Optical characteristics of LiNbO$_3$ implanted with Au$^+$ ions

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Optical characteristics of LiNbO$_3$ implanted with Au$^+$ ions at energy of 23 keV were studied. The color of the surface of the LiNbO$_3$ was changed to blue-green and a large absorption peak around 620 nm was observed. The surface morphology was also found to change with time. Metallic Au dots were observed on the surface after implantation and grew from day to day when the samples were held at room temperature. The absorption peak produced by Au$^+$ implantation was relatively stable toward thermal treatment compared to that of Cu$^+$ implantation into LiNbO$_3$. But as the sample was heated at temperatures higher than about 500 °C, this peak gradually decreased and finally disappeared. These characteristics were explained fairly well by the behavior of Au colloids formed in the surface layer of LiNbO$_3$. © *1996 American Institute of Physics.*
[S0021-8979(96)05012-8]

INTRODUCTION

In recent years, much work has been done on implanting ions into optical materials. The clusters of ions formed in the materials exhibit large third order optical nonlinearities and fast time response. These characteristics, which will be utilized for an optical switch in the future, are often attributed to colloids of the metal formed in the optical materials.[1–7]

The formation of metallic colloids in colorless and transparent materials can also give large absorption in the visible range. The peak position of the colloid band depends on the electron density of the metal colloids, the dielectric parameters of the host materials and the size of colloids. The wavelength for maximum absorption caused by colloids can be estimated by Doyle's equation.[8] Usually it gives a good explanation for the experimental results, especially in the case in which the colloids are so small that the volume fraction occupied by the colloids can be neglected. For higher doses, the effect of the volume fraction should be taken into account, as reported by Doremus.[9]

In the case of LiNbO$_3$, it shows interesting features, such as a large absorption peak in the visible region, bright beautiful color and formation of metallic dots on the surface when implanted with Au$^+$, Ag$^+$, or Cu$^+$ ions.[10,11]

EXPERIMENT

Metal ions were produced in the ion source using a radio-frequency discharge combined with direct-current sputtering and Au$^+$ ions were extracted from a small hole (0.1 mm diam) drilled at the center of the Au disk (30 mm diam) put on the cathode. The ions were accelerated up to 23 keV and then implanted into LiNbO$_3$ wafers (X-cut, 0.5 mm in thickness). The implantation was done at room temperature with the beam current density about 0.4 μA/cm^2. The dose was calculated by integrating the ion-beam-induced current flowing between the sample and the ground during implantation. The dose varied from 1×10^{16} to 4×10^{16} ions/cm^2.

The absorption spectrum was measured in the visible range. The light from a halogen lamp was irradiated on the sample and the transmitted light was directed to the spectrometer by means of an optical fiber. Heat treatment of the samples was done in an electrical furnace in air.

The pictures of the surface of LiNbO$_3$ were taken by differential interference microscopy. Dark field pictures were taken in order to emphasize the surface morphological changes.

EXPERIMENTAL RESULTS

After implantation, the surface of LiNbO$_3$ was changed to bright blue-green and its color grew richer with increasing dose.

Figure 1 shows the absorption spectra of LiNbO$_3$ implanted with Au$^+$ ions. Around 620 nm, a broad absorption peak is observed. As the dose increases, the absorption peak becomes sharper and its position shifts toward longer wavelengths. The intensity of maximum absorption increases with the dose. The peak shifts toward longer wavelengths by about 30 nm as the dose increases from 1×10^{16} to 4×10^{16} ions/cm^2.

Figure 2 shows the change of the surface state of the sample implanted with 1×10^{16} Au$^+$ ions/cm^2 and held at room temperature. Just after implantation, no fine structure is apparent on the surface. After one day, a fine structure appears and small particles can be observed as shown in Fig. 2(a). These white dots may be metallic Au precipitated on the surface. The number and the size of the particles grow with time as shown in Figs. 2(b)–2(d). Large dots may be formed by the aggregation of adjoining small dots.

While the blue-green color produced by Cu$^+$ ion implantation into LiNbO$_3$ is not stable if the samples are held at a temperature higher than room temperature, the color produced by Au$^+$ ion implantation is found to be stable up to relatively high temperatures. Annealing the samples at a temperature lower than 400 °C affects the absorption little. But heating at a temperature higher than 400 °C changes the absorption spectrum. As the heating temperature is raised to 500 °C, the change of the absorption spectrum is accelerated. Figure 3 shows a series of absorption spectra of LiNbO$_3$ implanted with 4×10^{16} Au$^+$ ions/cm^2 and annealed at 500 °C. Up to 4 h of total annealing time, the absorption
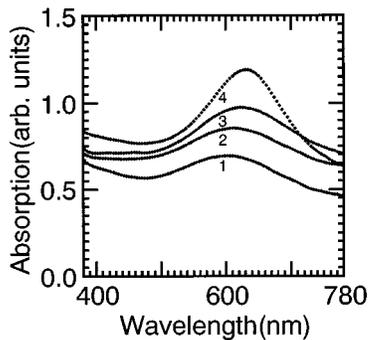
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FIG. 1. Absorption spectra of LiNbO$_3$ implanted with Au$^+$ ions at an energy of 23 keV with 1×10^{16}, 2×10^{16}, 3×10^{16}, and 4×10^{16} ions/cm^2 for 1–4, respectively.

FIG. 3. Change of the absorption spectra of LiNbO$_3$ implanted with 4×10^{16} Au$^+$ ions/cm^2. 1: the absorption before annealing, 2–6: the absorption after annealing at a temperature of 500 °C for 0.5, 4, 6, 8, and 10 h, respectively.

increases and its peak position shifts toward longer wavelengths. As the sample is annealed for times longer than 6 h, the absorption begins to decrease and the peak shifts toward shorter wavelengths.

Figure 4 shows a series of absorption spectra of the sample annealed at 600 °C. At this temperature the absorption decreases from the beginning of the anneal and the peak shifts toward shorter wavelengths. After annealing for 8 h, the peak position is shifted to about 590 nm, shorter by about 40 nm compared to that of as-implanted sample.
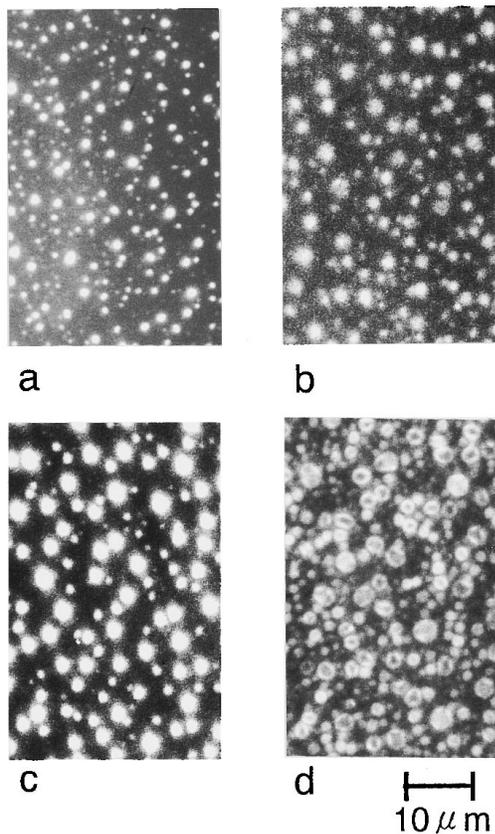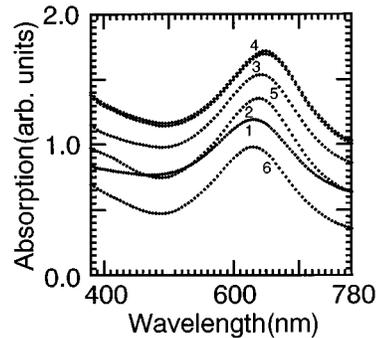
DISCUSSION

In our present work, all the absorption spectra of as-implanted samples have a broad peak around 620 nm, and the peak shifts toward longer wavelengths by about 30 nm as the dose varies from 1×10^{16} to 4×10^{16} ions/cm^2 as shown in Fig. 1.

According to Doyle's work, metal colloids which formed in alkali halide crystals produced a well defined and regular absorption band. The wavelength of the peak of the absorption band was predicted as follows:[8]

$$\lambda_0 = \frac{2\pi c}{\omega_p}(1 + 2n_0^2)^{1/2}, \qquad (1)$$

where ω_p is the plasma frequency of the metal, c is the velocity of light, and n_0 is the refractive index of the matrix. Applying this formula to our work, the absorption peak should appear at 460 nm, which is much shorter than our experimental value. To explain the peak position of the absorption of Au$^+$ implanted LiNbO$_3$ and the phenomenon of the peak shift toward longer wavelengths as the dose increases, the effect of the volume fraction occupied by the colloids must be taken into account.

Taking the volume fraction of colloids into account, the peak position of the absorption is modified as follows:[9]
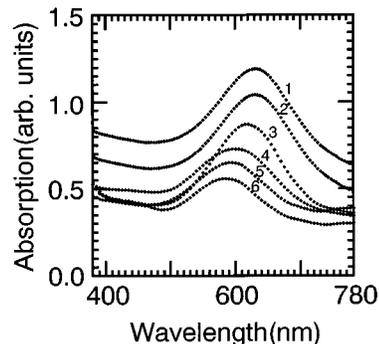

FIG. 2. Dynamical change of the surface morphology of LiNbO$_3$ implanted with 1×10^{16} Au$^+$ ions/cm^2 after implantation for (a) 1, (b) 3, (c) 5, and (d) 7 days.

FIG. 4. Change of the absorption spectra of LiNbO$_3$ implanted with 4×10^{16} Au$^+$ ions/cm^2. 1: the absorption before annealing, 2–6: the absorption after annealing at a temperature of 600 °C for 0.5, 1, 2, 4, and 8 h, respectively.

TABLE I. The wavelength of the absorption peak for experiment and Eq. (2), and the calculated radii of colloids for $LiNbO_3$ implanted with Au^+ ions.

Dose($\times 10^{-16}$) (ions/cm^2)	λ_{exp} (nm)	λ_D (nm)	$2R$ (nm)
1	603	492	3.0
2	613	530	3.4
3	626	577	3.8
4	632	633	4.2

$$\lambda_D = \frac{2\pi c}{\omega_p} \left(1 + \frac{2+Q}{1-Q} n_0^2 \right)^{1/2}, \qquad (2)$$

where Q is the volume fraction occupied by the colloids. The other parameters are the same as Doyle's.

To estimate λ_D using Eq. (2), the value of Q must be determined. Here we roughly assume that all Au^+ ions implanted into $LiNbO_3$ were formed into the colloids and distributed uniformly in the ion range and that the radius R of the colloids is much less than the mean free path of the free electrons in the metal. Then the radius of the colloids can be estimated by using the relation: $R = V_f / \Delta\omega_{1/2}$, where V_f and $\Delta\omega_{1/2}$ are Fermi's velocity of the metal and the half width of the absorption peak, respectively.[12]

Table I lists the wavelength for the maximum absorption of the experimental results, the values estimated by Eq. (2) and the average diameter of Au colloids for the spectra of Fig. 1. For the sample implanted with 4×10^{16} Au^+ ions/cm^2, the value of λ_D almost agrees with the experimental result. This indicates that the estimation of Q is fairly good for the samples with the high doses and that it is reasonable to attribute the absorption peak to the colloids. If we could estimate the volume fraction of colloids more precisely by taking the distribution of colloids into account for the samples implanted with lower doses, a better explanation for the experimental results might be achieved.

We observed a similar precipitation and growth of metallic dots in the case of Ag^+ or Cu^+ ion implantation into $LiNbO_3$.[10,13] To confirm what elements are involved in these dots, the samples implanted with Ag^+ ions were examined by inductive coupled plasma (ICP) spectroscopy. The samples with dots on the surface were immersed in nitric acid for several hours. The dots were clearly removed from the surface, and the ICP analysis showed Ag in the acid. Based on this analysis, we speculate that the small dots precipitated on the surface of Au^+ implanted $LiNbO_3$ are Au metallic particles. During implantation, Au^+ ions may aggregate into colloids and some of them exist as isolated atoms in the surface layer. After implantation, Au atoms implanted in the upper layer diffuse to the surface. Because of their large size and heavy mass, the colloids are immovable. The isolated Au atoms diffuse to the surface from the implanted layer, aggregating on the surface, to form the small Au metallic dots.

When the sample is annealed at 500 °C, at first, the peak becomes higher and shifts toward longer wavelengths. In this process the colloids may grow in size and some of the isolated atoms may aggregate. But further heating causes Au atoms to be released from the colloids and diffused to the surface. The decrease in size and number of colloids leads to reduction in the intensity of the absorption peak, and the peak shifts toward shorter wavelengths slightly. For annealing at higher temperature such as 600 °C, Au atoms, from the first, may be released from the colloids formed during the implantation and diffuse to the surface without reaggregating into colloids.

CONCLUSION

In conclusion, $LiNbO_3$ implanted with Au^+ ions shows a bright blue-green color and a large absorption peak at around 620 nm. The color grows rich, the intensity of the absorption peak increases and its peak position shifts toward longer wavelengths as the dose of Au^+ ions increases.

After implantation the Au atoms diffuse to the surface gradually and aggregate to form Au metal dots on the surface although the samples are held at room temperature.

For annealing at 500 °C, the absorption peak gradually increases and shifts toward longer wavelengths in the first 6 h, then it begins to decrease and come back toward shorter wavelengths. The absorption peak decreases from the initial stage and shifts toward shorter wavelengths for the annealing at 600 °C. These characteristic behaviors of the peak around 620 nm are attributed to the Au colloids formed in the implanted layer.

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