Photonics and Nanostructures – Fundamentals and Applications 29 (2018) 36–41

Contents lists available at ScienceDirect

Photonics and Nanostructures – Fundamentals and Applications

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

Photoluminescence of magnesium-associated color centers in LiF crystals implanted with magnesium ions

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ARTICLE INFO

Article history:
Received 21 June 2017
Received in revised form 9 August 2017
Accepted 30 January 2018
Available online 13 February 2018

Keywords:
Magnesium nanoparticles
Implanted crystal layer
Microscopy
Luminescing color centers
LiF:Mg crystal

ABSTRACT

In the present paper, the effect of magnesium nanoparticles implanted in a LiF crystal on the optical properties of color centers is studied. The transmittance spectra and AFM images demonstrate effective formation of the color centers and magnesium nanoparticles in an implanted layer of ~ 60–100 nm in thickness. Under thermal annealing, a periodical structure is formed on the surface of the crystal and in the implanted layer due to self-organization of the magnesium nanoparticles. Upon excitation by argon laser with a wavelength of 488 nm at 5 K, in a LiF crystal, implanted with magnesium ions as well as in heavily γ-irradiated LiF: Mg crystals, luminescence of the color centers at λ_{max} = 640 nm with a zero-phonon line at 601.5 nm is observed. The interaction of magnesium nanoparticles and luminescing color centers in a layer implanted with magnesium ions has been revealed. It is shown that the luminescence intensity of the implanted layer at a wavelength of 640 nm is by more than two thousand times higher than that of a heavily γ-irradiated LiF: Mg crystal. The broadening of the zero-phonon line at 601.5 nm in the spectrum of the implanted layer indicates the interaction of the emitting quantum system with local field of the surface plasmons of magnesium nanoparticles. The focus of this work is to further optimize the processing parameters in a way to result in luminescence great enhancement of color centers by magnesium nanoparticles in LiF.

1. Introduction

Over the last decades, diverse optical effects of the interaction between light and surface of metal nanoparticles (MNs) are intensively studied. These effects began to play a special role in the development of nanotechnologies after the discovery of the giant Raman scattering of molecules adsorbed on the nanoparticles surface. In addition, other effects associated with the interaction of molecules with metal nanoparticles are observed. Among them are the increase in the absorption cross section and in the luminescence intensity of molecular ions near the nanoparticle, and the transfer of excitation energy between nanoparticles and radiating centers [1–8].

Mechanisms of metal nanoparticles formation in dielectric matrixes, optical properties of heterogeneous materials, and nonlinear optical characteristics of these materials are discussed, for example, in works of Stepanov [9,10]. The studies of materials containing metal nanoparticles have shown that characteristics of the composite materials can be changed depending on type and concentration of nanoparticles and revealed fundamental effects of the interaction of the MN surface plasmons with quantum systems. However, the choice of model objects for researches of such interactions should be based on a possibility of efficient modeling of composite structures. It is difficult enough for the systems with a large amount of vibration modes, e.g. for organometallic compounds.

Convenient objects for the study of such effects are cubic crystals, in particular, alkali halide crystals with proper and impurities defects. In these crystals, MNs could be easily created using ionic implantation or vacuum precipitation techniques. MNs have high density in near-surface layer of 100–200 nm thick. At the same time, during the implantation, color centers are formed that play a role of chromophores. An important feature of such a system is the presence of very narrow zero-phonon lines in the absorption and luminescence spectra of color centers at low temperature. Measurement of the spectral parameters and the intensity of the

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https://doi.org/10.1016/j.photonics.2018.01.005
1569-4410/

zero-phonon lines enables to determine the degree of perturbation of the color centers due to interaction with nanoparticles or to deformation of the crystal matrix. The crystals and thin films of LiF are those objects which can contain luminescent color centers and nanoparticles of lithium, sodium, magnesium, nickel, cobalt, etc. depending on the growth conditions, the type and dose of radiation exposure and parameters of postradiation treatment [11–17]. It is known that metallic nanoparticles are actively formed if LiF crystals are irradiated with ion flows [18–21]. Here we tried to reveal the effect of implanted magnesium nanoparticles on the change of the optical properties of color centers in a LiF crystal.

2. Experimental techniques

2.1. Characteristics of crystal samples and ACM research method

The samples of lithium fluoride crystals grown by Kyropoulos method at air were chosen for the research. This growing method allows to obtain maximal concentrations of luminescent color centers. The samples surface was the natural cleavage along the cleavage plane [100]. The surface of all the samples before each analysis was treated with ethanol to remove organic "dirt" on the samples surface. All samples represented parallelepipeds with the following dimensions: length and width did not exceed 20 mm, height was not higher than 5 mm.

The crystal samples were irradiated with accelerated Mg^+ ions, with an energy of 80 keV, the current density in the ion beam was 4 $\mu A/cm^2$ in the dose ranging from 2.2×10^{16} to 7.5×10^{16} ion/cm^2. The target with samples was employed at room temperature. The average calculated depth of magnesium ions penetration into the crystal is of the order of 60 nm. The topology of the crystal surface was examined at all stages: before implantation, after implantation, after implantation and heat treatment.

The surface topology of the crystals was studied using an atomic force microscope (AFM) SOLVER P47-PRO (NT-MDT company). The scanning of the samples was carried out in a semi-contact mode using the cantilever NSG01. The value of the SetPoint parameter for the semi-contact was in interval 5.20 − 5.75. The images were treated with a non-linear filter Median 5 × 5 to eliminate artifacts and image inaccuracies. To improve sharpness of the images and to better represent boundaries of the relief, the images were also treated with the Prewitt Vertical filter. The choice of this mode and the scanning method was due to the fact that the semi-contact mode has less influence on the sample surface, and does not change the surface relief.

The initial untreated samples of LiF crystals before and after heat treatment as well as LiF crystals with implanted magnesium ions were studied before and after heat treatment.

2.2. Methods for measuring optical transmittance and luminescence spectra

Transmittance spectra in UV and visible spectral regions were measured using Perkin Elmer Lambda 950 and UV-3600 Shimadzu spectrophotometers. The equipment for the study of optical characteristics of crystals with nanostructures included an optical low-temperature helium cryostat SHI-4-1 (JANIS) operating at 4–400 K, an optical monochromator MDR-23, photodetectors (photomultipliers, silicon and germanium photodiodes), signals from which fall to the amplifier input and then to the inputs of the ADC board PCI6251 National Instruments.

The argon laser with 488 nm wavelength was used to excite the luminescence. Signals were recorded in synchronous detection mode, for which the radiation sources were modulated at 400 Hz. The reference channel for recording the incident radiation on the sample allowed controlling its intensity and correcting the absorption and luminescence spectra. The measurement results were treated using the LabVIEW graphical program, which allows the signal recording process to be optimized.

Since the absorption and luminescence bands of the color centers are strongly broadened at room temperature and it is difficult to observe the effects of broadening and shifting of the spectral position, the measurements were carried out at 5 K in a low-temperature cryostat with a recycling helium cycle.

3. Experimental results and discussion

3.1. ACM research

In Fig. 1a, b, AFM images of the cleavages of initial non-implanted and non-annealed LiF crystals are presented.

Roughness observed in the images is due to the crystals cleavage.

In Fig. 2a, b AFM images of the crystal surface before and after heat treatment are shown. The heat treatment was carried out by slow heating and annealing of the crystals at a temperature of 900 K for 5 min in air.

In Fig. 3, the image of sample after ion implantation with magnesium ions is presented.

To increase the contrast, a sample image was obtained with a display of the probe vibration phase (Fig. 3 b). In the images (Figs. 3a, b), structures with diameters of 100–500 nm on surface crystal are

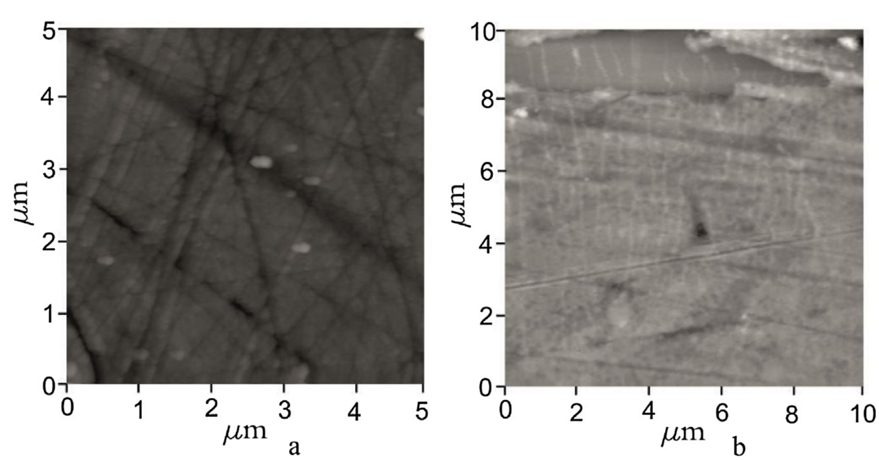

Fig. 1. AFM images of the cleavage in [100] plane of LiF crystals: (a) – the scan frame size is $5 \times 5\ \mu m^2$; (b) – the scan frame size is $10 \times 10\ \mu m^2$.