Optical Properties of Alkali Halides Crystals with Metallic Nanoparticles

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Abstract – Results of experiments on creation of layers consisting of nanosized metallic particles in LiF host are presented. Two techniques were used: implantation of Cu^{2+} ions with energies about 100 keV in bulk LiF samples by a special ion accelerator with the following annealing and deposition by thermal evaporation on surface of a substrate (silica glass, LiF, NaF, NaCl crystals) of multi layer films, consisting alternative layers of metal (Cu or Ag or Au) and LiF. By means of the absorption spectroscopy and transmission electron spectroscopy it was established that nanoparticles were produced in the near surface layer of both the bulk crystal and thin film of LiF. Average sizes of the Cu particles were of 10–30 nm and the average inter particle gap was 10–50 nm. Dependence of optical characteristics of the nanolayers on conditions of the film deposition and ions implantations was studied.

1. Introduction

Composite materials consisting of metallic clusters of nanometric scale embedded in an insulator host exhibit special optical, electrical and magnetic properties which have opened many possibilities for their use in various technological applications. In particular, inorganic crystals with nanosize metallic particles (NP) are a promising material for manufacturing of optical switches with the ultra fast response time. They have high non-linear optical third order susceptibility, especially at the frequencies closed to range of absorption by metallic nanoparticles, which is due to the surface plasmon resonance [1]. At present time a variety of the host materials for embedding of NP are being explored. In particular, wide studies are performed of characteristics for NP layers in silica of different composition [2], in $LiNbO_3$ crystals [3], in Al_2O_3 crystals and films [4]. It should be noted that the alkali halides crystals are a promising material for manufacturing of a variety of optoelectronic elements as well. These media have a set of merits, namely: high optical transmission in wide spectral range and high light irradiation resistively. Also, recently, it is has been found a feasibility to produce of planar waveguides on the LiF thin films by electron beam lithography [5]. The material is readily processed: in particular thin films of the material can result from thermal evaporation upon vacuum. The simple and low cost technique has a large commercial potential for fabrication of elements for integrated optics and waveguides. Finally, a variaty of laser media based on the alkali halides crystals with color centers have been developed last years. That suggests they are a promising material for manufacturing of communication fibers with distributed amplification.

In this paper we present the first results of development of a new type of optic media based of the alkali halides crystals and polycrystalline films with embedded sub-surface metallic NP. Objectives of the studies were

- To establish, in principal, a feasibility of formation of the metallic nanoparticle layers in bulk crystal and thin film of LiF.
- Study of conditions for formation of thin LiF films with metallic nanoparticle layers on a solid substrate by a thermal evaporation
- Study dependence of properties of the films on type of the substrate (amorphous or crystal), (ii) on type of the embedded metallic atoms (Cu, Ag or Au) and (iii) on conditions of the deposition process: temperature of the substrate, length of the deposition, intensity of atom flow. Special attention will be paid to studies of characteristics of thin alkaline-halogen films with NP layers.

2. Experimental

Two techniques were used to produce the NP layers in alkali halides host. The first one was intended for production of NP in matrix of the bulk LiF crystal. For the purpose we used the LiF samples of $10\times10\times1$ mm^3 sizes, which were implanted by Cu^{2+} ions by means of the special high energy ion accelerator. The ion fluencies were $5\cdot10^{16}$ and $1\cdot10^{17}$ ions/cm^2 with ion energy about 100 keV. After ion implantation an absorption band appears at 250 nm, which are caused the intrinsic lattice defects formation as the *F*-centers. The next stage was annealing of the irradiated crystals near the melting temperature. After annealing at the temperature up to

950 K, weak absorption band appears at 570 nm (see Fig. 1). Note, that at such high annealing temperature all absorption bands disappear in the irradiated crystals, because of destruction of the defects that have been formed by radiation and reconstruction of the regular lattice structure. On the other hand, location of the absorption band is closed to one, which has been observed earlier for surface plasmon resonance due to nanosized copper particles in amorphous silica glasses. Hence, it is naturally relate to the absorption band appearance at 570 nm in our case with surface plasmon resonance of the copper NP. Taking into account that depth of the embedded ions layer is near 60 nm, one can estimate of absorption coefficient in the maximum band near of $5\cdot10^5$ cm^{-1}.

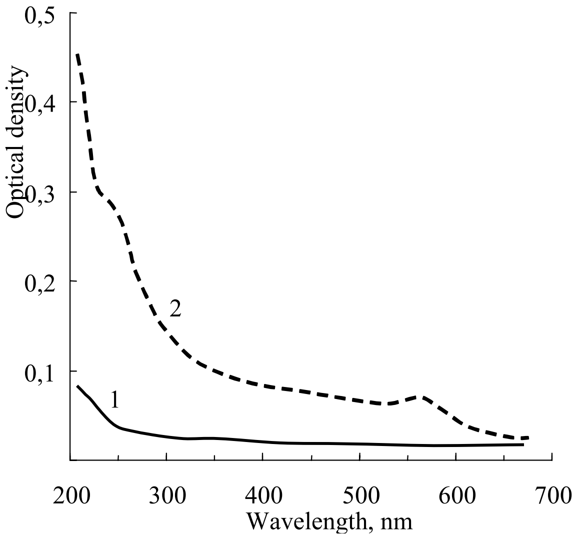

Fig. 1. Absorption spectra of LiF crystal before (1) and after (2) Cu^{2+} ions implantation with the subsequent annealing at 950 K

By means of the transmission electron microscopy (TEM LEO-906) it was shown that the copper particles distributed throughout the doped layer of the crystal are of a quasi spherical shape with 2–20 nm in diameter and average interparticles distance of 10–50 nm (see Fig. 2).

Several methods exist for introduction the metal into insulating substrates. One of the methods is presented in papers [4], where Al_2O_3 films with the embedded NP have been created by means of pulsed laser deposition on a substrate surface of the alternately ablated targets from the metal (Cu) or Al_2O_3. To produce LiF thin films with embedded metallic NP we used another type of technique. Low melting temperature of the LiF crystal (1140 K) let us to apply thermal deposition technique for fabrication of thin films with embedded NP layers. The commercial facilities were used to deposit films on a substrate from the thermally evaporated materials in vacuum $(2–6)\cdot10^{-5}$ Torr. The substrate could be heated while deposition up to 720 K by means of a special heater. Thickness of the deposited film estimated with the interferometer technique. To establish the influence substrate on properties of the film with NP layer we used both the amorphous (silica) and crystal (LiF and NaCl) substrates. The substrates were chemically cleaned and the films were deposited with alternate deposition of the subsequent metal (Cu or Ag or Au) and LiF layers, so that both stages were repeated up to three times. The control of deposition rate was performed with control of currents of the evaporators, which were hold for LiF charge and for charge of each type of the applied metal throughout the experiments. Gain of the deposited material was controlled by variation of the deposition time.

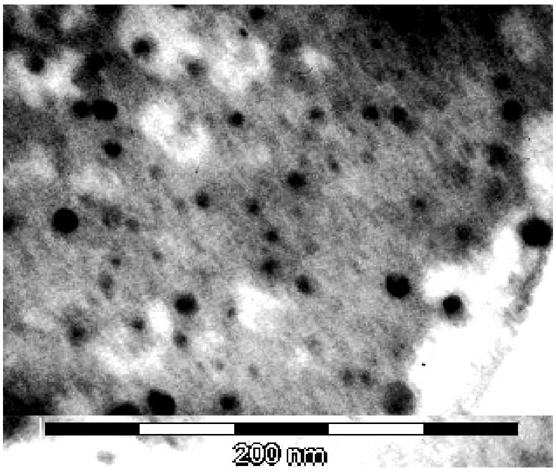

Fig. 2. TEM micrograph of the LiF crystal with the copper nanoparticles

The following results were obtained after experiments. To produce films of LiF host with copper NP layer we deposited on surface of the LiF substrate the layers of Cu and LiF, consequently, while deposition the substrate was hold at room temperature. After annealing of the sample at 950 K its absorption spectrum was obtained. The spectrum presented in Fig. 3 demonstrates the absence of any peculiarities in absorption. After that the sample was annealed additionally by irradiation of the second harmonic of the Nd:YAG laser (534 nm), and corresponding spectrum is presented in Fig. 3 (curve 2) as well. One can see that there appears the wide absorption band at 610 nm. We can conclude that in this case the NP layer is also created similar to results presented in section 2.1. Significant width and shifted position of its peak as compared with the usual position (570 nm) one can explain by a partial destruction of the NPs resulting from the laser irradiation effect. Note, that the similar experiments performed with the silica substrate did not result in formation of the band. Hence, we conclude that formation of NP layer in LiF matrix of a bulk sample or a polycrystalline film is possible just after realization of rather hard thermal processing as opposed to NP layer formation in silica [4].

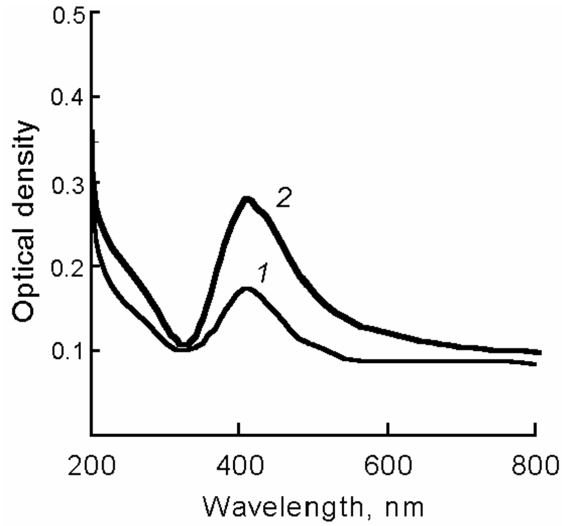

Fig. 3. Absorption spectra of LiF crystal with deposited LiF and Cu films at room temperature and subsequent annealing at 950 K (1), and the additional laser annealing (2). The arrow shows the location of the peak of plasmon resonance for Cu

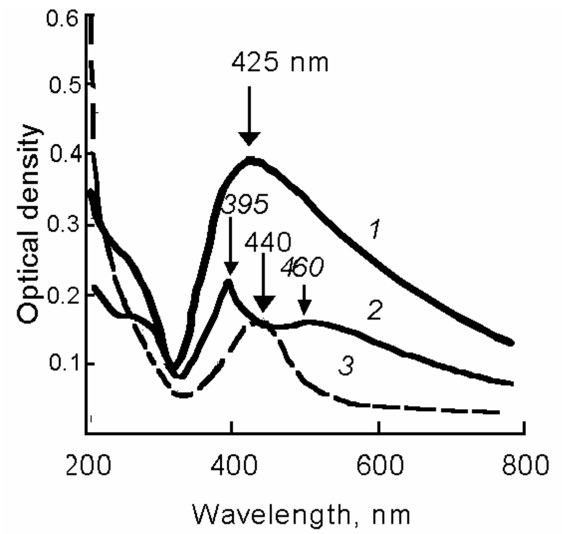

Fig. 4. Absorption spectra of LiF crystal with deposited LiF and Ag films at room temperature (1), after the subsequent annealing at 950 K (2) and with heating of the substrate in the process of deposition up to 650 K (3). Arrows show locations of peaks at the curves

The similar experiments were performed with deposition of the Ag and LiF film on surface of different substrates. Fig. 4 presents the absorption spectra of thin film that was composed from LiF and Ag atoms and was deposited on the LiF substrate held at room temperature. One can see the distinct peak at 425 nm that corresponds the Ag NP formation. The flattened right wing of the peak means that formation of NP layer is accompanied by conservation of 'islands' of the Ag film that results from the deposition. This suggestion is supported with the TEM image that is presented in Fig. 5. One can see that the film besides NP with the sizes being of the order of 10 nm or less includes also the islands with the sizes at the range of 50–100 nm. The following annealing at 950 K results in shift the peak to 395 nm and appearance of the additional peak at 460 nm. As theory of light scattering by NP says, that effect is, possibly, due to deformation of the NP resulting from the heating, so that its become ellipsoidal from the spherical one [6]. Fig. 4 also demonstrates effect of the substrate heating during the deposition process. As curve 3 shows, the heating results in more symmetric shape of the plasmon peak that means the less dispersion in sizes of NP and diminishing of the large metallic islands.

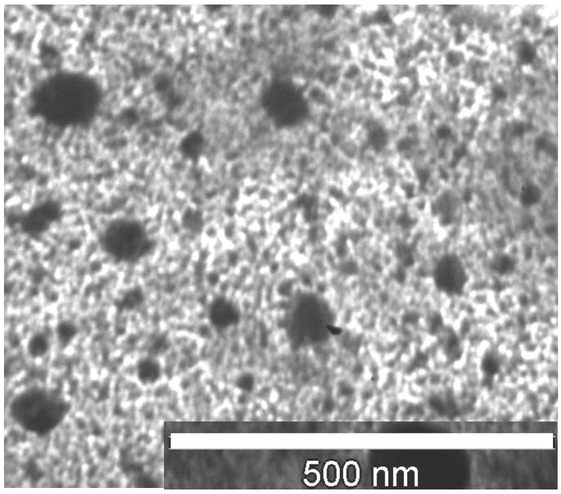

Fig. 5. TEM micrograph of the LiF crystal with deposited film of LiF containing Ag NP

Also, the same technique was applied with the NaCl substrate. The result presented in Fig. 6 shows that the plasmon peak here is a distinct and symmetric form. Also one can see that as the flow of Ag atoms increases (approximately two times) that amplitude of the absorption peak and hence, the density of NP, also increases two times.

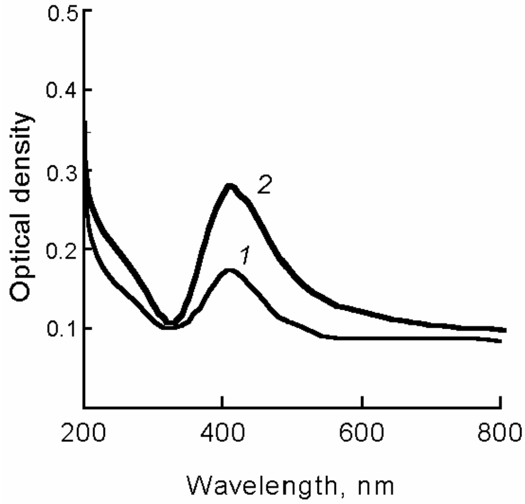

Fig. 6. Absorption spectra of NaCl substrate with deposited LiF and Ag films at room temperature with a given value of deposited flow of Ag atoms (1) and with the twice value of the flow (2)

To establish dependence of features of the film deposited on structure of the substrate (crystal or amorphous type) we applied the technique described about for creating of the Ag NP layers on a silica glass substrate. The results are presented in Fig. 7 and they show that as opposed to the crystal substrate in the given case there was not formed the plasmon resonance peak at the absorption curve immediately after the deposition on a substrate that was hold at room temperature, but just after the additional heating. Nevertheless, when the substrate was heated in the process of deposition, the NP layer was created.

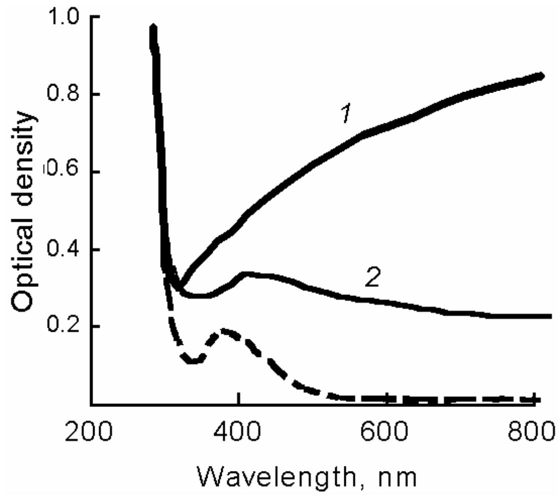

Fig. 7. Absorption spectra of SiO_2 substrate with deposited LiF and Ag films at room temperature (1), after the subsequent annealing at 950 K (2) and with heating of the substrate in the process of deposition up to 650 K (3)

Finally, we deposited on a surface of silica substrate by the thermal evaporation technique the film containing simultaneously LiF and Au. It was shown that there were no peculiarities at the absorption curve just after deposition. But after annealing of the sample, the distinct plasmon resonance peak, appears at the absorption curve. This means that Au NP are formed as a result of the annealing.

3. Discussion and conclusion

Results of the experiments presented here demonstrate, in principal, the possibility of fabricating of the NP layers in LiF host. Ion implantation of the high energy Cu ions is a way for creating of these layers in bulk sample. The process includes also a stage of high temperature annealing.

Nevertheless, the more promising technique for creating of thin films of LiF host, containing the metallic NP is a deposition of the film by means of the vacuum evaporation. It was established that:

1. These films could be fabricated for a series of metal: Cu, Ag and Au.
2. The most convenient matter for creating of the films is Ag, because of it is of low cost and relative simplicity of the technique of creating.
3. It more difficult to create the layers with Cu NP in LiF host. The process requires the additional laser annealing there with the NP layers are produced just on the LiF substrate while it was not found on the amorphous (silica glass) substrate. This result differs from one of the authors of paper [4], where Cu NP were produced on Al_2O_3 host by the alternately laser ablation of these samples. The difference is, possibly, due to the different structure of LiF and Al_2O_3 lattices, but this matter requires the additional studies.

It was shown that type of the substrate effects substantially on process of creating of the NP layer, in particular, the layer on amorphous substrate (silica glass) are produced just after high temperature annealing, while on substrate of the crystal type (LiF or NaCl) it is produced immediately in the process of the film deposition.

It was established also that heating of the substrate in the process of deposition improves structure of the NP layer because of decrease in dispersion of the NP sizes. Possibly, it results from preventing of formation of large metallic 'islands' in the process of deposition.

Finally, it was found that it is easy to control the density of NP layer by varying of intensity of the metallic atoms flow. The last is also easy to control by power of the evaporator.

So, the paper demonstrates that there are simple and highly efficient techniques for fabrication of the NP layers in LiF host. Hence, the matter is rather promising one for optoelectronics applications.

References

[1] P. Chacraborty, Journ. Materials Sci. 33 (1998) 2235.

[2] A.L. Stepanov, R.A. Ganeev, A.I. Ryasnyansky, N. Usmanov, Nucl. Instr. Methods Phys. Res. B 206 (2003) 624.

[3] S.R. Friderg, P.E. Smith, IEEE J. Quantum Electron. QE-23 (1987) 2089.

[4] R. Serna, T. Missana, J.M. Ballesteros et al, Appl. Physics. A. 66 (1998) 43.

[5] R.M. Montereali, Material Sci. Forum 239–241 (1947) 711.

[6] C.F. Bohren and D.R. Huffman, *Absorption and scattering of light by small particles.* Wiley-Interscience Publ. N-Y (1986) 660.