Optical waveguide in Nd:$Bi_{12}SiO_{20}$ crystal produced by multi-energy C ion implantation*

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We report the fabrication of a planar waveguide in the Nd:$Bi_{12}SiO_{20}$ crystal by multi-energy C ions at room temperature. The waveguide is annealed at 200 °C, 260 °C, and 300 °C in succession each for 30 min in an open oven. The effective refractive index profiles at transverse electric (TE) polarization are stable after the annealing treatments. Damage distribution for multi-energy C ion implanted in Nd:$Bi_{12}SiO_{20}$ crystal is calculated by SRIM 2010. The Raman and fluorescence spectra of the Nd:$Bi_{12}SiO_{20}$ crystal are collected by an excitation beam at 633 nm and 473 nm, respectively. The results indicate the stabilization of the optical waveguide in Nd:$Bi_{12}SiO_{20}$ crystal.

Keywords: ion implantation, Nd:$Bi_{12}SiO_{20}$ crystal

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1. Introduction

As a mature technology for semiconductor production, an ion beam from an accelerator has been widely used in optical communication devices. It is a very efficient and controllable way to modify the properties of the material in the near-surface region.[1] The ion beam provides several advantages over the traditional techniques as indicated by Townsend *et al.*[2] The typical ion-beam diameter is a few millimeters, and the electric scanning system is utilized to ensure homogeneous implantation of the sample surface.[3] Up to now, researchers have successfully fabricated ion-implanted waveguides of more than 100 optical materials, including glasses, ceramics, and crystals. However, the species and energies of the implanted ions are the key points for the penetration depth. With energies of MeV and fluences ranging from 10^{13} to 10^{15} ion/cm^2, the medium-mass ions (C, O, etc.) have been successfully used for fabricating the waveguide structures in crystals.[3] For the waveguide structure fabrication, the damage induced by electronic energy loss of medium-mass ions has been formed at the surface of the sample. The Raman, fluorescence, XRD, and absorption spectra have been reported in the $LiNbO_3$, BBO, and YVO_4 crystals before and after different ion implantations, which can be used to gain the information about the structure affected by ion implantation process. Both the optical crystal and the emerging two-dimensional materials irradiated by ions can be analyzed by the above spectra.[4]

As an important part of materials, optical crystals play an important role in optical transmission and integrated photonic applications, serving as signal transmission and storage, laser gain media, etc. As a class of stabilized derivative of γ-Bi_2O_3, bismuth oxide crystal has body-centered cubic structure and space group symmetry I_{23}, with a formula $Bi_{12}MO_{20}$ (M = Ge, Si, Ti). By multi-energy C ion implantation, we fabricated the $Bi_{12}SiO_{20}$ crystal waveguide structure, which is an attractive crystal for optical data processing, image correction with four-wave mixing inversion, and other nonlinear photorefractive optical applications.[5] $Bi_{12}SiO_{20}$ crystal is also piezoelectric semiconductor with a larger energy gap (3.25 eV), which possesses pronounced piezoelectric, electro-optical, and elasto-optical properties.[6] The Raman and infrared phonon spectra, and mechanical properties of Nd:$Bi_{12}SiO_{20}$ crystal have been reported.[5,6] Waveguide structures in Nd:$Bi_{12}SiO_{20}$ crystal fabricated by He and C ions have been reported in our earlier work.[7]

In this work, multi-energy C ions are used to fabricate waveguide structure in Nd:$Bi_{12}SiO_{20}$ crystal. The effective refractive index with the intermittent thermal annealing treatment is investigated in the Nd:$Bi_{12}SiO_{20}$ crystal. The Raman and fluorescence spectra are also measured before and after

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the multi-energy C ion implantation.

2. Experimental details

The Nd:$Bi_{12}SiO_{20}$ crystals in our work were grown and provided by State Key Laboratory of Crystal Materials at Shandong University, which was doped with less than 0.1 at.% Nd^{3+} ions. One of the larger facets of the crystal was stuck on a copper disc and cleaned with alcohol before the ion implantation process. The optically polished technology was used to treat the unimplanted opposite sides of the crystal with the dimensions of $8 \times 5 \times 2$ mm^3. With the ion-beam adjustment, carbon ions with three energies and fluences were implanted on the other larger facet of the crystal at Peking University, China. The C ions were implanted into the Nd:$Bi_{12}SiO_{20}$ crystal with the energies of 4 MeV, 4.5 MeV, and 5 MeV, and with the fluences of 3×10^{14} ion/cm^2, 3×10^{14} ion/cm^2, and 8×10^{14} ion/cm^2, respectively. The Nd:$Bi_{12}SiO_{20}$ crystal on the copper disc was tilted by 7° off the ion beam direction. The angle can minimize the channeling effect in the ion-implanted process. Thermal annealing treatment in the open oven was performed to investigate the optical transmission characteristics in the implanted layer.

Profiles of the effective refractive indices were investigated by *m*-line technique, using the prism-coupling method, with the help of the Model 2010 Prism Coupler (Metricon). The Raman and fluorescence emission spectra of the bulk and modified layers in the Nd:$Bi_{12}SiO_{20}$ crystal were recorded by using a spectrometer (Horiba/JobinYvon HR800).

3. Results and discussion

The Model 2010 prism couple (Metricon, USA) is used to record the profiles of the effective refractive indices. In the setting, the polished and implanted facet is pushed by air pressure and clamped to a specific rutile prism. A red laser beam with a wavelength of 633 nm strikes the margin of contact surface and is reflected to a silicon photodetector. As recorded, the effective refractive index at the wavelength of 633 nm of the unimplanted Nd:$Bi_{12}SiO_{20}$ crystal is 2.5281, which is omitted in the paper. The effective refractive index profiles with the measured relative intensity of the red light at TE polarization, reflected from the rutile prism versus the effective refractive index of the multi-energy C ion implanted layer in Nd:$Bi_{12}SiO_{20}$ crystal is shown in Fig. 1. Judging from the deep dips in Fig. 1(a), the layer on Nd:$Bi_{12}SiO_{20}$ crystal after multi-energy C ion implantation could carry five optical modes. The values of the effective refractive index of the modes are lower than those in the unimplanted crystal, which implies that a waveguide structure with an optical barrier can exist in the implanted layer. To investigate the influence of annealing treatment, the implanted crystal is annealed at 200 °C, 260 °C, and 300 °C in succession each for 30 min in an open oven. The value of fundamental mode is increased by the annealing treatment, while the number of modes is still maintained. Table 1 also presents the effective refractive indices of TE modes in Nd:$Bi_{12}SiO_{20}$ crystal after the intermittent thermal annealing treatment. The results indicate the stabilization of optical modes in Nd:$Bi_{12}SiO_{20}$ crystal.

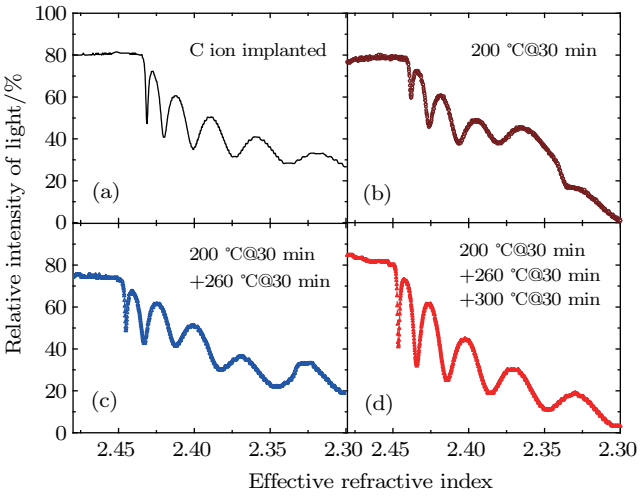


Fig. 1. (color online) Plots of relative intensity of light versus effective refractive index of the Nd:$Bi_{12}SiO_{20}$ waveguide with multi-energy C ion implantation and after the intermittent thermal annealing treatment.

Table 1. Values of optical modes in Nd:$Bi_{12}SiO_{20}$ crystal after the intermittent thermal annealing treatment.

Temperature/°C	Time/min	Effective refractive index of TE mode			
		0	1	2	3
Substrate		2.5281			
As implanted		2.4312	2.4197	2.4010	2.3734
200	30	2.4379	2.4261	2.4065	2.3811
260	30	2.4451	2.4329	2.4120	2.3824
300	30	2.4464	2.4343	2.4140	2.3855

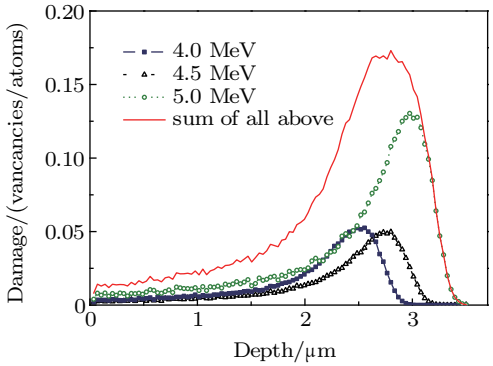


Fig. 2. (color online) Damage distribution for multi-energy C ion implanted in Nd:$Bi_{12}SiO_{20}$ crystal, calculated by SRIM 2010.

To reduce the damage and maintain crystallinity in the waveguide layer to a great extent, the fluences of the middle-light-mass ions (C, O, Si) should be lower than those of the light ions (H, He).[8] The process of C ion implantation into the Nd:$Bi_{12}SiO_{20}$ crystal was simulated by SRIM 2010, which was simplified by "transport and ranges of ions in matter".[9]

The damage distributions in Nd:$Bi_{12}SiO_{20}$ crystal induced by C ion implantation with different conditions are shown in Fig. 2, where the parameters are as follows: the energy of 4 MeV at a fluence of 3×10^{14} ion/cm^2, the energy of 4.5 MeV at a fluence of 3×10^{14} ion/cm^2, the energy of 5 MeV at a fluence of 8×10^{14} ion/cm^2, and the sum of the damage distributions is also shown in the figure. Compared with single energy ion implantation, the multi-energy C ion implantation increases the damage range. For the total damage in Fig. 2, a minimum damage of 0.00817 vacancies/atom is calculated near the surface, and a maximum of 0.17307 vacancies/atom is produced at about 2.8 μm beneath the surface, which is the peak position on the total profile. The results imply that the region near the surface is slightly affected by the multi-energy C ion implantation.

The micro-Raman spectra of the Nd:$Bi_{12}SiO_{20}$ crystal are collected by an excitation beam at 633 nm and room temperature. The laser resolution is about 1 μm. The Raman spectrum of the bulk and the implanted layer near the surface after final annealing treatment are shown in Fig. 3. The experimental spectrum is in a range of 50–870 cm^{-1}. By comparing the results with the literature values,[10,11] we find that all the peak positions correspond to the modes of SiO_4 and Bi_3O_4 units with Raman spectra active in $Bi_{12}SiO_{20}$ crystal. "A sphere" of 12 heavy bismuth atoms surrounds the tightly bound SiO_4 tetrahedron, and the vibration peak intensities of the Bi_3O_4 tetrahedron are stronger than those of SiO_4.[10] The results for the micro-Raman spectra of the substrate and the implanted layer after final annealing treatment in Nd:$Bi_{12}SiO_{20}$ crystal show no microstructural changes. There are two reasons for the results in Fig. 3, i.e., the low irradiation fluence of the C ions is unable to produce suitable damage in the surface of the layer and the damage is recovered after annealing treatment. According to Raman spectra of ion-implanted waveguides[12] and the results in Fig. 2, we can conclude that there is slight damage with hardly any peak change in Fig. 3 on the surface of Nd:$Bi_{12}SiO_{20}$ crystal.

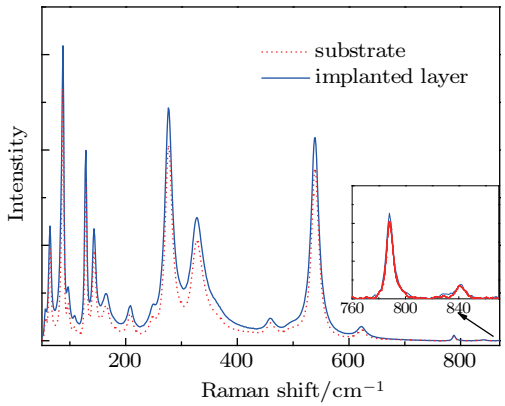


Fig. 3. (color online) Raman spectra of (a) bulk Nd:$Bi_{12}SiO_{20}$ crystal (dotted line) and (b) implanted Nd:$Bi_{12}SiO_{20}$ crystal layer (dashed line) by using an excitation beam at 633 nm.

When the laser wavelength is tuned to 473 nm, the fluorescence spectra of the Nd:$Bi_{12}SiO_{20}$ crystal from the wavelengths ranging from 810 nm to 970 nm at room temperature are shown in Fig. 4. Figure 2 presents the bulk and the implanted layer near the surface after final annealing treatment. As reported in Refs. [13] and [14], the localized disorders, damage, defects, and changes in the unit cell volume of the crystal can be reflected by the line width, the fluorescence intensity reduction, and the spectral shift of the fluorescence line, respectively. As shown in Fig. 4, the two spectra are almost consistent except for the fluorescence intensity reduction at 946 nm in the implanted layer. The results show that the weakened peak at 946 nm is sensitive to the slight damage to the implanted layer on the surface. For Nd^{3+} ions, laser transition from $^4F_{3/2}$ to $^4I_{9/2}$ corresponds to laser emissions at about 900–950 nm.[15,16] Because of the attention to the generation of blue light by second harmonic generation, the $^4F_{3/2}\rightarrow{}^4I_{9/2}$ transition of Nd^{3+} ion is widely studied and this opens the door for plenty of applications, such as submarine communications and high-density optical-data storage, water vapor detection, etc.[15,17]

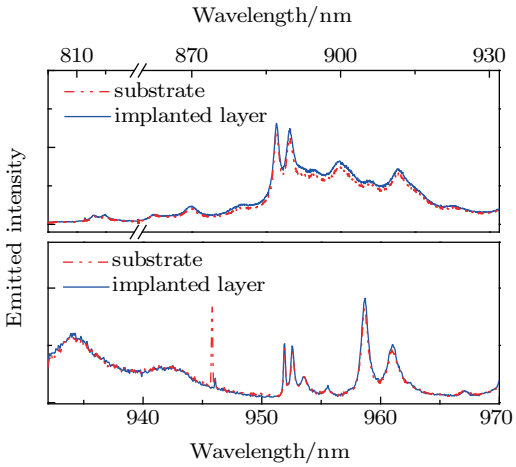


Fig. 4. (color online) Room temperature fluorescence emission spectra correlated to the Nd^{3+} ions in (a) bulk (dotted line) and (b) implanted Nd:$Bi_{12}SiO_{20}$ crystal layer (dashed line) obtained after annealing treatments.

4. Conclusions and perspectives

Multi-energy C ions with an energy of 4 MeV at a fluence of 3×10^{14} ion/cm^2, an energy of 4.5 MeV at a fluence of 3×10^{14} ion/cm^2, and an energy of 5 MeV at a fluence of 8×10^{14} ion/cm^2 are used to implant and fabricate the waveguide structure in the Nd:Bi_{12} SiO_{20} crystal. The effective refractive index profiles at TE polarization show the stabilization of optical modes in Nd:$Bi_{12}SiO_{20}$ crystal. Damage to the implanted layer is simulated by SRIM 2010. Multi-energy ion implantation can increase the damage range, but the region near the surface is slightly affected by the C ion implantation. The Raman spectrum at 633 nm is collected and it hardly shows any change on the surface of Nd:$Bi_{12}SiO_{20}$

crystal. Also, the fluorescence spectrum at 473 nm shows the weakened peak at 946 nm.

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