Nonlinear change of refractive index of Co_3O_4 thin films induced by semiconductor laser ($\lambda = 405$ nm) irradiation

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Nonlinear change of the refractive index (n) and extinction coefficient (k) of Co_3O_4 thin films induced by a laser with $\lambda = 405$ nm ($h\nu = 3.06$ eV) irradiation was evaluated using equipment having an ellipsometric optical configuration. Nonlinear refractive index (n_2) and extinction coefficient (k_2) were $+1.0\times10^{-10}$ m^2/W (positive) and -2.6×10^{-11} m^2/W (negative), respectively. n_2 and k_2 at $\lambda = 650$ nm ($h\nu = 1.91$ eV) were -5.5×10^{-11} m^2/W and -8.7×10^{-11} m^2/W (both have negative signs). From these results and the fact that the Co_3O_4 thin film has the band-gap energy of 2.06 eV, the band filling effect can be seen as one of the most probable models describing the large nonlinear change of n and k of Co_3O_4 thin film. [DOI: 10.1063/1.1498144]

Co_3O_4 thin film has great optical nonlinearity and its refractive index (n) and extinction coefficient (k) change significantly with laser irradiation.[1–7] Recently, we reported a large nonlinear change of n and k of Co_3O_4 thin film at a 650 nm irradiation wavelength,[6,7] n decreased from 3.35 to 3.03 and k decreased from 1.10 to 0.38. The change of n and k corresponded to nonlinear refractive index (n_2) and extinction coefficient (k_2) of -5.5×10^{-11} m^2/W and -8.7×10^{-11} m^2/W, respectively. Since this film has such a great optical nonlinearity it can be applied as a superresolution film for optical recording media having high recording density.[5]

The mechanism of the optical nonlinearity is not clear. Previous papers have mentioned that the band filling effect is one of the most probable.[1,7] However, it is hard to decide the mechanism from the change of refractive index at only a single wavelength, and other evidence is necessary. One way to confirm the change mechanism of refractive index is examination of the wavelength dependence of the optical nonlinearity.

Recently, a GaN semiconductor laser with a 405 nm irradiation wavelength was developed, and it is expected that this laser will be used as the optical source for next generation optical recording disks. Therefore evaluation of the nonlinear optical property of Co_3O_4 thin film at 405 nm should provide further information about the mechanism of the change of refractive index and the application possibility to optical disks. Accordingly, in the present study, we investigated the change of the refractive index at 405 nm, and considered the mechanism of the optical nonlinearity of Co_3O_4 thin film.

The change of n and k of Co_3O_4 thin film was measured using an ellipsometer (DHA-NP, Mizojiri Optical Co Ltd.)[6,7] coupled with a GaN semiconductor laser (Nichia Corporation) with an irradiation wavelength of 405 nm. Pulse width was 100 ns. Laser intensity (I) for measuring n_0 and k_0 in the ground state was under 0.25 GW/m^2, and between 1.0 and 8.2 GW/m^2 in the excited state.

The Co_3O_4 film was obtained by rf magnetron sputtering on borosilicate glass substrates at room temperature. An SPF-750HL sputtering device (Anelva Techno Business Co. Ltd.) was used for this. 99.9999% argon gas was used as sputtering gas. Sputtering power was 1.0 kW on a 152.4 mm ϕ Co_3O_4 target. Each film was about 70 nm thick. Back pressure was under 3.0×10^{-5} Pa, and the pressure during sputtering was 7.0×10^{-1} Pa.[6,7]

Nanostructure of the obtained thin film was characterized by x-ray diffraction (XRD) and transmission electron microscopy (TEM) with energy dispersed x-ray spectroscopy. XRD and electron diffraction images revealed Co_3O_4 precipitates in the thin film. The bright field TEM images indicated that the film consisted of nanoscale Co_3O_4 particles having 10 nm diameter.[8]

Figure 1 shows the change of (a) n and (b) k of Co_3O_4 thin film when the pulse laser ($\lambda = 405$ nm) beams of having several peak intensities were irradiated. Intensity of the pulse laser for measuring n_0 and k_0 in the ground state was 0.25 GW/m^2 in the time range of $t<0$. The intensity of the pulse laser started to increase at t (time)$=0$ (i.e., before the laser irradiation), and it rose to the desired peak intensity (from 1.1 and 8.2 GW/m^2) after 10 ns. n_0 and k_0 in the ground state were 1.91 and 0.86, respectively, and they were constant for $t<0$. n increased with increasing laser intensity for $t>0$, and it saturated at a value that depended on the peak intensity. The saturated n value also increased with increasing peak

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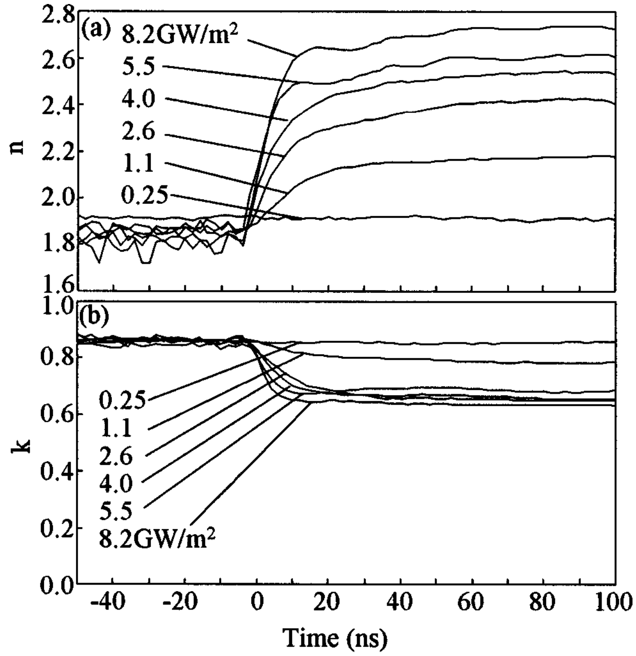

FIG. 1. Change of (a) n and (b) k of the Co_3O_4 thin film when irradiated by the pulse laser ($\lambda = 405$ nm).

intensity, and n measured with the 8.2 GW/m^2 laser was 2.73. On the other hand, k decreased with increasing laser intensity as shown in Fig. 1(b), and k at 8.2 GW/m^2 was 0.65.

Figure 2 shows the refractive index (n) of the Co_3O_4 thin film calculated from the data shown in Fig. 1(a) as a function of the laser intensity. The change of n induced by the 650 nm laser is also given Fig. 2.[6,7] These curves were the average of n and k within the time range from 50 to 100 ns. n_0 at wavelengths of 650 and 405 nm were 3.34 and 1.91, respectively, indicating the Co_3O_4 thin film has an anomalous dispersion, which is consistent with the tendency reported by Cook and van der Meer.[9] The value of n decreased with increasing laser intensity irradiated at 650 nm, and it reached 3.03 in the excited state when the laser power was 6.0

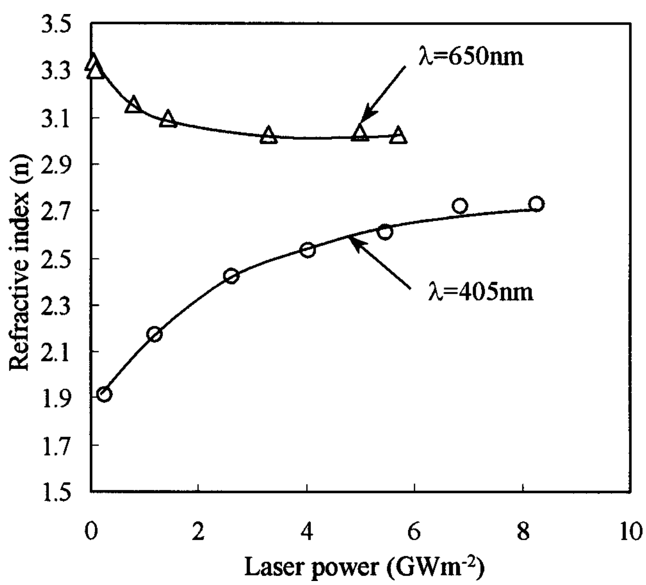

FIG. 2. Refractive index (n) of the Co_3O_4 thin film as a function of the laser intensity.

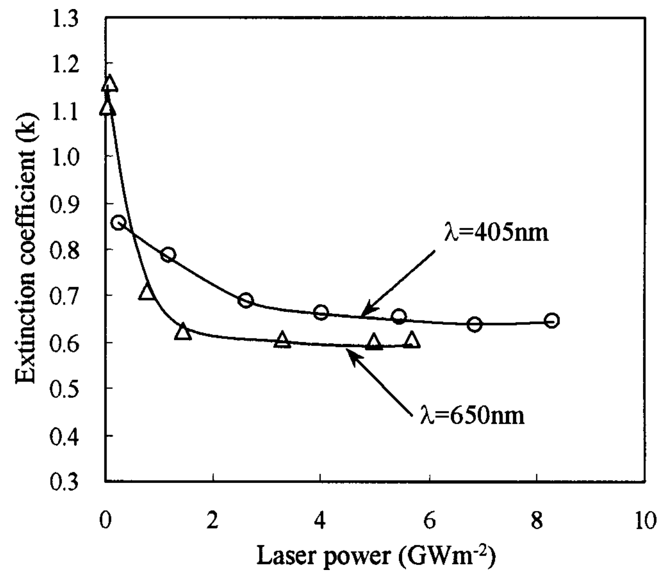

FIG. 3. Extinction coefficient (k) of the Co_3O_4 thin film as a function of the laser intensity.

GW/m^2. On the other hand, n increased as a function of the laser power, and it saturated at 2.73 for a 8.2 GW/m^2 laser irradiation at 405 nm.

Figure 3 shows the change of extinction coefficient (k) calculated from the data shown in Fig. 1(b) as a function of the laser intensity. k values at 405 and 650 nm in the ground state were 0.85 and 1.15, respectively. Both decreased with increasing laser intensity, and were 0.60 and 0.65 in the excited state, respectively.

The nonlinear refractive index (n_2) and extinction coefficient (k_2) were calculated using these results. n_2 and k_2 at 405 nm were calculated as $+1.0\times10^{-10}$ and -2.6×10^{-11} m^2/W, respectively. On the other hand, n_2 and k_2 at 650 nm were -5.5×10^{-11} m^2/W and -8.7×10^{-11} m^2/W as we mentioned above.

From these results, we can discuss the mechanism of the large nonlinear change of n and k of Co_3O_4 thin film. One of the most probable models that can describe the phenomenon is the band filling effect.[10,11] Figure 4 shows a schematic diagram of the change of (a) k and (b) n by the band filling effect. The band filling effect is due to by the transition of electrons from the ground state to the excited state, which is induced by laser irradiation having an energy near the band gap, E_g. Excitation of electrons widens the band gap from E_g to $E_g'(E_g'>E_g)$. Therefore the absorption edge shifts to high energy, and then a blue shift of the absorption spectrum occurs. Consequently, the extinction coefficient decreases for all wavelengths. The refractive index was calculated from the extinction coefficient using Kramars–Kronig relation, which gives a peak for n at $h\nu=E_g$. When the absorption coefficient shifts from E_g to $E_g'(E_g'>E_g)$, the peak for n also shifts to E_g'. Therefore n in the energy range near E_g decreases and n in the higher energy range would increase due to the band filling effect.[10]

Co_3O_4 has E_g of 2.06 eV which is assigned as a charge transfer from $O^{2-}(\pi^*\Gamma)$ to $Co^{2+}(\sigma^*t^2)$.[12,13] When the film was irradiated by the laser having the energy ($h\nu$) of 1.91 eV ($\lambda = 650$ nm), the band filling effect and blue shift of absorption both occurred. In this case, $h\nu$ is close to E_g of

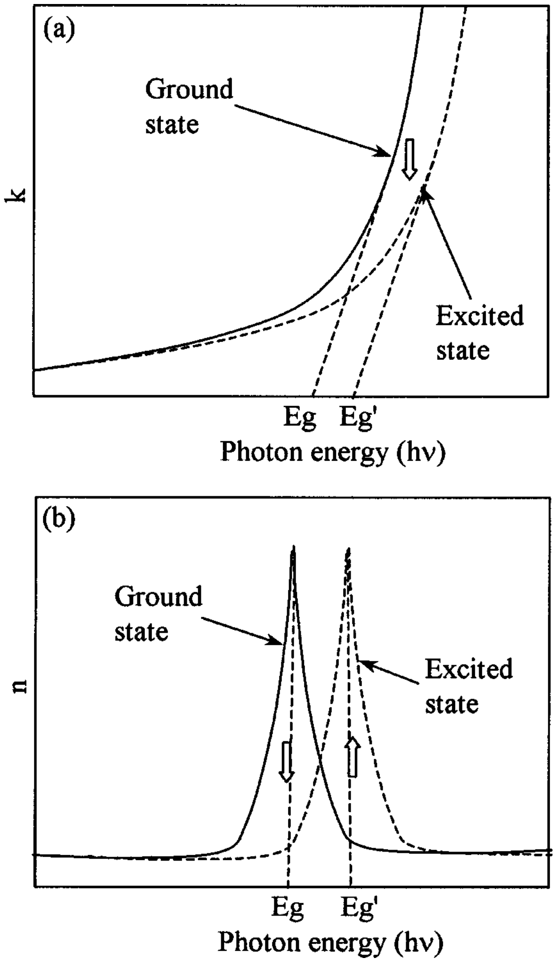

FIG. 4. Schematic diagram of the change of *n* and *k* by the band filling effect.

Co_3O_4, so the absorption coefficient decreases in proportion to the extinction coefficient decrease. As we mentioned above, the change of refractive index at the wavelength close to E_g decreases, and it increases in the range of higher energy. The results of the present study indicate that the 405 nm laser irradiation also leads to the band filling effect in the Co_3O_4 thin film, and k decreases and n increases.

In conclusion, Co_3O_4 thin film had a large nonlinear change of n and k, and the sign of n_2 and k_2 depended on the wavelength of the irradiated laser. n_2 was positive and k_2 was negative for laser irradiation wavelength of 405 nm; on the other hand, both n_2 and k_2 were negative for the 650 nm irradiation. Since Co_3O_4 has a band gap of 2.06 eV, these results could be explained using the band filling theory for semiconductors.

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