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Kyoto University
Nonlinear change of refractive index of Co₃O₄ thin films induced by semiconductor laser (λ = 405 nm) irradiation

Hiroki Yamamoto and Shuhei Tanaka

Nonlinear change of refractive index (n) and extinction coefficient (k) of Co₃O₄ thin films induced by a laser with λ = 405 nm (hv = 3.06 eV) irradiation was evaluated using equipment having an ellipsometric optical configuration. Nonlinear refractive index (n₂) and extinction coefficient (k₂) were +1.0 × 10⁻¹⁰ m²/W (positive) and −2.6 × 10⁻¹¹ m²/W (negative), respectively. n₂ and k₂ at λ = 650 nm (hv = 1.91 eV) were −5.5 × 10⁻¹¹ m²/W and −8.7 × 10⁻¹¹ m²/W (both have negative signs). From these results and the fact that the Co₃O₄ thin film had 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 Co₃O₄ thin film. © 2002 American Institute of Physics. [DOI: 10.1063/1.1498144]
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, and $k$ at 8.2 GW/m$^2$ was 0.65.

Figure 2 shows the refractive index ($n$) of the Co$_3$O$_4$ 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 in Fig. 2. The values 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$_3$O$_4$ thin film has an anomalous dispersion, which is consistent with the tendency reported by Cook and van der Meer. 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 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 extinction coefficient ($k$) of the Co$_3$O$_4$ thin film as a function of the laser intensity. The $k$ 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 $+1.0 \times 10^{-10}$ and $-2.6 \times 10^{-11}$ m$^2$/W, respectively. On the other hand, $n_2$ and $k_2$ at 650 nm were $-5.5 \times 10^{-11}$ m$^2$/W and $-8.7 \times 10^{-11}$ 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$_3$O$_4$ thin film. One of the most probable models that can describe the phenomenon is the band filling effect. Figure 4 shows a schematic diagram of the change of $n$ and $k$ by the band filling effect. The band filling effect is due to 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 Kramers–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.

Co$_3$O$_4$ has $E_g$ of 2.06 eV which is assigned as a charge transfer from $O^{2-}(\pi^*\Gamma)$ to Co$^{2+}(\sigma^*\sigma^2)$. 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
Co$_3$O$_4$, 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$_3$O$_4$ thin film, and $k$ decreases and $n$ increases.

In conclusion, Co$_3$O$_4$ 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$_3$O$_4$ has a band gap of 2.06 eV, these results could be explained using the band filling theory for semiconductors.

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