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STUDY OF THE EFFECTS OF MEV AG, CU, AU AND SN IMPLANTATION ON THE OPTICAL PROPERTIES OF LINBO$_3$.

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ABSTRACT

We present the results of characterization of linear absorption and nonlinear refractive index of Au, Ag, Cu and Sn ion implantation into LiNbO$_3$. Ag was implanted at 1.5 MeV to fluences of 2 to 17 x 10^{16}/cm^2 at room temperature. Au and Cu were implanted to fluences of 5 to 20 x 10^{16}/cm^2 at an energy of 2 0 MeV Sn was implanted to a fluence of 1.6 x 10^{17}/cm^2 at 160 kV Optical absorption spectrometry indicated an absorption peak for the Au implanted samples after heat treatment at 1000°C at ~620 nm The Ag implanted samples' absorption peaks shifted from ~450 nm before heat treatment to 550 nm after 500°C for 1h Heat treatment at 800°C returned the Ag implanted crystals to a clear state. Cu nanocluster absorption peaks disappears at 500°C No Sn clusters were observed by opotical absorption or XRD The size of the Ag and Au clusters as a function of heat treatment were determined from the absorption peaks The Ag clusters did not change appreciably in size with heat treatment The Au clusters increased from 3 to 9 nm diameter upon heat treatment at 1000°C. TEM analysis performed on a Au implanted crystal indicated the formation of Au nanocrystals with facets normal to the c-axis. Measurements of the nonlinear refractive indices were carried out using the Z-scan method with a tunable dye laser pumped by a frequency doubled mode-locked Nd·YAG laser. The dye laser had a 4 5 ps pulse duration time and 76 MHz pulse repetition rate (575 nm)

INTRODUCTION

Introducing metal colloids into a glass or other transparent material matrix has been used to change their color for decoration and more recently for fabricating optical filters and other fast optical devices In recent years, ion implantation has been used to introduce nonlinear optical properties [1-10] in layers near the surface of optical materials. To form nanoclusters after ion implantation the material may need to be thermally annealed or laser annealed [11]. An attractive feature of ion implantation is that the metal colloids can be placed in a well defined space near the surface and that by using focused ion beams, point quantum confinement may be accomplished

It has long been known that small metallic particles or colloids embedded in dielectrics produce colors associated with optical absorption at the surface plasmon resonance frequency [12,13] For a collection of spherical clusters with diameters much smaller than the wavelength of the incident light the absorption coefficient (cm^{-1}) of the composite can be calculated from [12]

$$\alpha = \frac{18\pi Q n_o^3}{\lambda}\,\frac{\varepsilon_2}{(\varepsilon_1+2n_o^2)^2+\varepsilon_2^2}\,, \qquad (1)$$

where Q is the volume fraction occupied by the metallic particles, n_o is the refractive index of the host medium, and ε_1 and ε_2 are the real and imaginary parts of the frequency-dependent dielectric constant of the bulk metal Equation 1 is maximized at the surface plasmon resonance frequency (ω_p) when $\varepsilon_1 = -2n^2$ if ε_2 is well behaved in this region.

Using tabulated values [14,15] of ε_1 for Cu, Sn, Ag and Au as a function of the photon wavelength, and using $n_0 = 2.2$, Equation 1 predicts that the wavelengths for the surface plasmon resonance frequencies should be about 520 nm for Ag and near 620 nm for Cu and Au and at ~350 nm for Sn

If the metal spheres are small compared with the wavelength of the incident light, their radius estimated from the optical absorption spectrum is $r = A_m v_f / \Delta\omega_{1/2}$ [1,16], where v_f is the Fermi velocity of the metal and $\Delta\omega_{1/2}$ is the full width at half maximum of the absorption band and A_m is a constant that varies for different metals. For Ag we have taken $A_m = 1$ and for Au we have used $A_m = 1.5$ [16].

EXPERIMENTAL PROCEDURES

Single crystal, 1mm thick $LiNbO_3$ wafers were obtained from Crystal Technology Inc., (Palo Alto, CA). We used 1.5 MeV Ag and 2.0 MeV Au and Cu with beam currents of 2 to 3 $\mu A/cm^2$ and the samples were maintained at room temperature Ag was implanted to fluences ranging from $2 \times 10^{16}/cm^2$ to $1.7 \times 10^{17}/cm^2$ while Au and Cu were implanted from $5 \times 10^{16}/cm^2$ to $2\ 0 \times 10^{17}/cm^2$. Sn was implanted at 160 keV to fluences up to $1.6 \times 10^{17}/cm^2$.

Optical absorption photospectrometry was done soon after implantation and immediately after heat treatment using a Cary model 3e spectrophotometer. Heat treatments were done in air at temperatures of 300°C to 1000°C for times from 0.5 to 14 hours. Average radii were measured from these spectra.

To investigate the effects of the implantation on the third order nonlinear optical coefficient, n_2, we used the z-scan technique [17, 18] employing a tunable pulsed dye laser pumped by a frequency doubled mode locked Nd.YAG laser run to give a wavelength of 575 nm and a pulse width of 4.5 ps at a repetition rate of 76 MHz. The average power was 70 to 350 mW, giving a power density applied to the sample in the range of 0.02 to 0.1 GW/cm^2.

RESULTS AND DISCUSSION.

The damage and modification of the optical properties are directly proportional to the atomic number and fluence of the bombarding ion [19, 20]. The $LiNbO_3$ samples implanted with Ag at fluences of less than $8 \times 10^{16}/cm^2$ were yellow/brown immediately after implantation but turned blue after 1 hr heat treatment at 500°C, whereas a sample implanted at $1.7 \times 10^{17}/cm^2$ remained almost black The gold samples were much darker and changed to a dark purple after heat treatment at temperatures above 700°C. The lower fluence Cu samples were red and the Sn implanted samples were light to dark gray The surfaces of all of the Ag implanted samples were also noticeably textured by the implantation; the higher fluence samples even functioned as poor quality diffraction gratings The Au implanted $LiNbO_3$ also showed some surface texturing but not to the same extent as the Ag samples The texturing remained in the 2×10^{17} Au/cm^2 sample after 10 hours at 1000°C.

The absorption spectra for Cu and Sn implanted $LiNbO_3$ are shown in Figure 1. The peak due to Cu clusters disappears after 500°C heat treatment for one hour. After 400°C for 1 h in air the Sn spectrum is the same as a virgin crystal. RBS analysis of the Sn implanted sample shown no significant diffusion at these low temperatures XRD analysis did not indicate the presence of Sn crystals

The absorption spectra from a Ag implanted sample at a fluence of $5 \times 10^{16}/cm^2$ is shown in Figure 2 The absorption peaks decreased in height and shifted to longer wavelengths, with the

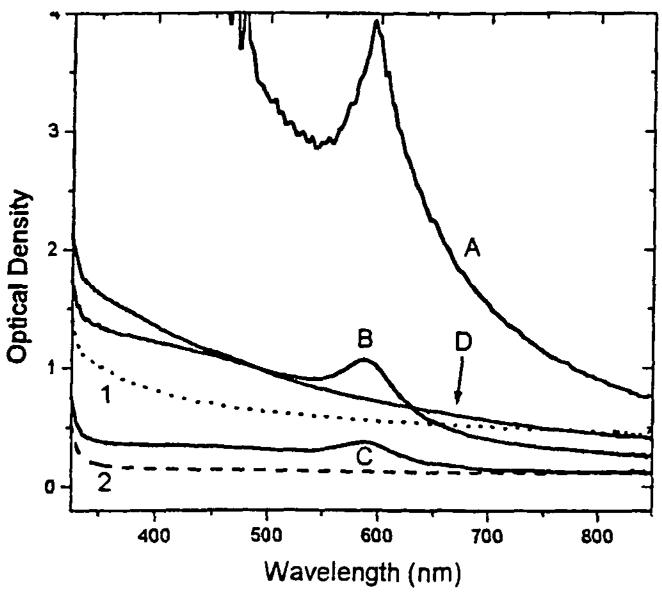

Figure 1 Optical absorption spectra from 2.0 Mev Cu, A) 2 x 10^{17}/cm^2, B) 5 x 10^{17}/cm^2, C) 2 x 10^{16}/cm^2, D) 2 x 10^{17}/cm^2 heated to 500°C and from 160 keV Sn, 1.6 x 10^{17}/cm^2. 1) As Implanted, 2) 400°C, 1 hr

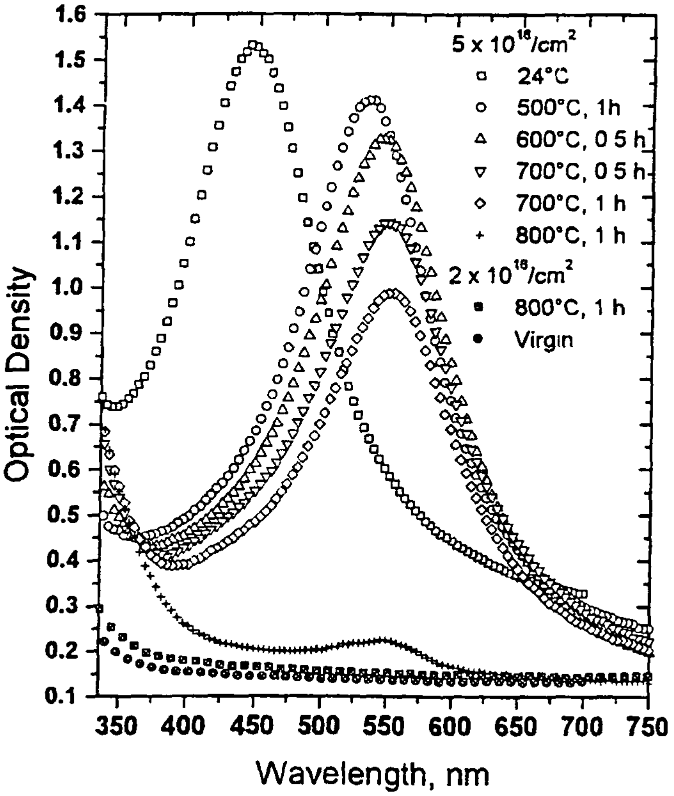

Figure 2 Optical absortion spectra of 1.5 MeV Ag implanted $LiNbO_3$ after various heat treatments The calculated radius increased from 1.1 nm at 24°C to 1.6 nm at 700°C

greatest shift occuring during the initial 500°C heat treatment. After 800°C heat treatment the 2 x 10^{16} Ag/cm^2 implanted sample's absorption spectrum was very close to that of a virgin crystal. The change in height of the spectra may be due to a reduction in the number of Ag clusters as Ag diffuses atomistically into the substrate The wavelengths of the Ag absorption peaks and the radii of the clusters are shown in Table 1 for each fluence and heat treatment. The radii are initially the same for all three fluences, then increase from 30 to 60 percent after heat treatment. Another increase in radius is seen just before the aborption spectra disappear.

In the as-implanted state the absorption peaks were at a wavelength shorter than that expected from theory (~520 nm). This blue shift may be caused primarily by end of range damage, which has been shown [23] to decrease the index of refraction by over 5 percent. From Equation 1, changing the host index by 5 to 10 percent would result in a shift of the expected absorption peak of 20 to 40 nm Heat treatment works to remove much of this implantation damage and restores the refractive index $LiNbO_3$ implanted with Ag 1 x 10^{17}/cm^2 at 190 keV has been shown to undergo full epitaxial regrowth after heat treatment at 400°C [24], but an anneal of 800°C for 1 h is necessary for full removal of the implantation damage. Prism coupling results indicate that for a Ag fluence of 2 x 10^{16}/cm^2 and heat treatment at 500°C the refractive index is increased by over 5 percent, sufficient to move the plasmon resonance peak position from the expected 520 nm to the experimentally observed 542 nm

The absorption spectra for a 5 x 10^{16} Au/cm^2 implanted sample is shown in Figure 3 No absorption peak is visible prior to heat treatment There was little

Fluence, ions/cm^2	Temp °C	Optical Density at 575 nm	Nonlinear index, n_2, 10^{-8} cm^2/W
2×10^{16}	500	0.39	0.96
2×10^{16}	800	0.15	0.35
5×10^{16}	500	1.0	2.90
5×10^{16}	800	0.2	0.38
17×10^{16}	500	1.87	6.81

Table 1. Nonlinear index of refraction as measure by z-scan method for varoius fluences of 1.5 MeV Ag in $LiNbO_3$

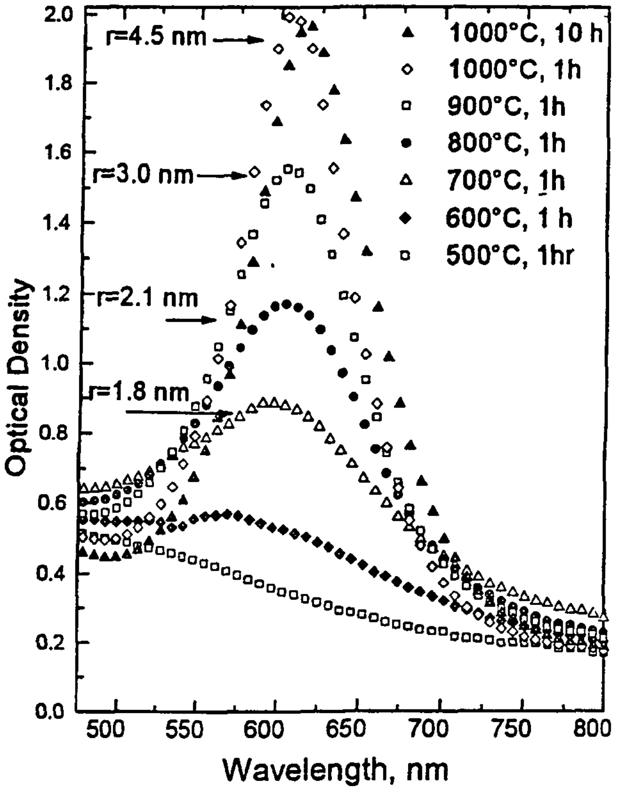

Figure 3. Optical absorption spectra from 5×10^{16} Au/cm^2 at 2.0 MeV into z-cut $LiNbO_3$. The radius calculated from each spectrum is indicated.

change in the spectrum from the 5×10^{16} Au/cm^2 sample after 0.5 and 14 h at 500°C but for higher fluence samples (9×10^{16}/cm^2 and 2.0×10^{17}/cm^2) the 500°C for 0.5 h heat treatment resulted in an absorption spectrum typical of Au. At 700°C and above the peak positions shift to longer wavelengths and increase dramatically in height. Shang, et. al. [21] observed a decrease in peak height at 600°C for Au implanted into $LiNbO_3$ at 23 keV. In their case heat treatment at 600°C for up to 8 hr resulted in a blue shift and a large decrease in the peak height with the expectation that the absorption spectrum would disappear with further heat treatment, as is the case for Ag in $LiNbO_3$. For the two higher fluence samples mentioned above we observed a slight decrease in peak height at 650°C. Analysis of the absorption spectra indicates that the clusters begin to grow significantly larger at 800 to 900°C and appear to reach a maximum size at 1000°C.

TEM analysis of the 5×10^{16}/cm^2 Au implanted sample after heat treatment at 1000°C for 10 h shows (Figure 4a) that the Au clusters are in a ~380 nm thick band 100 nm below the surface. Figure 4b shows the faceting of the Au crystals normal to the c-axis. Very few of the crystals are smaller than 9 nm in diamter, many are approximately 9 to 11 nm diameter and they range in size up to 40 nm in diameter. This agrees reasonably well with the cluster sizes determined from the absorption spectra since in that method the width of the resonance is inversely proportional to the cluster size. The absorption spectrum from mixture of large and small clusters should differ little from the spectrum of small clusters only.

The results of the z-scan for the Ag implanted samples are shown in Table 1. The thickness of the colloidal layer used in the calculation of n_2 (240 nm for 1.5 Mev Ag) was estimated using SRIM96 [25]. For both Ag and Au the magnitude of the nonlinear index increased with increasing fluence and optical density. For the low fluence (2×10^{16}/cm^2) Ag implanted sample yet a significant postive nonlinear index is seen. This is not the intrinsic nonlinear index of $LiNbO_3$, which is negative, as was confirmed by a z-scan of an unimplanted area. The nonlinear indices reported here are at least one order of magnitude greater than those reported for other silver clusters in the literature [26]. This indicates the presence of the cumulative thermal self-focussing effect which can still occur for the short pulses used in this work due to the relatively high pulse repetition rate (76 MHz versus 3.8 MHz in Ref. [26]). For the Au implanted $LiNbO_3$ a positive n_2 was seen prior to heat treatment as well as after cluster formation was observed.

CONCLUSIONS

The Cu, Sn, Ag and Au implanted $LiNbO_3$ reacted differently to heat treatment as observed in the optical absorption spectra. Silver clusters disappeared at a heat treatment temperature of 800°C, Cu clusters dissappeared at 500°C and Sn clusters were not observed. Heat treatment of the Au implanted samples was necessary to see the expected absorption spectrum from Au clusters. Au clusters grew at heat treatment temperatures up to 1000°C and formed crystals with facets normal to the c-axis. For Ag implanted $LiNbO_3$ the Ag absorption peak appears without heat treatment (Figure 2) and disappears upon heat treatment at 800°C but enhancement of the nonlinear index remains after reduction of the absorption.

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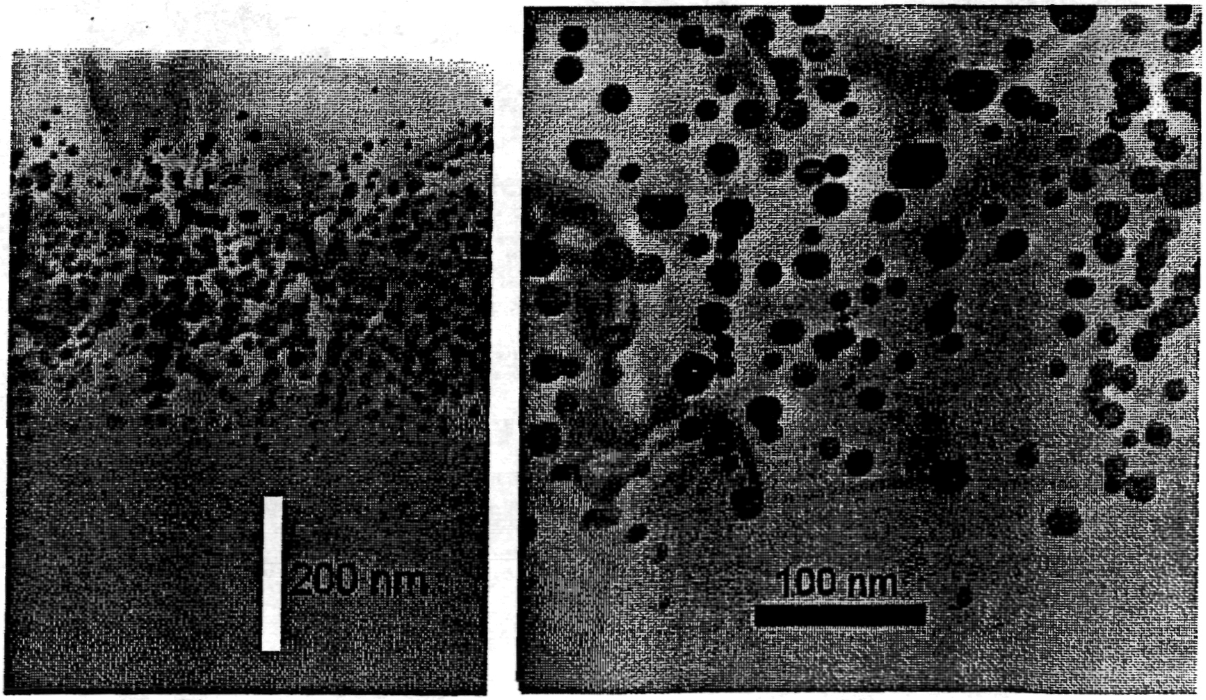

(a) (b)

Figure 4. TEM micrographs of Au clusters in z-cut $LiNbO_3$. The Au fluence was $5 \times 10^{16}/cm^2$, heat treatment was 1000°C for 10 hr. The facets in the Au nanocrystals are normal to the c-axis.

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