Synthesis and Characterization of a Nano (CdO)$_{0.94}$:(In$_2$O$_3$)$_{0.06}$/Si gas Sensor

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Abstract

In this work, a (CdO)$_{0.94}$:(In$_2$O$_3$)$_{0.06}$ film was developed on a glass substrate using Q-switching pulse laser beam (Nd:YAG; wavelength 1064 nm). The quantitative elemental analysis of the (CdO)$_{0.94}$:(In$_2$O$_3$)$_{0.06}$ thin film was achieved using energy dispersive X-ray diffraction (EDX). The topological and morphological properties of the deposited thin film were investigated using atomic force microscope (AFM) and field emission scan electron microscopy (FESEM). The I-V characteristic and Hall effect of (CdO)$_{0.94}$:(In$_2$O$_3$)$_{0.06}$ thin films were used to study the electrical properties. The gas sensor properties of the film prepared on n-Si were investigated for oxidization and reduction gases.

Keywords: Gas nanosensors, (CdO)$_{0.94}$:(In$_2$O$_3$)$_{0.06}$ thin film, morphological properties, electrical property and pulsed laser deposition technique.

Introduction

In recent years, transparent thin films of conductive oxides (TCOs), such as PbO, CdO, ZnO, SnO$_2$, In$_2$O$_3$, and MoO$_3$, of semiconductor materials have been used in various applications, including transistors, optical storage devices, gas sensors, phototransistors, and photo-thermal and photovoltaic converters [1,2]. Most of the studies related to transparent conducting metal oxides were performed on anion deficient (oxygen deficient) materials and, hence, always produced n-type conductors [3, 4]. It is well known that high carrier mobility ($\mu_H$) is essential for manufacturing TCOs with good electro-optical properties [5].

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The preparation of thin films of nanometeric size is important because of their potential applications in various science and technology fields, such as electronics, optics, space, aircraft and other industries [6, 7]. Nanofilms are different from those made of either the bulk materials or single atoms [8]. These oxide films showed an extraordinary important because of their potential applications in electronics, gas sensing, and photonic devices [9].

Cadmium oxide (CdO) film is an n-type that belongs to the II - VI group, with face center cubic crystal structure (FCC) (rock-salt crystal structure) [5]. The CdO film is one of the most promising TCO semiconductors due to its high electrical conductivity and high carrier concentration, which make it useful for various applications, such as photodiodes and gas sensors [10, 11]. It is well known that the electrical properties of CdO films can be improved by the movement of interstitial cadmium atoms and oxygen vacancies [12].

Indium oxide (In$_2$O$_3$) is a significant translucent conducting oxide of intrinsic semiconductor. It has a considerable chemical stability and high electrical conductivity. Therefore, it is used for the fabrication of many types of devices, such as liquid crystal displays (LCD), light emitting diodes (LEDs), solar cells, gas sensors, and anti- reflective coatings [13-15].

Indium oxide is an n-type degenerate semiconductor with a cubic bixbyite structure [16-18]. Many researchers over the last few years have demonstrated that the metal–oxide–semiconductors can be widely used as sensors to detect various gases. The sensing properties of sensors need to be enhanced to achieve excellent selectivity with fast response and recovery time to detect low concentrations of materials in the environment [10].

In this study, the topology, morphology, and electrical and gas sensing properties of a nano (CdO)$_{0.94}$: (In$_2$O$_3$)$_{0.06}$ film prepared by pulsed laser deposition technique were investigated.

**Materials and Methods**

A pellet was prepared from 94 wt% CdO and 6 wt% In$_2$O$_3$ powders (Sigma Eldritch; 99.98 purity) with dimensions of 9 mm diameter and 5 mm thickness. Thin film of (CdO)$_{0.94}$:(In$_2$O$_3$)$_{0.06}$ was prepared using pulsed laser deposition technique with 600 mJ energy. The Nd:YAG laser of 1064 nm wavelength was operated at 6 Hz repetition rate and 7 ns pulse duration. The target-to-substrate distance was 2 cm.

The quantitative elemental analysis of the (CdO)$_{0.94}$:(In$_2$O$_3$)$_{0.06}$ thin film was examined using energy dispersive X-ray (EDX) (DeyPetronic Co.) which provides information about the composition of the prepared films. The topological surface analysis was carried out by using atomic force microscope (AFM) (AA3000 Scanning Probe Microscope SPM, tip NSC35/AIBS, Angstrom Ad-Vance Inc).

Field emission scanning electron microscopy (FESEM) is equipped with energy-dispersive produce by MIRA3 model-TE-SCAN, (DeyPetronic Co.), was used to provide morphology and elemental information.

The electrical properties of the prepared (CdO)$_{0.94}$:(In$_2$O$_3$)$_{0.06}$ film were studied using the measurements of I-V characteristics and Hall effect. The I–V measurement was taken in the dark and in room light at room temperature (RT) using a system that consists of a Keithley source meter, which is used as the electrode contact material for the film. Two strip contacts were made by the deposition of aluminum on the prepared film surface, using the thermal evaporation technique. The film contact configuration had 1 cm length and 1 cm width. Silver paste was used to fix the two contact wires.

Two main parameters were taken into account throughout the fabrication of (CdO)$_{0.94}$:(In$_2$O$_3$)$_{0.06}$/n-Si gas sensor, namely the response and recovery time. The testing system for the proposed gas sensor consisted of cylindrical stainless steel test chamber. It has an inlet for allowing the tested gas to flow in, along with an air admittance valve to allow the flow of atmospheric air after evacuation. A multi-pin feed through was used at the base of the chamber to allow the electrical connections to be established to the hot plate heater, K-type...
thermocouple, and sensor electrodes. A PC-interfaced digital multimeter (UNI-T UT81B) and a laptop PC were used to record the variation of the sensor resistance when exposed to the mixing ratios of air-NO₂ or H₂S gas at various operating temperatures (RT, 323, 373, 423, and 473 K).

Results and Discussion

The results of the quantitative elemental analysis of the (CdO)₀.₉₄:(In₂O₃)₀.₀₆ thin film are shown in Figure 1, which were deduced from data measured by using the EDX technique. The values of the constituent elements of the prepared film were 8.0, 12.6, and 79.4 wt.% for In, O, and Cd, respectively. No other elemental peaks appeared in the EDX spectrum, which indicates the high purity of the prepared thin film [19]. It can be observed that oxygen deficiency may enable the sample to adsorb a large amount of oxygen species, which is one of the reasons of the improved electrical conductivity of the films [20].

![Figure 1-Quantitative elemental analysis of (CdO)₀.₉₄:(In₂O₃)₀.₀₆ thin film](image)

The nanostructured (CdO)₀.₉₄:(In₂O₃)₀.₀₆ thin film were topologically characterized using the atomic force microscope technique. Figures 2 (a and b) show the two and three-dimensional images, respectively, whereas Figure 3 presents the distribution of granularity accumulation of the prepared (CdO)₀.₉₄:(In₂O₃)₀.₀₆ thin film deposited on a glass substrate at room temperature. One can observe clearly that the film exhibits a granular structure, distributed almost homogeneously on the surface. The small spherical grain agglomerates are uniformly distributed in shape and size along the film surface. Also, one can notice that the film possesses a high grain density distribution with tightly packed grains [7]. The fine topology and roughness of the film were observed by other researchers [10]. The root mean square (RMS), roughness, peak to peak, and average grain size values for the CdO₀.₉₄: In₂O₀.₀₆ thin film were found to be 25.1nm, 21.2nm, 101.1nm, and 88.7 nm, respectively. It is clear that the prepared film has a high roughness value, indicating that it possesses a high specific surface area of the sensing material (maximum roughness). This outcome usually has positive effects on the gas-sensing performance [10].
Figure 2- AFM images for (CdO)_{0.94}(In_{2}O_{3})_{0.06} thin film a- 2D image, b- 3D image.

Figure 3- Granularity accumulation distribution for (CdO)_{0.94}(In_{2}O_{3})_{0.06} thin films.

Field emission scanning electron microscopy (FESEM) images of the prepared (CdO)_{0.94}(In_{2}O_{3})_{0.06} thin film are shown in Figure 4. It is clear that the particles are in the nano-size with a spherical structure. They are uniformly distributed and highly agglomerated in nature, due to the aggregation or overlap of smaller particles. The highest particle size is 183.1 nm, whereas the lowest is 24.56 nm [21].
Figure 4-FESEM images for (CdO)_{0.94}:(In_2O_3)_{0.06} thin film.

I–V measurement of the prepared (CdO)_{0.94}:(In_2O_3)_{0.06} film was recorded in the forward and reverse bias at RT in the dark and room light, within a voltage range of 1.0 to -1.0 V, as displayed in Figure 5. As shown in this figure, the relation between the current and the applied voltage is linear, and nearly symmetrical in nature. This indicates that aluminum forms Ohmic contacts for the (CdO)_{0.94}:(In_2O_3)_{0.06} thin film. This result is in line with other publications [22].

Hall coefficient (R_H), carrier concentration (n_H), carrier conductivity, and Hall mobility (\mu_H) were calculated from the measurement of Hall effect for the (CdO)_{0.94}:(In_2O_3)_{0.06} thin film deposited on a glass substrate. The n_H and \mu_H values for the prepared film were calculated by using the following relations [23]:

\[ n = \frac{1}{eR_H} \tag{1} \]
\[ \mu_H = \frac{\sigma}{R_H} \tag{2} \]

where e is the electronic charge and \sigma is film conductivity.
Hall measurement showed that the prepared film has a negative Hall coefficient, i.e. it has n-type charge carriers. This might be due to the fact that CdO has defects, such as interstitial cadmium atoms and oxygen vacancies. These defects can be easily ionized and the electrons induced by this process can contribute to the conduction of electricity, causing the film to act as an n-type semiconductor [10, 24]. The carrier concentration of (CdO)_{0.94}(In_{2}O_{3})_{0.06} film is 5.253 x10^{19} cm^{-3} and the sheet concentration is 2.101 x10^{15} cm^{-3}. The mobility (μ), resistivity, and conductivity values of the film were found to be 2.367 cm²/V.s, 5.021 x 10^{-2} Ω.cm, and 19.92 S.cm, respectively.

The mechanism of sensing is based on the changes in the resistance of the film, which is controlled by gas species. The sensitivity (S) of the n-type metal oxide semiconductor is defined as the ratio of difference between the surface resistance of the film in air (Rₐ) and test gas (R₉) to its resistance in air or gas, as shown in the following equations [7, 25]:

\[ S = \left| \frac{R_a - R_g}{R_a} \right| \times 100\% \quad \text{for oxidization gases} \]  
\[ S = \left| \frac{R_a - R_g}{R_g} \right| \times 100\% \quad \text{for reduction gases} \]  

The temperature is an important parameter for gas sensing materials and the design of the sensor. The response time (t_{res}) is defined as the time required to reach 90% of the response signal, whereas the recovery time (t_{rec}) denotes the time needed to recover 90% of the original baseline signal, as extracted using the following relations [7]:

\[ \text{Response time} = \left| t_{gas(on)} - t_{gas(\text{off})} \right| \times 0.9 \]  
\[ \text{Recovery time} = \left| t_{gas(\text{off})} - t_{gas(on)} \right| \times 0.9 \]

where \( t_{gas(\text{on})} \) is the time when the gas is on and \( t_{gas(\text{off})} \) is the time when the gas is off.

Figures 6 and 7 illustrate the sensing properties for (CdO)_{0.94}(In_{2}O_{3})_{0.06} thin film deposited on n-Si substrate at different operation temperatures (RT, 323, 373, 423, and 473 K) for the reducing gas (H₂S) and oxidization gas (NO₂), respectively. For the reducing gas, Figures 6a-d show a decrease in the resistance value when the gas is on, then it increases when the gas is off. For the oxidization gas, the operation is reversed, i.e. a decrease in the resistance value when the gas is off, followed by an increase when the gas is on, as shown in Figures 7 a-e. The figures show the variation of resistance as a function of time with on/off gas for
(CdO)$_{0.94}$: (In$_2$O$_3$)$_{0.06}$/n-Si sensor. Figures 8 and 9 a, b, c show the values of sensitivity, response time, and recovery time for the prepared sensor at different operation temperatures for H$_2$S and NO$_2$ gases, respectively. One can draw from these figures the best conditions that should be used to fabricate the gas sensor. Also, one should highlight the role of the operating temperature, as far as gas-sensor sensitivity is concerned, for detecting gases in the environment. The highest value of sensitivity of the prepared sensor for H$_2$S gas was 51.9 at 373 K operating temperature, with equal values of response and recovery time (0.9s). Whereas for the sensing of NO$_2$, the sensitivity value was 93.9 at RT, with 3.6 sec response time and 6.3 sec recovery time. Hence, the prepared gas sensor is more sensitive to oxidizing than reducing gases.
Figure 6- Resistance vs. time for (CdO)$_{0.94}$:(In$_2$O$_3$)$_{0.06}$ /n-Si sensor for H$_2$S gas at different operating temperatures; a-RT, b- 323K, c- 373K, d-423K.
Figure 7-Resistance vs. time for (CdO)_{0.94}:(In_{2}O_{3})_{0.06} /n-Si sensor for NO\textsubscript{2} gas at different operating temperatures; a- RT, b- 323K, c- 373K, d- 423K, e-473K.
Figure 8-Variations in (a) sensitivity, (b) response time, and (c) recovery time for \((\text{CdO})_{0.94}(\text{In}_2\text{O}_3)_{0.06}/\text{n-Si}\) sensor of H$_2$S gas at different operating temperatures.

Figure 9-Variations in (a) sensitivity, (b) response time, and (c) recovery time for \((\text{CdO})_{0.94}(\text{In}_2\text{O}_3)_{0.06}/\text{n-Si}\) sensor of NO$_2$ gas at different operating temperatures.
Conclusions
A thin film of (CdO)$_{0.94}$:(In$_2$O$_3$)$_{0.06}$ was successfully deposited on a glass substrate using the pulsed laser deposition technique at room temperature. The quantitative elemental analysis of the film demonstrated the presence of the constituent elements of In, O, and Cd. The topology of the prepared film displayed a granular structure and an almost uniform dimension distributed over the film. The film morphological analysis showed spherical grains. Aluminum is used to form Ohmic contacts for the (CdO)$_{0.94}$:(In$_2$O$_3$)$_{0.06}$ thin film. The prepared film is n-type with $5.253 \times 10^{19}$ cm$^{-3}$ carrier concentration and low mobility. The (CdO)$_{0.94}$:(In$_2$O$_3$)$_{0.06}$/n-Si gas sensor possesses higher sensitivity for the oxidizing gas of NO$_2$ than that for the reducing gas of H$_2$S.

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