Highly Transparent and Conductive Zn_{0.86}Cd_{0.11}In_{0.03}O Thin Film Prepared by Pulsed Laser Deposition

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Abstract Zn_{0.86}Cd_{0.11}In_{0.03}O alloy semiconductor film was deposited on quartz substrate by pulsed laser deposition technique. Cd is used to change the optical band gap and In is used to increase the carrier concentration of the ZnO film. XRD studies confirm that the structure of Zn_{0.86}Cd_{0.11}In_{0.03}O is hexagonal wurtzite structure without CdO phase appeared. FE-SEM shows that the grain size of Zn_{0.86}Cd_{0.11}In_{0.03}O film is smaller than that of ZnO. These films are highly transparent (∼85%) in visible region. Most importantly, the electrical properties of Zn_{0.86}Cd_{0.11}In_{0.03}O film highly improved with In doped. It has low resistivity (4.42 × 10^{-3} Ω cm) and high carrier concentration (5.50 × 10^{19} cm^{-3}) that enable this film a promising candidate for window layer in solar cells and other possible optoelectronic applications.

Keywords Zn_{0.86}Cd_{0.11}In_{0.03}O film · Pulse laser deposition · Transparent conductor oxide · Hall effect

1 Introduction

ZnO is a promising candidate for future high quantum efficiency light-emitting/detecting devices because of its large exciton binding energy of 60 meV and wide band gap of 3.4 eV [1, 2]. To further widen the useable wavelength range and improve the efficiency of quantum confinement structures, band gap engineering by alloying is an effective technique. Cadmium oxide (CdO) is also an II–VI compound semiconductor with a narrower band gap of 2.3 eV. So, by adding proper amount of Cd to ZnO, the band gap of ZnO may gain tunable while keeping the crystalline structure and lattice parameter close to ZnO, which is available for constructing appropriate heterostructures like ZnO/Zn_{1-x}Cd_xO/ZnO to realize double confinement actions for both electrons and photons [3].

To date, there have been a few reports on ZnCdO thin films grown by spray pyrolysis [3], molecular-beam epitaxy [4], electrodeposition [5], and thermal evaporation [6]. Sakurai et al. have found distinct blue luminescence from textured ZnCdO films, clearly visible to the eye under weak excitation of He–Cd laser, with a photoluminescence peak around 2.65–2.80 eV [5]. It is also found that ZnCdO films have lower resistivity than ZnO film due to the high conductive CdO [7]. However, the resistivity of ZnCdO films still high, in the order of 10–10^{-1} Ω cm, compared with other conductive films (like ITO). Hence, an attempt in this work has been made to obtain the highly conductive ZnCdO films. Indium has been widely used as a suitable dopant for other transparent conducting films to increase the concentration of conduction electrons and improve the electrical conductivity, but there is no report on In and Cd codoped ZnO thin films by pulse laser deposition technique. In this communication, we are reporting the structural, optical, and electrical properties of Cd and In codoped ZnO (ZCIO) film. Cd is used to change the band gap and In is used to increase the carrier concentration of ZnO films.

2 Experimental Procedure

High purity indium (99.99%), cadmium (99.99%), and zinc (99.99%) powder were mixed thoroughly in the correct atom
ratio. The powder mixture was cold pressed using hydraulic press at 2.5 × 10^7 Pa load to make a disk, which could be used as a target for the PLD deposition. 3 at% indium and 11 at% cadmium codoped ZnO film was prepared on quartz glass substrate by pulse laser deposition. CdO, ZnO and Zn_{0.89}Cd_{0.11}O films were also prepared for comparison. Pulsed Nd: YAG laser with a wavelength of 1064 nm was used. The repetition rate is 10 Hz and the fluency on target was set at 60 J/cm² for all samples. The distance between the target and the quartz substrate was kept at 2.5 cm. The chamber was evacuated first to a base pressure (below 5 × 10⁻⁶ Pa) using a turbo molecular pump and then the gas pressure was kept at 10 Pa by feeding oxygen gases (99.99% purity) into the chamber. The deposition time of 30 min was maintained for all tests. The films were deposited at a fixed temperature of 300 °C.

The crystal structure of the films was analyzed by XRD (Rigaku Dymax) with a Cu target and a monochromator at 40 kV and 250 mA. The atomic composition of doped film was analyzed by X-ray photoelectron spectroscopy (XPS) with an ESCALAB Mk II (Vacuum Generators) spectrometer using unmonochromatized Al Ka X-rays (240 W). Cold field emission scanning electron microscope (FE-SEM, JSM-6700F) was used to characterize the surface morphology of the film. The optical properties of the films were characterized by UV-Visible spectrophotometer. The resistivity (ρ) and Hall coefficient (R_H) were measured by a standard four-probe technique (Lakeshore’s 7704 Hall system). Indium contacts were used for all electrical measurements. The film resistivity has been determined by taking the product of resistance and film thickness. The thickness of the films was measured by Stylus Profiler (Veeco Dekatak 150). The Hall Effect was measured with the magnetic field applied perpendicular to film surface in the Van der Pauw configuration [8]. The type of the conducting carriers was confirmed to be n-type for all samples from the observed negative slope in magnetic field versus Hall voltage plots. The carrier concentration (n) and the Hall mobility (μ) were calculated from the electrical resistivity (ρ) and the Hall coefficient (R_H) was using the following relations:

\[ n = 1/eR_H; \quad \mu = 1/ne\rho \quad \text{(1)} \]

All measurements were done at room temperature.

3 Results and Discussion

3.1 Structural Properties

The X-ray diffraction patterns of Zn_{0.86}Cd_{0.11}In_{0.03}O (ZCIO), Zn_{0.89}Cd_{0.11}O (ZCO), ZnO, and CdO thin films are shown in Fig. 1. It is clearly seen that the ZCIO and ZCO films have c-axis orientation and wurtzite phase without any impurity phase, keeping the crystalline structure and lattice parameters close to those of ZnO film. But there is a slight shift of 2θ in (002) diffraction toward lower Bragg angle from 34.41° for pure ZnO to 33.96° for ZCIO. According to the Bragg formula: \[ \lambda = 2d \sin \theta, \] where λ is the X-ray wavelength (0.1541 nm), d is the crystalline plane distance for indices (hkl) and θ is the diffraction angle of the (002) peak. It can be understood that the observed lattice plane distance d values for doped films are larger than the standard d values of ZnO, which will result in the decrease of the diffraction angle. In our present work, this may be due to addition of Cd and In into ZnO lattice that would substitute Zn ion. And the radii of Cd ionic (0.97 nm) and In ionic (0.81 nm) are larger than that of Zn ionic (0.74 nm), resulting in a change in lattice constant.

In order to evaluate the average grain size of the films, we adopted the Debye–Scherrer formula using the full width at half maximum (FWHM) value of the XRD diffraction peaks. The Scherrer formula is

\[ D = \frac{0.9\lambda}{B\cos \theta} \quad \text{(2)} \]

where D, λ, θ, and B are the mean grain size, the X-ray wavelength, Bragg diffraction angle, and the FWHM of the diffraction peak of ZnO film (002) direction at 34.41, respectively. The mean grain sizes are 47 and 20 nm for the ZnO and ZCIO films, respectively. This result indicates that an obviously decrease in the grain size with Cd and In codoped ZnO. However, the mean grain size estimated using the Debye–Scherrer formula is smaller than the actual value. This may be due to the internal, strain, lattice distortion or defects can also broaden the XRD peaks [9–11].

The lattice constants c is used to estimate the strain (ε) in the films along c-axis given by the following equation [12]: