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Synthesis of ferromagnetic Bi-substituted yttrium iron garnet films by laser ablation

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Bismuth-substituted yttrium iron garnet (Bi:YIG) films were deposited on gadolinium gallium garnet substrate by laser ablation using the ArF excimer laser. This is the first report on the preparation of Bi-substituted YIG films by laser ablation. Films have a garnet single phase above the substrate temperature of 490 °C, and the film composition does not deviate largely from the target composition and it is almost constant in the temperature range between 490 and 580 °C. The saturation magnetization of the film is 1500 G at room temperature. Faraday rotation angle θ_F at a wavelength of 830 nm at room temperature is -0.3×10^4 °/cm.

Rare-earth iron garnet (RIG) films are of great interest in device applications such as magneto-optical memory device and waveguide optical isolator, because of its transparency in near-infrared region and excellent magneto-optical properties such as anomalously large Faraday rotation angle in the region from visible to near infrared. Especially in yttrium iron garnet (YIG), Faraday rotation angle θ_F at a wavelength of 633 nm at 295 K is $+835$°/cm.[1] An increase in the amount of Bi substituted for Y makes Faraday rotation angle change linearly at a rate of -2.1×10^4 °/cm(1 Bi atom/f.u.), where f.u. represents formula unit.[1] In fully Bi-substituted iron garnet [$Bi_3Fe_5O_{12}$:(BIG)], θ_F of greater than -6.2×10^4 °/cm can be expected. Moreover, the incorporated Bi ions do not reduce the transparency of the film. Therefore, Bi-substituted YIG (Bi:YIG) films attracts a great attention from the viewpoints of both materials science and applications. For use in magneto-optical memory devices, the films are required to have magnetic anisotropy perpendicular to the film plane. In many cases, films have been epitaxially deposited on (111) plane of paramagnetic garnet substrate because (111) axis of these ferromagnetic garnet materials is the axis of easy magnetization. Conventionally, Bi:YIG films have been prepared by liquid phase epitaxy (LPE),[2] reactive ion beam sputtering (RIBS),[3,4] and rf-magnetron sputtering.[5,6] These methods, however, have some disadvantages such as the problems of impurity admixture, low deposition rate, and large fluctuation in composition, respectively.

On the other hand, it has been indicated that laser ablation has great advantages in preparing multielement oxide thin films such as superconducting thin films and ferroelectric thin films.[7–9] The most promising characteristics of this preparation method are the following: (1) Even materials with a high melting-point can be easily deposited if the materials strongly absorb the laser light. (2) Deposition in high oxygen pressure is possible because of the absence of energy sources in the system. (3) There is little difference in the composition between the target material and the deposited film. So far, our group has prepared Ba-Y-Cu-O superconducting thin films [10,11] and lead-zirconate-titanate (PZT) ferroelectric thin films[12,13] with the excellent properties using laser ablation. Considering these features, Bi:YIG film, which is a multielement oxide ferromagnetic thin film, is expected to be successfully prepared by laser ablation.

In this letter, we report the results of the structural and ferromagnetic properties of Bi:YIG films prepared by laser ablation using the ArF excimer laser.

Details of the equipment for the preparation of Bi:YIG films are almost the same described in a previous letter.[12] The substrate is heated up by focusing the infrared ray emitted from the lamp exterior to the vacuum chamber. The film deposition was carried out by the ablation of a Bi:YIG ceramic target in the vacuum chamber with an oxygen gas pressure of 27–133 Pa using an ArF excimer laser (Shibuya SQL2240, 193 nm wavelength, 10 ns pulse width, 5 Hz repetition rate). The ceramic target is a pellet of $Bi_{1.5}Y_{1.5}Fe_5O_{12}$. In order to ablate always the fresh target surface, the target was continuously moved during the film deposition. A (111) plane of gadolinium gallium garnet [$Gd_3Ga_5O_{12}$: (GGG)] was used as a substrate. The distance from the target to the substrate is about 30 mm. The substrate temperature, measured by thermocouple on the substrate surface and radiation thermometer, was controlled between 200 and 580 °C. The laser energy for the ablation was 70 mJ/shot, which corresponds roughly to a laser fluence of 3.5 J/cm^2 shot. After the ablation, films were cooled to room temperature in 3 h. X-ray diffraction (XRD) measurements were carried out using Cu $K\alpha$ to investigate the film structure. The film composition was measured by inductively coupled plasma spectroscopy (ICP). Film morphology was inspected using scanning electron microscopy (SEM). The measurement of Faraday rotation angle was carried out at a wavelength of 830 nm. The ferromagnetic resonance (FMR) measurement was carried out at a frequency of 9.472 GHz using Varian E-109 X-band spectrometer. These measurements were carried out at room temperature.

Typical film thickness is about 0.5 μm and the film deposition rate is in the range of 0.7–1.3 Å/s at the preparation conditions mentioned above. The deposition rate is about five times larger than that for the RIBS[14] and the same as that for the rf-magnetron sputtering.[5]

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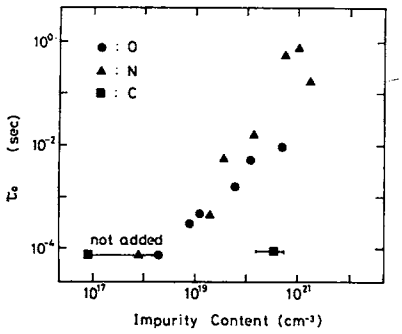

FIG. 4. Decay time τ_0 as a function of O, N, and C contents.

thought to result from the upward shift of E_F.[10] For the N incorporation, σ_F increases with the N content from 10^{-5} to 10^{-3} S/cm, while σ_d from 10^{-10} to 10^{-6} S/cm. For the O incorporation, σ_d increases with the O content from 10^{-10} to 10^{-4} S/cm, while σ_d increases from 10^{-10} to 10^{-8} S/cm. Therefore, the photosensitivity σ_P/σ_d decreases from 10^5 to 10^3 for the N incorporation, and from 10^5 to 10^4 for the O incorporation.

The results of light-induced ESR measurements at 77 K also show that the density of charged dangling bonds increases with an increase in the O and N contents, whereas the density of neutral dangling bonds remains unchanged. The results of the measurement of optical absorption due to defects using the constant photocurrent method (CPM) also suggest the increase in the density of charged dangling bonds.

Finally, the photocurrent decay from the steady state after the switching-off of the steady illumination was investigated. We define a decay time τ_0 as a time when the photoconductivity $\sigma_P(t)$ decays to $1/e$, where the steady state σ_P is fixed to be 1×10^{-6} S/cm by changing the illumination intensity.[3] Figure 4 shows the decay time τ_0 as a function of the impurity content. It is revealed that the N incorporation dramatically increases τ_0 by 4 orders, and the O incorporation by 2 orders. Such a degradation in the photoresponse should be suppressed for the application to *a*-Si:H optical sensor devices which need a rapid response. The degradation of the photoresponse shows a formation of a new trap state below the conduction band by the N or O incorporation.

The present results mentioned above are reasonably explained in terms of the following model.[1] Some of the N and O atoms incorporated in *a*-Si:H become fourfold-coordinated N_4^+ and threefold-coordinated O_3^+, respectively, acting as a donor. According to our model,[1] a photoexcited electron is captured at N_4^+ or O_3^+, resulting in the bond breaking. Then N_4^+ or O_3^+ changes to N_3^0 or O_2^0, respectively, creating neutral Si dangling bonds Si_3^0 at the neighboring site.[3] This appears to be the origin of the light-induced ESR signals. The increase in τ_0 due to the N or O incorporation shown in Fig. 4 is attributed to a trapping of photoexcited electrons by N_4^+ or O_3^+.[3] Figures 2 and 3 indicate that the N incorporation increases both σ_d and τ_0 more prominently than the O incorporation. However, the increase in σ_d by the N incorporation is far smaller than that by the P or As incorporation.[5] Through the present study it is found that C atoms do not have a prominent effect in moving the Fermi level.

In summary, both O and N impurities were found to increase the dark conductivity by decreasing its activation energy in *a*-Si:H films. Furthermore, it was found that both of them delay the photoresponse. C impurity, however, has no appreciable effect on them. These findings suggest that O and N impurities shift the Fermi level upward and form a trapping state for photoexcited electrons, supporting our O_3^+ and N_4^+ model.[1]

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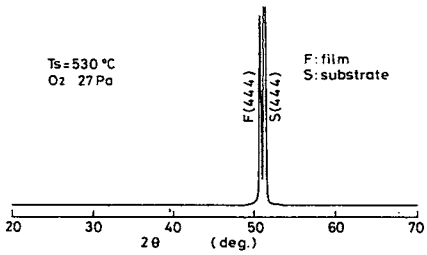

FIG. 1. XRD spectrum of the Bi:YIG film on GGG (111) plane prepared at $T_s = 530$ °C and oxygen pressure of 27 Pa.

XRD spectrum of the Bi:YIG film on GGG(111) plane prepared at a substrate temperature of 530 °C and an oxygen pressure of 27 Pa is shown in Fig. 1. Only the peak for the (444) plane of the Bi:YIG film is observed besides the peak for the (444) plane of GGG substrate. From this spectrum, it is confirmed that the film has a garnet single phase and ⟨111⟩ axis, which is the axis of easy magnetization, is perpendicular to the film plane. At oxygen pressure of 27 Pa, below the substrate temperature of 510 °C, all the films were found to be amorphous. When oxygen gas pressure increases to 133 Pa, however, the film is crystallized and has a garnet single phase above 490 °C. The full width at half maximum (FWHM) of the (444) diffraction for the film prepared at the pressure of 133 Pa is slightly smaller than that for 27 Pa. From these FWHM values, we estimated the crystallite size of these films to be about 1000 Å.

SEM photographs of the films prepared at the different conditions are shown in Fig. 2. In the case of the gas pressure of 133 Pa, although droplets with submicron size exist on the film surface, the size of the grain in the film is

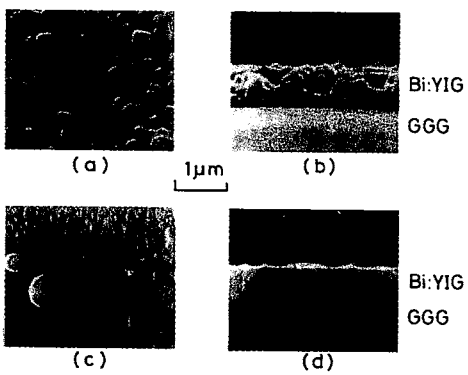

FIG. 2. SEM photographs of the films. (a) and (b) show the film surface and the sectional view, respectively, of the film prepared at $T_s = 530$ °C and oxygen pressure of 27 Pa. (c) and (d) show the film surface and the sectional view, respectively, of the film prepared at $T_s = 510$ °C and oxygen pressure of 133 Pa.

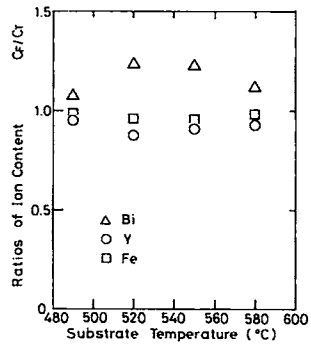

FIG. 3. Substrate temperature dependence of the ratio of the ion content in the film (C_F) to those in the target (C_T). Films were prepared at oxygen pressure of 133 Pa.

uniform and the film surface is smooth in comparison with the case of the gas pressure of 27 Pa. The smoothness of the film surface is important for employing these films in the magneto-optical devices. The sectional views also show that the film prepared at the pressure of 133 Pa has a uniform and dense structure. From the XRD measurement and the film morphology, it can be seen that the oxygen pressure of 133 Pa is suitable for preparing Bi:YIG films.

Ratios of the ion contents in the films (C_F) to those in a target (C_T) plotted as a function of substrate temperature at the oxygen pressure of 133 Pa are shown in Fig. 3. Although around 20% of excess Bi ions is found in the film, the film composition is roughly constant in the temperature range between 490 and 580 °C.

Figure 4 shows the magnetic field dependence of Faraday rotation angle of the film prepared at a substrate temperature of 510 °C and the pressure of 133 Pa. The measurement was carried out at 830 nm wavelength. At the magnetic field of about 2 kOe, the rotation angle becomes maximum and from this maximum value we obtain $\theta_F = -0.3 \times 10^4$ °/cm. In this measurement, the polarized light reflected at the interface between the film and the

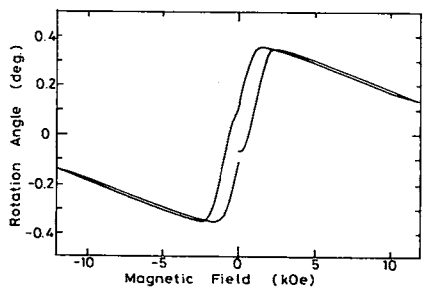

FIG. 4. Applied magnetic field dependence of Faraday rotation angle, measured at a wavelength of 830 nm at room temperature. Films were prepared at $T_s = 510$ °C and oxygen pressure of 133 Pa.

substrate was detected, so that the calculation was carried out by considering twice the film thickness as the light path.

The magnetization measurement revealed that the film has the axis of easy magnetization parallel to the film plane, in spite of the ⟨111⟩ axis orientation perpendicular to the film plane. This is explained by the fact that the anisotropy field perpendicular to the film plane is overcome by the demagnetizing field ($4\pi M_s$) in the film. The saturation magnetization ($4\pi M_s$) is about 1500 G, which is similar to that for Bi:YIG film prepared by RIBS.[14] From the magnetization and the ferromagnetic resonance (FMR) measurements, the anisotropy field is calculated to be 985 G under an assumption of uniaxial isotropy. Considering these values of the anisotropy field and the demagnetizing field, it is expected that the films with a magnetic anisotropy perpendicular to the film plane can be obtained by reducing the saturation magnetization of the films. It is realized by substituting paramagnetic ions such as Al^{3+} or Ga^{3+} for Fe^{3+} in Bi:YIG.[5]

In summary, Bi-substituted YIG films with a (111) orientation were successfully grown on the (111) plane of GGG substrate by laser ablation using the ArF excimer laser. The following results were obtained: (1) The saturation magnetization ($4\pi M_s$) of the film is about 1500 G and Faraday rotation angle is -0.3×10^4 °/cm at a wavelength of 830 nm. (2) The film composition does not deviate largely from the target one, and it is almost constant in the substrate temperature range of 490–580 °C. (3) The oxygen gas pressure influences the crystallization temperature, film structure, and morphology. A relatively high oxygen gas pressure is suitable for preparing the garnet films.

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