Pulsed Laser Deposition of Crystalline Cd$_2$SnO$_4$ Thin Film

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Thin films of cadmium stannate (Cd$_2$SnO$_4$) have been deposited on glass substrates by pulsed Nd:YAG laser at room temperature. The deposited film was crystalline in nature and highly oriented in the (311) direction. Using this method, Cd$_2$SnO$_4$ films with the Hall mobility of 25 cm$^2$ V$^{-1}$ s$^{-1}$ and the carrier concentration of 6×10$^{20}$ cm$^{-3}$ corresponding to the conductivity of 2.4×10$^{-3}$ S cm$^{-1}$ have been prepared without post-deposition thermal annealing. The films exhibited average optical total transmission of 70% in the visible region. The optical band gap was found to be 3.18 eV. [DOI: 10.1380/ejssnt.2007.152]

Keywords: Cadmium stannate; Thin film; Pulsed laser deposition

I. INTRODUCTION

Transparent conducting oxides (TCOs) are promising materials for optoelectronic devices, e.g. flat panel displays, organic light emitting-diodes, solar cells, and photodetectors [1–4]. Indium tin oxides (ITOs) were the best materials for optoelectronic applications, but high price of indium element and chemical interface instability in photovoltaic applications limit its usage in wide range [5]. It makes sense, therefore, to develop TCOs not based on indium. Among the most promising candidates for the photovoltaic applications is cadmium stannate (Cd$_2$SnO$_4$), and it has been subjected of extensive investigations [6, 7].

Several methods have been adopted to prepare Cd$_2$SnO$_4$ thin films such as radio frequency magnetron sputtering [7], radio frequency reactive sputtering [8], dip coating [9], sol-gel [10], metal organic chemical vapor deposition (MOCVD) [11]. Pulsed laser deposition (PLD) technique was used successfully to grow ITO and TCO materials [12–14]. The PLD of Cd$_2$SnO$_4$ has been demonstrated to exhibit enhanced performance when compared with film prepared with other methods. However, detailed investigation on fundamental understanding of growth behavior of this film by PLD have not been made. Pulsed laser deposition of Cd$_2$SnO$_4$ thin films have many advantages: (i) accurate stoichiometry, (ii) good film-to-film reproducibility, (iii) smoothness of the deposited film, (iv) good adhesion of film with substrate, (v) highly oriented films, and (vi) good film quality deposited at relativity low temperature.

From this point of view, in this paper we have prepared Cd$_2$SnO$_4$ thin film on glass substrate at room temperature using Nd:YAG laser pulses. Furthermore, the structural, electrical and optical characteristics of grown film were investigated and analyzed.

II. EXPERIMENT

Cd$_2$SnO$_4$ thin film was deposited on cleaned corning glass substrate using PLD technique. The laser beam with deposition parameters listed in Table I was focused using a 20 cm positive lens onto a rotated hot-pressed and sintered CdO-SnO$_2$ pellet (with purity of 99.99% provided from BDH chemical company) with molarity 2:1 respectively located at 45° angle of incidence. The target rotation is necessary to avoid the depletion of material at the same spot continuously and to obtain highly uniform film [15]. The sintered pellet has a diameter of 3 cm and thickness of 5 mm, the schematic diagram of experimental set-up presented in Fig. 1. To ensure a constant irradiation energy density during film deposition, the laser pulse energy was measured before and after each film deposition with a laser power meter.

The conductivity at different temperatures and mobility of the grown films were investigated using four point probe FPP 5000 (Veeco) and Hall measurements. Ohmic contacts have been made on Cd$_2$SnO$_4$ film by deposition of Al film through special mask. The crystalline structure of the film was investigated using CuK$_\alpha$ XRD system (θ-2θ scan) with the scan speed of 3°/min. The transmittance of the films was investigated in the spectral range of 400-900 nm using UV-VIS Shimatzu double beam spectrophotometer. The film thickness was measured using...
TABLE I: Laser deposition parameters.

| Deposition parameters     | Specification |
|---------------------------|---------------|
| Laser type                | Nd:YAG        |
| Wavelength                | 1.06 µm       |
| Pulse duration            | 20 ns         |
| Energy density            | 2 J/cm²       |
| Repetition frequency      | 10 Hz         |
| Target rotation           | 15 Hz         |
| Target-substrate distance | 5 cm          |
| Substrate temperature     | 300 K         |
| Deposition Pressure       | 5 × 10⁻⁶ Torr |

FIG. 1: A schematic diagram of the PLD system.

III. RESULTS AND DISCUSSION

Figure 2 shows the XRD spectrum of grown Cd₂SnO₄ film. The film has a cubic polycrystalline phase and the grains are highly oriented in the (311) direction. The FWHM of the (311) peak was found to be as narrow as 0.65°. All the diffracted peaks are belonging to the Cd₂SnO₄ film except a small amount of CdO may be responsible for the broad (400) reflection at 35.5°. On the other hand, no diffracted peaks related to SnO₂ elements have been noticed in XRD spectrum. These results agree well with that for film prepared by MOCVD technique [10].

Figure 3 demonstrates the optical transmission plot of the grown film. Estimated average transmission of 70% in the visible and near-infrared regions has been obtained. Low transmission in the visible region (60%) may be due to the metallic traces of Cd and Sn phases (they did not detected by the XRD spectrum because may be they are amorphous in nature). From the transmittance data, the absorption coefficient $\alpha$ of the film was determined using the relation:

$$\alpha = \frac{\ln \left( \frac{1}{T} \right)}{t},$$

where $T$ is the film transmittance and $t$ the thickness of the film. For evaluating the optical band gap of the Cd₂SnO₄ film $(\alpha h \nu)^2$ is plotted versus photon energy as shown in Fig. 4. Cd₂SnO₄ material has a direct band gap and for such band to band transition the $\alpha$ is function of photon energy $h \nu$ according to the following relationship:

$$(\alpha h \nu)^2 = A(h \nu - E_g),$$

where $A$ is a constant and $E_g$ is the energy gap.

From Fig. 4 the band gap of the grown film was calculated and found to be 3.18 eV which is in good agreement with reported results [10]. The electrical measurements revealed that the deposited film was $n$-type and the variation of electrical conductivity with operating temperature is depicted in Fig. 5. The room temperature conductivity and mobility are 2400 S cm⁻¹ and 25 cm² V⁻¹s⁻¹ corresponding to $6 \times 10^{20}$ cm⁻³ carrier concentration. This high electrical conductivity of grown film is probably due
to metallic phases of both Cd and Sn (this point needs detailed study) presented in film. On the other hand, no significant variation of conductivity with temperature has been observed which indicate the degenerate semiconductor behavior. Gathering the sheet resistance $R_S$ and optical transmittance data of the film, figure of merit ($T/R_S$) was calculated and found to be about $3 \times 10^{-2}$ S.

IV. CONCLUSIONS

Transparent and electrically conductive $n$-type Cd$_2$SnO$_4$ (CTO) thin films having sheet resistance of 17 $\Omega$ and transmittance of 70% were deposited by pulsed laser deposition (PLD) technique. The grown film exhibits high degree of crystallinity without need post-deposition thermal annealing as in the case of other deposition methods which would complicate large scale device fabrication. The large value of figure of merit data suggests the fact that Cd$_2$SnO$_4$ film grown by PLD are very promising materials for optoelectronic applications. The effect of laser deposition parameters on the film characteristic is underway.

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