Effect of oxygen concentration on the photoluminescence spectrum of CdIn2O4 films

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Effect of oxygen concentration on the photoluminescence spectrum of $CdIn_2O_4$ films

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The photoluminescence of transpartent and conductive $CdIn_2O_4$ thin films formed by rf sputtering has been investigated as a function of oxygen concentration. The photoluminescence peaks show a "red shift" as the oxygen concentration is increased. This is due to the Burstein–Moss effect in conductive degenerate oxide semiconductors.

Thin films of cadmium–indium oxide ($CdIn_2O_4$) are broad-band-gap semiconductors that show remarkable properties such as low electrical resistivity, good transmission in the visible region of the light spectrum and high reflectivity in the near-IR [1–6]. These films can be used as transparent electrodes, antistatic layers or heat mirrors in optoelectronics and solar energy conversion technology.

In this Letter, we report the experimental photoluminescence results for $CdIn_2O_4$ thin films. The studies indicate that the photoluminescence peaks of $CdIn_2O_4$ thin films are moved to long wavelengths as oxygen concentration is increased. These results are discussed briefly.

$CdIn_2O_4$ thin films were prepared by rf sputtering from 34 at% Cd + 66 at% In alloy targets at different oxygen concentrations (O_2/Ar) in a reactive Ar + O_2 atmosphere. The rf power was in the range 100–400 W. The pressure of the Ar + O_2 mixture was about 6 Pa. Thin films were deposited on cleaned glass substrates mounted to a water-cooled sample holder equipped with a heater. The substrates were heated at 473 K for 15 min in vacuum before sputtering was performed. The water-cooled target to substrate spacing was kept at 60 mm.

Fig. 1 shows an X-ray diffraction pattern of $CdIn_2O_4$ thin film with an oxygen concentration of 10% (ratio of O_2/Ar in the sputtering gas). X-ray diffraction analysis revealed that the $CdIn_2O_4$ thin films were mostly polycrystalline with the majority of the film in the spinel phase, with only a small concentration of In_2O_3. The lattice constant was $a = (0.9161–0.9201) \pm 0.0005$ nm which changes little with increasing oxygen concentration.

The optical transmission spectrum of a $CdIn_2O_4$ film is shown in fig. 2. As can be seen, the optical transmission in the visible region of the light spectrum is greater than 90% with electrical conductivity of the order of $10^5\ \Omega^{-1}\ m^{-1}$. The transmission slightly decreased with increasing oxygen concentration.

Fig. 3 shows the photoluminescence spectrum of a $CdIn_2O_4$ thin film with an oxygen concentration of 10% which is the ratio of O_2/Ar in the sputtering gas. The spectrum was measured in the wavelength range from 0.4 to 0.9 μm using a Hitachi 850 fluorescence spectrophotometer. Light of wavelength 450 nm with a photon density of $5 \times 10^{20}\ cm^{-2}\ s^{-1}$ was used as exciting source at a temperature of 77 K. From fig. 3, we can see that there are three emission bands centered at wavelengths of 576, 680 and 750 nm. However, the emission peaks of the $CdIn_2O_4$ thin films showed a red shift with increasing oxygen concentration. The photoluminescence peaks centered at wavelengths of 576 and 750 nm are moved to the peaks occurring at 579 and 751 nm as the oxygen concentration increased by 10 to 50%, but the peak at 680 nm shows no change. These results are shown in fig. 4.

From the abovementioned results, the photolu-

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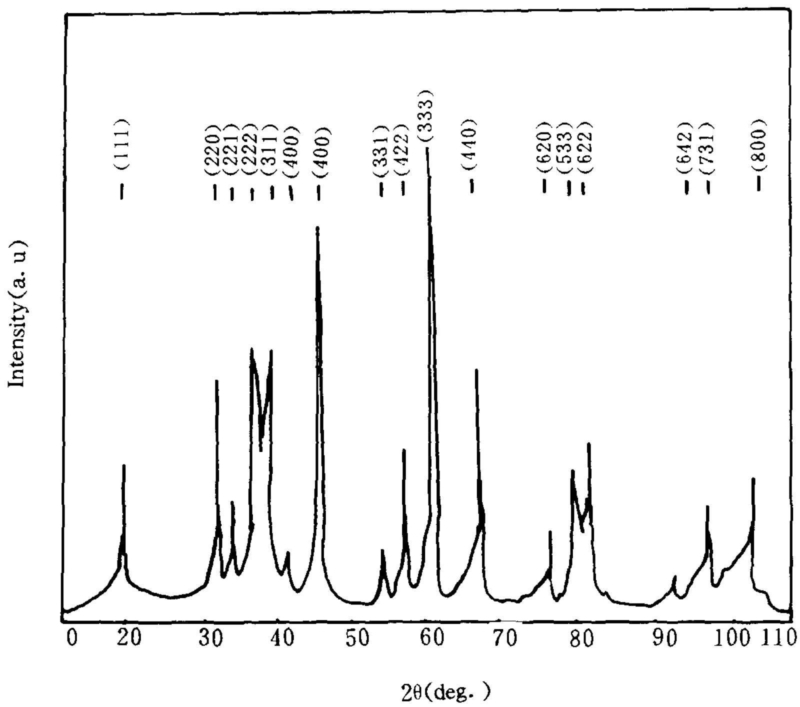

Fig. 1. X-ray diffraction pattern of a $CdIn_2O_4$ thin film with an oxygen concentration of 10% (ratio of O_2/Ar in the sputtering gas). The 4th and 6th indices are In_2O_3 lines.

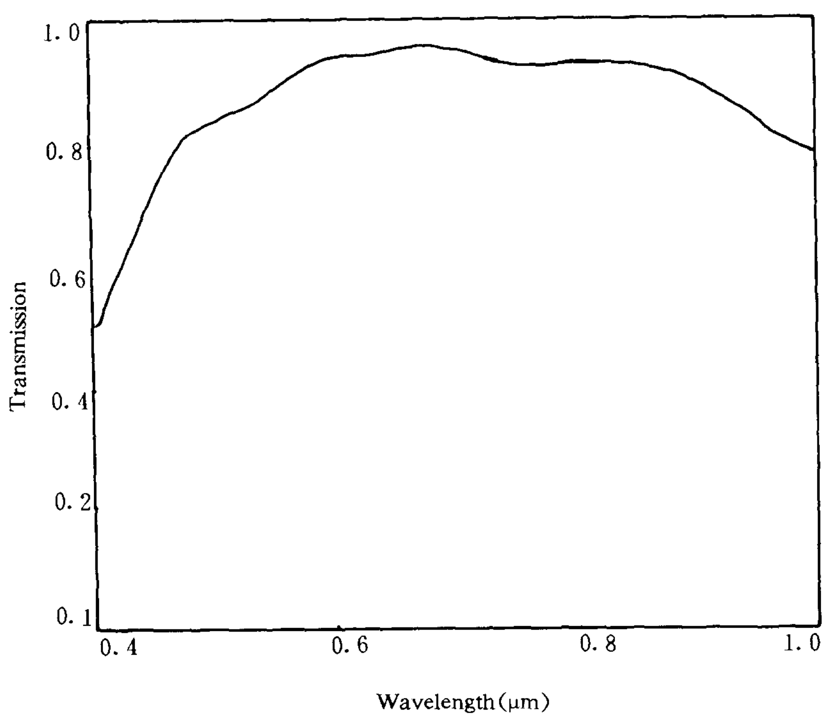

Fig. 2. Optical transmission spectrum of a $CdIn_2O_4$ thin film with 10% O_2.

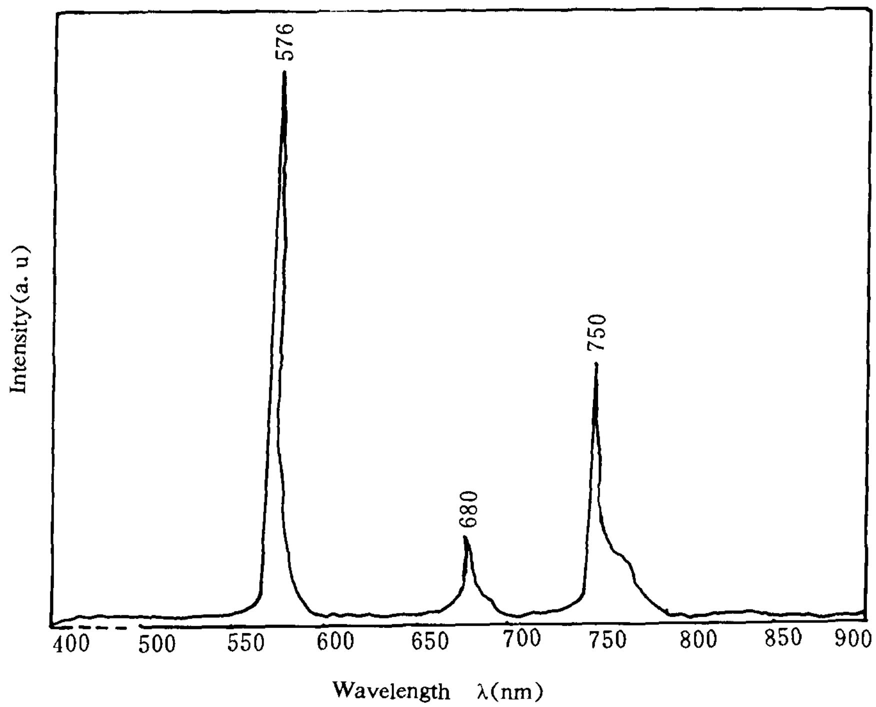

Fig. 3. Photoluminescence spectrum at 77 K of a $CdIn_2O_4$ thin film with an oxygen concentration of 10%.

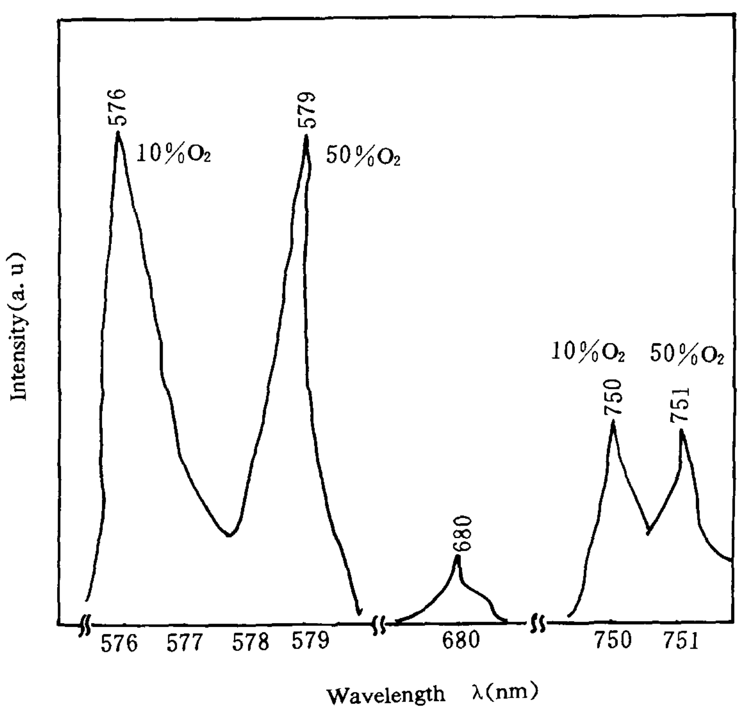

Fig. 4. Photoluminescence change with oxygen concentration.

minescence spectrum of $CdIn_2O_4$ thin films is very similar to that of SnO_2 thin films [7]. From fig. 3, it can be seen that a direct transition occurs at about 576 nm, an indirect transition at about 750 nm, and there is an impurity peak at about 680 nm.

Undoped $CdIn_2O_4$ thin films are highly degenerate n-type semiconductors [8]. The conductivity of the films is attributed to the presence of oxygen vacancies which produce donor states in the forbidden gap [9–11]. Plasma sputtering in a low-oxygen-concentration plasma easily generates oxygen vacancies. Thus, carrier concentration increases with decreasing oxygen concentration. The conduction-electron effective mass for $CdIn_2O_4$ films is about 0.24–0.34 m_e. Semiconductors with a low effective mass favour the generation of a conduction band with high curvature. The density of states at the bottom of the conduction band will be low in such a system. They can be saturated at relatively small free-carrier concentrations, and force optical emission to proceed at high energy.

According to the Burstein–Moss effect in degenerate semiconductors, the band-gap shift is given by [12,13],

$$\Delta E^{\mathrm{BM}} = \frac{h^2}{2m^*}\left(\frac{3n}{\pi}\right)^{2/3},$$

where n is the free-carrier concentration, ΔE^{BM} the Burstein–Moss shift, and m^* the effective mass of the conduction electron. From this expression, it is quite apparent that the photoluminescence of $CdIn_2O_4$ thin films also changes due to the band-gap shift that occurs with variation of oxygen concentration.

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