Journal of Luminescence 129 (2009) 1731–1734

Contents lists available at ScienceDirect

Journal of Luminescence

journal homepage: www.elsevier.com/locate/jlumin

Enhanced photo-response of thin-film structures with nanocrystals

Olga Goncharova [a,b,*], Rosa Maria Montereali [b], Giuseppe Baldacchini [b]

[a] NASB, Institute of Physics, Independence Avenue 68, Minsk 220072, Belarus
[b] ENEA, Frascati Research Center, Via E. Fermi 45, Frascati 00044, Rome, Italy

ARTICLE INFO

Available online 7 May 2009

PACS:
78.20.−e
78.67.Bf
42.65.−k

Keywords:
Nanocrystals
Thin films
Intrinsic defects
Absorption
Luminescence
Subpicosecond transient absorption

ABSTRACT

Thin-film multilayers with dielectric and semiconductor nanolayers of 200–10 nm thicknesses have been deposited by thermal evaporation onto irradiation-resistive substrates using pure crystals as evaporated targets. Some multilayers were γ-irradiated in air at room temperature with dose of 83 kGy. X-ray diffraction and microscopy studies reveal that the multilayers consist of nanometer-sized crystals with cubic structure and defined size. Film structures were oriented along the (1 1 1) plane. Absorption spectra of non-irradiated LiF nanocrystals of 100 nm size and those of initial crystals give evidence of metal colloids presence. Photoluminescence spectra of γ-irradiated nanostructures with various LiF content show the enhancement of F_3^+-colour centres excitation in the region of metal colloids absorption and the increase is observed between emission intensities of F_3^+ and F_2 centers with respect to initial crystals γ-coloured in identical conditions. Emission intensities of both centers under excitation in the *M* band correlate with LiF content. These effects, which are related to high-quality nanocrystals, but at the same time depend strongly on the defect content, especially as far as their 1–2 ps nonlinearities are concerned, could depend on nanocrystal purity and metal excess collection in their boundaries regions.

1. Introduction

Nano-sized layers and crystals play an important role in future technology as they exhibit different and often unique properties with respect to the initial macroscopic materials. Semiconductor and metal nanocrystals formed in dielectric layers are being extensively studied because of ultrafast optical nonlinearities [1,2] and specific photo-response due to metal content [2,3]. The local electric field inside and near metal nanoparticles is greatly enhanced due to the resonant absorption of surface plasmons, and it leads to a strong absorption, third-order susceptibility and subpicosecond response. The composition of metal, dielectric and semiconductor nanostructures can give extra peculiarities to these properties [4,5]. Moreover, irradiated dielectric and semiconductor nanocrystals exhibit novel effects, such as a higher efficiency of *F*-aggregate colour centers (CCs) formation [6–8] and 1–2 ps decay components of absorption saturation [7].

Film structures with nanocrystals [9–12] have drawn much attention owing to their applicability for switching devices, detectors, efficient dosimeters, emitters and solar cells [1,7,13]. The possibility of using these nanostructures not only for fundamental studies, but also for novel devices fabrication, is stimulating the efforts to control the nanocrystal size, shape, structure, space arranging [1] as well as their composition and structural defects [2,7,13]. Unfortunately, not only bulk, but boundary (surface) states of nanocrystals affect strongly their physical properties as their size reduces [14]. The properties of thin layers and nanocrystals as prepared and post-growth processed by different methods can be affected by the presence of impurities, crystal defects and aggregation of impurities and intrinsic defects to the colloids in the bulk and surface regions [13,15–20] related to the used preparation technique.

Several physical deposition methods are used for preparation of thin-film nanostructures such as thermal or electron-beam evaporation from composite targets [10], sequential sputtering or evaporation [1,9]. Ion implantation [17], thermal treatments [18] and ionising radiation bombardment (combined with special annealing [15,16,19,20]) are established tools for metal nanoparticles formation in solids. Understanding the structural evolution during the preparation of nanocomposites can be of great help in understanding how to control the characteristics of the final products.

Lithium fluoride is a well-known material which, after irradiation by electrons, X-rays, γ-rays, or laser light, is characterized by *F*-CC aggregates and metal colloids formation sensitive to the content of oxygen, hydroxyl and divalent metal ions in initial crystals [15,16,19,20]. Clusters of *F*-CCs (lithium colloids) and impurity colloids can be created in LiF at temperatures where diffusion of point defects and impurities is possible [18–20]. Even though the actual mechanism of the formation of such colloids is

* Corresponding author at: National Academy of Sciences of Belarus (NASB), Institute of Physics, Independence Avenue 68, 220072 Minsk, Belarus.
Tel.: +375 29 1273712; fax: +375 17 2840879.
E-mail address: OlgaGoncharova08@gmail.com (O. Goncharova).

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doi:10.1016/j.jlumin.2009.04.062

still an open question, a lot of attention was devoted to study the optical properties of the crystals (nanocrystals) containing these metallic aggregates.

Since nanocrystal defects have been studied only in a limited way [2,13,14], in this paper, we carried out the following measurements to investigate them.

2. Experimental

2.1. Samples preparation

The investigated samples consist of films composed by dielectric or/and semiconductor nanocrystals. The samples are multilayers [9,10,12] and interferometers (TFI) with intermediate multilayers [11]. Samples with various "sensitizing" nanocrystals are grown on radiation-resistant, flat substrates by multi-step deposition of alternate nanolayers [9,10]. "Sensitizing" nanolayers are prepared with thicknesses equal to nanocrystal sizes [9]. To avoid radiative coloration, thermal evaporation was the preferred fabrication technique. Undoped crystals, 99.999% pure, are used as starting materials. The substrates were kept at room temperature (RT) on a copper holder, and the vacuum pressure in the evaporation chamber was about 10^{-6} Torr. The films thicknesses were measured by interference method. As-prepared (fresh) samples are kept for seven days in a dry box before starting the optical measurements in the open atmosphere at RT at about 50% humidity. Crystals and films produced in standard way were used as reference samples. After the growth some samples were γ-coloured at RT up to 83 kGy [7,15].

2.2. Measurements

Microstructural and optical characteristics of different film samples are summarized in Fig. 1.

The microstructure of film samples is determined by X-ray phase analysis, scanning electron microscopy (SEM) and atomic force microscopy (AFM). Optical transmittance (T) spectra of samples are measured with a Cary 500 Scan and a Lambda 19DM Perkin-Elmer spectrophotometers in the spectral range 190–3300 nm. Optical absorption (OA) (Fig. 2) is derived from transmittance and is used to estimate the defects in nanocrystals with respect to initial crystals. The photoluminescence (PL) measurements were carried out by using a Jobin Yvon Fluorolog-3 spectrofluorometer with the front-face detecting geometry, and by exciting the samples at 458 nm (M band), see Fig. 3. Nonlinear properties were detected using a pump-probe setup and 3-ps and 150-fs laser pulses, and reported in Fig. 4. All measurements were performed at RT.

3. Results and discussion

X-ray diffraction (XRD)-, SEM- and AFM-results show that non-irradiated multilayers are structures with definite size of nanocrystals. Presence of (111) and (222) peaks in XRD data of the multilayers indicates that they have strong c-axis orientation perpendicular to the substrate surfaces. The XRD pattern of LiF multilayers, see Fig. 1a, shows an intense (111) peak at $2\theta = 38.7^\circ$ and a considerably less intense (222) peak at $2\theta = 83.1^\circ$.

Not-presented here XRD-, SEM- and AFM-results validate the fact that irradiation neither causes a change in the packing nor increases in the size of nanocrystals. The (111) peaks prevail in the XRD-patterns and γ-irradiation with the dose of 83 kGy only improves the crystalline quality of nanostructure (increase in the intensities of (111) peaks).

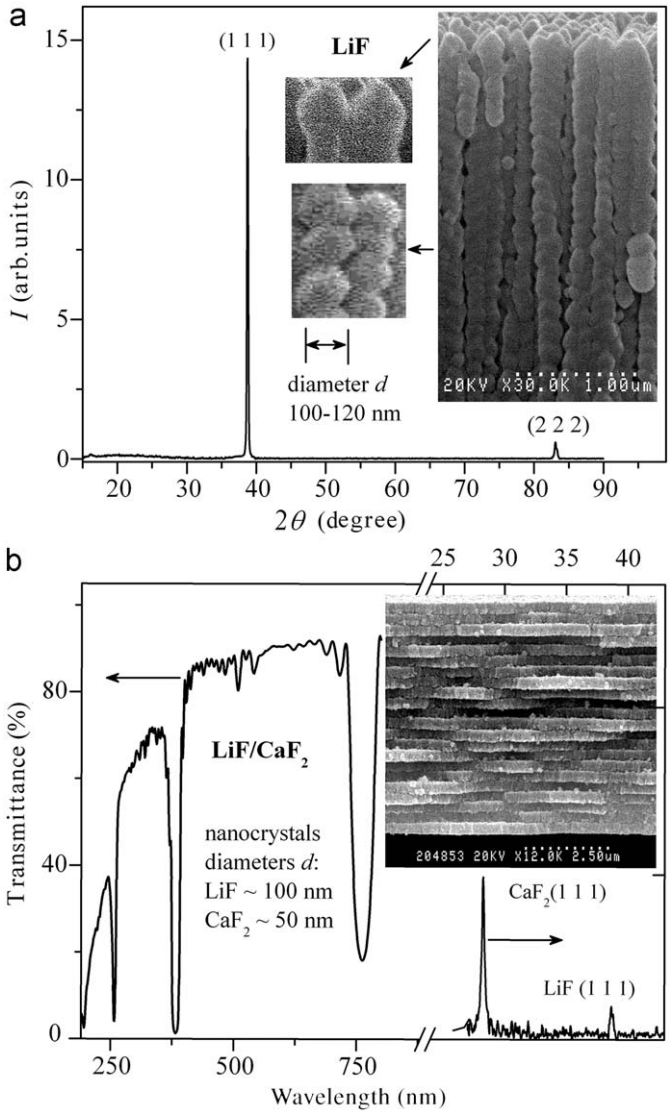

Fig. 1. c-oriented nanostructures consisting of LiF (a) and LiF and CaF_2 nanocrystals and (b) with sizes d~100 and 50 nm, respectively.

To establish the influence of content of LiF nanocrystals with given size on photoluminescence of multilayers, two LiF/CaF_2 structures have been prepared (Fig. 1b). The first is the 24-period structure consisting of 100 nm LiF-layers and 220 nm CaF_2-layers. The next is the 48-period structure of 100 nm LiF-layers and 50 nm CaF_2-layers. Both multilayers were composed of 100 nm LiF and 50 nm CaF_2 nanocrystals and were c-oriented structures. High-reflectivity and transmissivity bands are provided by the structures. Spectral positions of the bands were not changed after γ-irradiation but can be shifted to short-wavelength region by increasing the angle of incidence of light.

OA spectra of non-irradiated LiF nanostructures and initial crystals with small content of Mg^{2+}, O^{2-} and OH^- ions [13] show well-resolved absorption of Mg^{2+} colloids [19,20] (Fig. 2). (The non-irradiated and γ-irradiated substrates remain non-absorbing in the above spectral range.) According to the literature, besides Mg colloids with the absorption band peaked at 4.4–4.6 eV, the low-wavelength absorption band at 3.6–4.1 eV related to formation of more large Mg colloids or intrinsic Li colloids [19,20], are reliably distinguished in non-irradiated LiF nanostructures (Fig. 2) and initial crystals γ-irradiated with