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in Metal Cluster Composites Produced by Ion Beam Implantation**

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MECHANISMS OF FORMATION OF NONLINEAR OPTICAL LIGHT GUIDE STRUCTURES IN METAL CLUSTER COMPOSITES PRODUCED BY ION BEAM IMPLANTATION

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ABSTRACT

We report the results of characterization of linear and nonlinear optical properties of a light guide structure produced by MeV Ag ion implantation of LiNbO₃ crystal (z-cut) in relation to the mechanisms of formation.

INTRODUCTION

Ion implantation has been shown to produce a high density of metal colloids in glasses and crystalline materials. The high-precipitate volume fraction and small size of metal nanoclusters formed leads to values for the third-order susceptibility much greater than those for metal doped solids [1]. This has stimulated interest in use of ion implantation to make nonlinear optical materials. On the other side, LiNbO₃ has proved to be a good material for optical waveguides produced by MeV ion implantation [2]. Light confinement in these waveguides is produced by refractive index step difference between the implanted region and the bulk material. Implantation of LiNbO₃ with MeV metal ions can therefore result into nonlinear optical waveguide structures with great potential in a variety of device applications. We describe linear and nonlinear optical properties of a waveguide structure in LiNbO₃-based composite material produced by silver ion implantation in connection with mechanisms of its formation.

EXPERIMENT

The sample was made of 1-mm thick LiNbO₃ (z-cut) implanted with 1.5-MeV Ag ions to a dose of $2.0 \times 10^{16} \text{ cm}^{-2}$. Implantation was done at room temperature. Fig.1 presents the distribution of the implanted silver along the depth of the sample calculated by the Monte-Carlo simulation program TRIM96 [3]. The position of the peak of the distribution defines the depth of the implanted layer at 0.41 μm and FWHM of the distribution gives an estimate of 0.24 μm for the thickness of the layer.

Light transmission along the implanted layer (treated at 500°C) was studied using the prism coupling technique [4]. The technique is based on light tunneling from a prism with high refractive index (rutile, index is 2.8643) to the implanted light guiding layer through a small air gap (Fig. 2). The phase matching condition for light coupling is

$$n_p \sin \theta_m = N_m, \quad (1)$$

where n_p is the prism refractive index; θ_m is the angle of incidence; N_m is the propagation

Fig. 1. The concentration of the implanted Ag ions versus the depth of the LiNbO₃ sample calculated by the Monte-Carlo method. The energy of the Ag ions is 1.5 MeV, the fluence is $2.0 \times 10^{16} \text{ cm}^{-2}$.

Fig. 2. Scheme of the prism coupling experiment.

number for the m -th order mode in the waveguide. Energy channeling to a guided mode leads to the drop of the intensity of the light outcoupled from the prism which is monitored with a photo detector. Measuring the intensity dependence on the incidence angle, it is possible to obtain θ_m and then to calculate N_m . The implanted layer refractive index n_f and thickness h_f can be found from the solution of the system of dispersion equations at least for two modes. For s -polarization (TE - modes) these equations can be written as:

$$\frac{2\pi h_f}{\lambda} (n_f^2 - N_m^2)^{1/2} - \tan^{-1} \left(\frac{N_m^2 - n_c^2}{n_f^2 - N_m^2} \right)^{1/2} - \tan^{-1} \left(\frac{N_m^2 - n_s^2}{n_f^2 - N_m^2} \right)^{1/2} - m\pi = 0 \quad (2)$$

where λ is the light wavelength, n_s and n_c are the substrate and the cladding (air) refractive indices respectively. Similar equations can be formulated also for TM-modes. The ~~prism~~ coupler Metricon 2010 was used in our measurements. Fig. 3 shows experimental results which

Fig. 3. Intensity of the light outcoupled from the coupling prism versus the propagation number of modes injected into the light guiding implanted layer. Curve 1 corresponds to virgin LiNbO₃ crystal, where point (a) marks the threshold of total internal reflection which determines the refractive index at 2.2867. Curves 2 and 3 correspond to two different locations in the implanted crystal. Points (b) and (c) mark the dips related to the zeroth order and the first order propagating modes in the first location with propagation numbers $N_0 = 2.3652$ and $N_1 = 2.3003$ respectively. Points (d) and (e) mark the modes $N_0 = 2.3938$ and $N_1 = 2.3029$ for the second location. The average refractive index and thickness of the implanted layer in the first location is calculated to be 2.3887 and 0.748 μm respectively while the same parameters for the second location are 2.4254 and 0.6228 μm . All the measurements are taken at 633 nm.

indicate that the light guiding layer with the index greater than that of the substrate (2.2867) is spread along the depth up to 0.75 μm and therefore goes beyond the limits of the 0.24- μm -wide nuclear stopping region where the implanted Ag ions were originally located (Fig. 1). This is indicative for silver ion diffusion out of the original location during heat treatment accompanied by the increase of the refractive index of the crystal.

The linear optical absorption spectra of the implanted sample are shown in Fig. 4. The spectrum right after implantation exhibits the prominent single surface plasmon peak near 430 nm which is the signature of nanometer size clusters of metallic silver formed in the host. The radius of the clusters can be estimated by using the relation $R = V_f / \Delta\omega_{1/2}$, where V_f and

Fig. 4. Optical absorption spectra of the Ag implanted LiNbO₃ sample.

$\Delta\omega_{1/2}$ are Fermi's velocity of silver (1.39×10^8 cm/s [5]) and the half width of the absorption peak, respectively [6]. In our case $R \approx 1.1$ nm. Heat treatment after the implantation at 500°C for 1 hour lead to the red shift of the absorption peak to 550 nm (Fig. 4) without significant change of $\Delta\omega_{1/2}$ (and, correspondingly, of the radius R). Shang, et. al. proposed to explain this effect as a result of the volume fraction increase due to Ag precipitation near the surface [7]. Another likely contributing factor is that the heat treatment is working to remove implantation damage [8]. LiNbO₃ implanted with 190 KeV Ag at 1×10^{17} -cm⁻² fluence has been shown to undergo full epitaxial regrowth after heat treatment at 400°C but an anneal of 800°C for 1 h is necessary for full removal of the implantation damage [9]. At the end of range ions implanted into LiNbO₃ have been shown [2, 8] to decrease the index of refraction by over 5 percent. Reducing the host index by 5 to 10 percent would result in a shift of the expected absorption peak for Ag from 520 nm to approximately 480 nm.

The nonlinear refractive index of the sample after heat treatment was characterized using the Z-scan technique [10]. The laser source was a tunable dye laser (with laser dye Rhodamine 6G) pumped by a frequency-doubled mode-locked Nd:YAG laser (76-MHz pulse repetition rate). The tuning range was 555 to 600 nm. The average power of the laser radiation applied to the sample varied from 100 to 350 mW. The laser pulse duration (FWHM) was 4.5 ± 0.8 ps. The beam diameter was 3.0 mm. Estimated laser peak power density in the sample placed near the focus of the lens (125-mm focal distance) in the Z-scan experiment was 0.025 to 0.088 GW/cm². The closed aperture Z-scan demonstrated typical behavior of a nonlinear refractive medium with positive nonlinear refractive index [10]. The open aperture Z-scan showed saturation of nonlinear absorption of the sample (optical transmission peak) at the distance $z = 0$ from the focus. The measured nonlinear refractive index of the sample is plotted against the wavelength in Fig.5 (circles). It repeats the linear absorption spectrum fraction of which is depicted by a solid line 1. This is a typical picture when the surface plasmon resonance contributes to the intrinsic nonlinear

response of nanoclusters originated from interband, intraband, and hot electron photo excited transitions [11].

Fig. 5. Nonlinear refractive index of the Ag:LiNbO₃ sample (circles) and Cu:silica reference sample (squares) versus wavelength. Solid lines 1 and 2 represent optical absorption spectra of Ag:LiNbO₃ and Cu:silica respectively.

The nonlinear refractive index of the silver implanted LiNbO₃ sample was compared against Cu-implanted silica sample as a reference. The sample was prepared at the conditions similar to those in Ref. 1. The energy of the Cu ions and the fluence were 2.0 MeV and $1.0 \times 10^{17} \text{ cm}^{-2}$ respectively. Implantation was performed at room temperature. Heat treatment was done at 1000°C in the air for 1 hour. The nonlinear refractive index of the reference sample was characterized with the Z-scan technique at the same conditions as the Ag-implanted LiNbO₃ sample. It is plotted together with the absorption spectrum in Fig. 5 (squares and solid line 2 respectively). The nonlinear refractive index of the reference also repeats the shape of the Cu surface plasmon resonance peak in full agreement with Ref. 1. The nonlinear index of the Ag-implanted sample is approximately two times greater than the index of the reference. The optical density is greater as well. At the same time, the fluence used to implant the silver sample is 5 times less than the fluence used for the reference. We believe that this enhancement of the nonlinear refractive index and the optical density can be attributed to the high volumetric density of Ag nanoclusters in the ion-implanted layer remaining even after intensive heat treatment and possible recrystallization of the nuclear damage region in the LiNbO₃ matrix. The absolute values of the nonlinear index of both samples ($(8.21 \pm 0.20) \times 10^{-9} \text{ cm}^2/\text{W} \leq n_2 \leq (12.82 \pm 0.52) \times 10^{-9} \text{ cm}^2/\text{W}$ and $(4.02 \pm 0.30) \times 10^{-9} \text{ cm}^2/\text{W} \leq n_2 \leq (6.82 \pm 0.28) \times 10^{-9} \text{ cm}^2/\text{W}$ for silver and copper respectively) are at least one order of magnitude greater than those for similar materials reported in the literature [1] possibly due to the cumulative thermal self-focusing effect at relatively high pulse repetition rate (76 MHz versus 3.8 MHz in Ref. 1).

CONCLUSIONS

We have fabricated a planar nonlinear optical waveguide using implantation Ag ions in LiNbO_3 . The implanted composite light guiding layer exhibits a Kerr-type nonlinear susceptibility. The nonlinear refractive index for the $\text{Ag}:\text{LiNbO}_3$ composite compares well to other metal colloid composites prepared by ion implantation. It is particularly twice as high as the index for $\text{Cu}:\text{silica}$ composite.

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