Nuclear Instruments and Methods in Physics Research B 403 (2017) 1–6

Contents lists available at ScienceDirect

Nuclear Instruments and Methods in Physics Research B

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

Formation of metal nanoparticles in MgF_2, CaF_2 and BaF_2 crystals under the electron beam irradiation

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ARTICLE INFO

Article history:
Received 5 February 2017
Received in revised form 22 April 2017
Accepted 25 April 2017

Keywords:
Crystal
Alkali-earth metal
Nanoparticle
Electron beam
Plasmon resonance

ABSTRACT

It is shown experimentally that electron beam action with electrons energies of 50 and 70 keV on MgF_2, CaF_2 and BaF_2 crystals results in local formation in the crystal near-surface layer of Mg, Ca or Ba nanoparticles which possess plasmon resonance. In the case of MgF_2 spheroidal nanoparticles are formed, in the cases of CaF_2 and BaF_2 – spherical. The formation of metal nanoparticles is confirmed by computer simulation in dipole quasistatic approximation. The dependence of absorption via electron irradiation dose is non-linear. It is caused by the increase of nanoparticles concentration and by the increase of nanoparticles sizes during irradiation. In the irradiated zones of MgF_2 crystals, for irradiation doses less than 80 mC/cm^2, the intense luminescence in a visible range appears. The practical application of fabricated composite materials for multilevel optical information recording is discussed.

1. Introduction

Composite materials containing metal nanoparticles (NPs) with plasmon resonances [1,2] are widely used in photonics. In glasses, containing metal nanoparticles, such as Ag, Au and Cu, a pronounced non-linear optical properties are observed and they can be used as an active media in the ultrafast optical switches [3,4]. Such composite materials are perspective for the creation of optical composite metamaterials with negative permittivity and superlenses [5,6]. Alkali and alkali-earth metal NPs also provide sharp plasmon resonances [1] and are promising from the view point of non-linear optical materials and metamaterials development. It was shown in [7–16] that irradiation of LiF, NaF, NaCl and CaF_2 crystals by γ- or X-ray radiation, by electrons with energies of 0.5–200 MeV or by UV laser intense radiation results in metal NPs formation in crystal bulk. In CaF_2 crystals colloids of Ca NPs can be formed by additive coloring – i.e. by thermal treatment in Ca vapor [17]. The formation of color centers in the mentioned crystals by irradiation makes it possible optical information recording. To increase data recording density different methods can be used [18–20], including multilevel optical information recording [21]. The last method makes possible to record information not in binary code, but in high-order codes (i.e. octal or hexadecimal codes). In an integrated optical and nanoplasmonic devices and for optical information recording it is important to form NPs or color centers locally in submicron region and near substrate surface.

As it was shown in [22,23] the irradiation by electrons with relatively low energies E = 5–50 keV of Ag- and Na-containing silicate glasses and the subsequent thermal treatment above the glass transition temperature result in the formation of Ag and Na NPs in the near-surface layers of glasses. The main mechanisms of this effect are as follows [22–24]: (i) the accumulation during electron irradiation of thermalized electrons and the resultant formation of negatively charged region under the glass surface; (ii) the field migration of mobile positive metal ions into this negatively charged region; This is the main peculiarity of low energy electron irradiation – in contradiction to γ- or X-ray, high energy electron and UV laser irradiation. The appearance of local charged region and field migration of metal ions result in their spatial redistribution in crystal – the concentration of metal ions in the irradiated zone increases, and in the surrounding areas decreases; (iii) the reduction of metal ions to neutral state; and (iv) the growth of metal nanoparticles during the thermal treatment. The main advantage of this method is the possibility of nanoparticles formation locally, in the region with the required shape and located at the required depth.

In the given paper, we report the results on the formation of metal nanoparticles in MgF_2, CaF_2 and BaF_2 crystals under the

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http://dx.doi.org/10.1016/j.nimb.2017.04.085
0168-583X/

effect of electron beam with relatively low electron energies and discuss the properties of these nanoparticles. In the discussion we payed attention to the abilities of multilevel optical information recording in crystals by electron beam.

2. Experimental

In our experiments we used polished plates of single crystal MgF_2, CaF_2 and BaF_2 2 mm thick. The choice of materials was determined by the fact that Mg, Ca and Ba metals are from the II group of Mendeleev periodical table of elements, but differ significantly in atomic mass: atomic mass of Mg is 24.3, of Ca – is 40.1 and of Ba – is 137.3. Their material densities also differ significantly. The advantage of the chosen crystals, in contradiction to alkali halide crystals, is in that they are not dissolved in water, which is important for practical applications. The electron irradiation was carried out in a JEBD-2 scanning electron microscope, the electron energy E was 50–70 keV, the irradiation doses Q was 7–100 mC/cm^2 for the electron current density of 50 μA/cm^2. The dose of irradiation was determined by the irradiation duration. The electron irradiation was carried out at a room temperature. The calculation has shown that the temperature of near-surface glass layers during the electron irradiation for E = 50 keV and Q = 50 mC/cm^2 does not exceed 150–200 °C. The electron beam diameter on the glass surface was 1.5–2 mm. Electron beam diameter was chosen for the convenience of optical measurements. For very small diameters of irradiated zones the errors during optical density measurements significantly increase if standard spectrophotometer is used. But it must be noted, however, that the electron beam of scanning electron microscope can be focused into a spot with a diameter less than 10 nm, which is important for optical information recording with high density. Al films of 80 nm thick were deposited on the samples surfaces for removing the surface charge, which appear on a crystal surface during electron irradiation. After irradiation, these films were removed by etching in an aqueous solution of KOH. The optical density spectra of samples under study were recorded within the 250–800 nm spectral region using Lambda 650 (Perkin–Elmer) spectrophotometer at a room temperature. During optical density measurements the samples were covered with masks with the hole sizes equal to the sizes of irradiated zones. Curve 5 in Fig. 1 and curve 4 in Fig. 4 were smoothed using ORIGIN™ software to delete noise. For luminescence measurements EPP2000-UVN-SR (StellarNet) fiber spectrometer was used, the luminescence being excited by a semiconductor laser with λ = 405 nm.

3. Experimental results

3.1. MgF_2 crystals

Electron irradiation of MgF_2 crystals with E = 50 keV results in the appearance of several absorption bands on optical density spectra (Fig. 1). It can be seen from the figure that overlapping absorption bands appear at 250, 300 and 325 nm. Two pronounced overlapping bands appear at 375 and 400 nm, and two weak absorption bands appear at 470 and 520 nm. For Q = 100 mC/cm^2 the absorption significantly increases in the whole spectral range. At λ = 350–400 nm for Q = 100 mC/cm^2 the value of optical density is near 4. For electron energy of 50 keV all processes during irradiation take place in the near-surface layer approximately of 12–20 μm thick (see below). It means that the absorption coefficient in this case exceeds 5000 cm^{-1}. Arise of absorption bands led to the coloration of crystals from weak-yellow for Q < 50 mC/cm^2 to black for Q = 100 mC/cm^2 (see inset in Fig. 1).

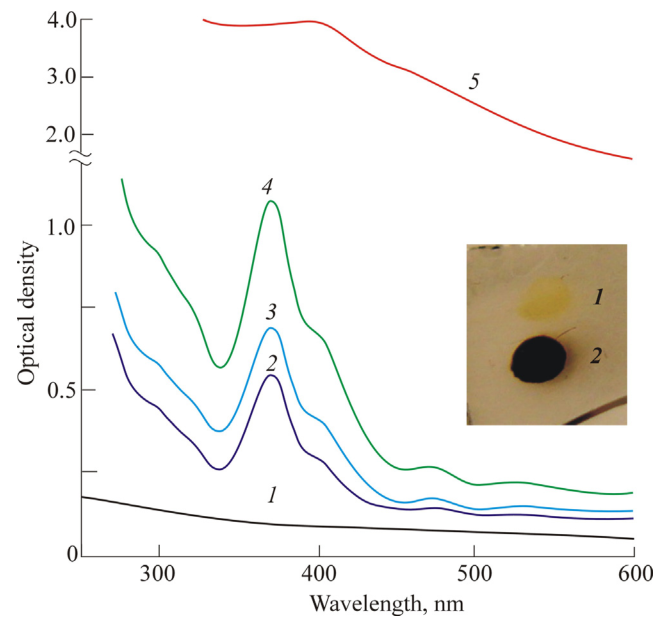

Fig. 1. Optical density spectra of irradiated zones of MgF_2 for E = 50 keV and different irradiation doses. *1* – before irradiation, *2* – 50 mC/cm^2, *3* – 60, *4* – 80, *5* – 100. Inset: photo of irradiated zones for Q = 50 mC/cm^2 (*1*) and 100 mC/cm^2 (*2*). Diameters of irradiated zones are 2 mm.

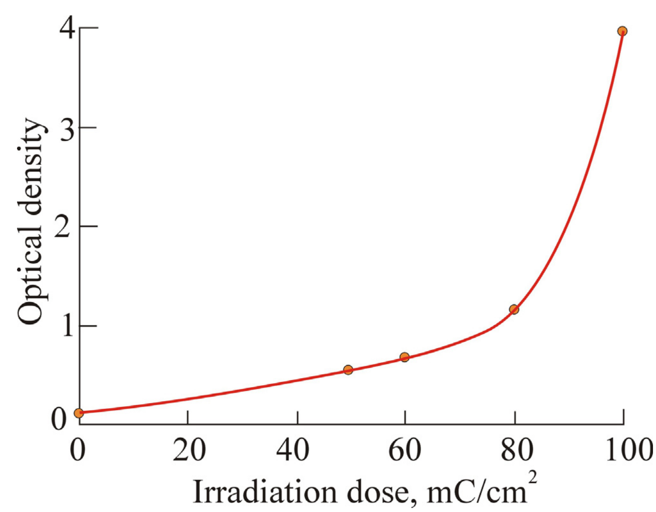

Fig. 2. Optical density of MgF_2 at 375 nm via electron irradiation dose. E = 50 keV.

Fig. 2 shows the optical density of MgF_2 at 375 nm via electron irradiation dose for E = 50 keV. It can be seen that the dependence is non-linear and strong increase of the absorption is observed for Q > 60 mC/cm^2. The analysis has shown that for Q > 50 mC/cm^2 the dependence is near exponential.

Electron irradiation of MgF_2 crystals results not only in the increase of absorption, but also in the appearance of luminescence in a visible range. Fig. 3 shows luminescence spectrum of MgF_2 for E = 50 keV and Q = 50 mC/cm^2 for the excitation wavelength of 405 nm. It can be seen from figure that wide luminescence band appears at spectral region of 500–700 nm with maximum at 570 nm. One can see from inset in Fig. 3 that for Q = 50 mC/cm^2 luminescent centers fill the whole irradiated area, while for Q = 100 mC/cm^2 luminescence is observed only at perimeter of irradiated zone. It is evident, that strong absorption in the central part of irradiated zone results in the absorption of excitation and