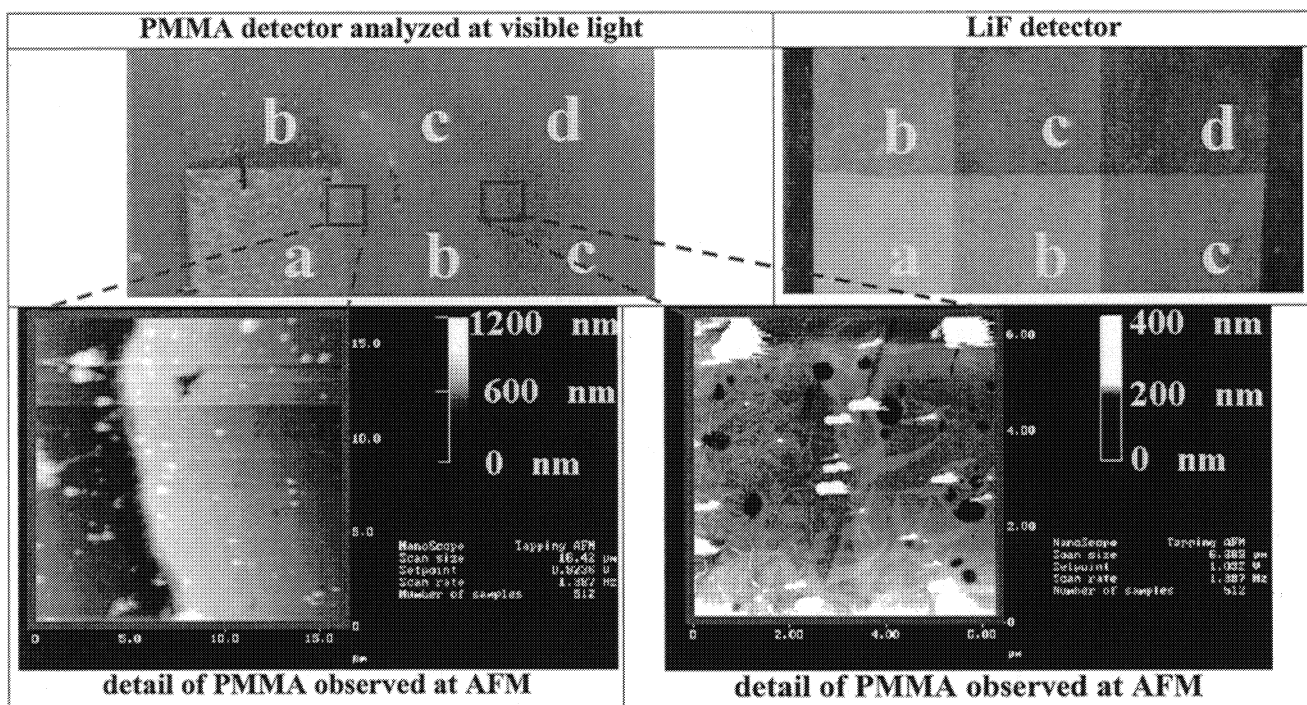


Fig. 5: Micro-radiography of a step-shaped polypropylene phantom on PMMA photoresist and on LiF film exposed in the same conditions (600 mJ/cm^2). The phantom step-structure reduced the soft X-ray fluence by a factor 0, 150, 300 and 600 for areas a,b,c and d, respectively. The PMMA has been developed 0.5 minutes in MIBK developer. Its original thickness was 600 nm while after development resulted (from AFM analysis as shown in the details) 200 nm for zone-a, 588 nm for zone-b and ~ 600 nm for both zones c and d.

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