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Evaluation of an Nd doping effect on characteristic properties of tin oxide

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ABSTRACT

In the present work, transparent and conductive Nd doped SnO_2 thin films were deposited via spray pyrolysis. Crystallographic, morphological, optical and electrical characterizations of SnO_2 were researched as a function of Nd doping. The XRD analysis indicated the films had tetragonal cassiterite tin oxide structure and (211) preferential direction for NdTO-0, NdTO-1, NdTO-2 and NdTO-3 samples changed to (110) plane for NdTO-4 and NdTO-5 samples. The crystalline size and strain analysis were made by using a Williamson–Hall method. The SEM micrographs showed that all films had homogenously scattered pyramidal and small densely nanoparticles. The optical analysis indicated optical band gap value of undoped film increased with 1 at% Nd doping and then it decreased with more Nd content. The Hall measurements indicated that the highest electrical conductivity was obtained for 2 at% Nd doping content.

1. Introduction

Until today, transparent conductive oxide (TCO) materials such as SnO_2, In_2O_3, ZnO, TiO_2 have attracted a major attention [1,2]. TCOs have been wide-spread used in solar window materials [3], heat reflectors [4], gas sensors [5], Li-ion batteries and dye-sensitized solar cells etc. owing to their high electrical conductance, good optical transmittance in visible region and reflectance in infrared region, chemically inertness and mechanical rigidity [6,7]. Although Al doped ZnO (AZO), F doped SnO_2 (FTO), indium tin oxide (ITO) have commercially sold in the industrial markets as well as their usage in various devices, a lot of studies are still being made to fabricate more efficiency TCO materials. Tin oxide, one of the first transparent conductors [8,9], is a degenerate n-type semiconductor because of intrinsic defects (O vacancies or Sn interstitials) [10–13] and its properties can be highly tailored with suitable dopant elements. In earlier studies, SnO_2 structure has been doped with various dopant elements such as antimony (Sb), niobium (Nb), vanadium (V), fluorine (F), molybdenum (Mo), cadmium (Cd), indium (In), aluminum (Al), yttrium (Y), boron (B) and iron (Fe) [1,3,13,14–22] and the effect of these elements on some TCO characteristic properties of SnO_2 has been investigated. As a result of these studies, it has been found that effectual displacement of Sn^{4+} and O^{2-} ions in SnO_2 structure by A^{x+} ($x>4$) and B^- ions can improve electrical conductivity and optical transparency. Neodymium (Nd) can be considered as another dopant element for SnO_2 structure. When SnO_2 is doped with neodymium, if Sn^{4+} ions [23] are replaced by Nd^{6+} ions like Mo and W [9,14,15, 24–26], they will contribute two free electrons to SnO_2 structure. Thus, they bring about an improvement in electrical and optical properties.

In the literature, there are a few studies about Nd doped SnO_2 structure. The gas sensing properties of Nd doped

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SnO_2 powders were investigated by Shinde et al. [27]. Rinnert et al. [28] investigated the photoluminescence and conductivity properties of Nd doped SnO_2 thin films fabricated by electron beam evaporation. Joseph et al. [29] also made a study on investigation of structural, electrical and optical properties of Nd doped SnO_2 films. For their study, a vapor deposition technique which is similar to spray pyrolysis has been used to deposit Nd doped SnO_2 thin films. Unlike spray pyrolysis, at first $SnCl_2 \cdot 2H_2O$ salt has thermally been evaporated to create $SnCl_2$ vapor and then $SnCl_2$ vapor sprayed on preheated substrates by means of air pomp. However, in a spray pyrolysis process, solutions containing of precursor material are pulverized on substrates [30]. Because there are very limited studies on Nd doping on SnO_2, the study on Nd doped SnO_2 thin films (NdTO) is very essential to figure out clearly the effect of Nd dopant on features of tin oxide. Therefore, in the present study, it is aimed to fabricate NdTO films and explore the influence of Nd content on the crystallographic, morphological, electrical and optical characteristics of tin oxide. And this study has been the first work on deposition of NdTO films with spray pyrolysis.

2. Materials and methods

2.1. Synthesis of NdTO thin films

Nd doped SnO_2 thin films with different Nd doping contents from 0 at% to 1 at% in step of 1 at% were deposited by a spray pyrolysis technique. 0.7 M tin (II) chloride dehydrate ($SnCl_2 \cdot 2H_2O$) and 0.7 M neodymium (III) chloride hexahydrate ($NdCl_3 \cdot 6H_2O$) salts dissolved in ethanol solvent were used to be SnO_2 starting and Nd doping materials, respectively. These solutions were utilized in the required amounts in order to prepare undoped and 1 at%, 2 at%, 3 at%, 4 at%, 5 at% Nd doped SnO_2 thin films. The microscopic glasses with dimensions of 1 mm × 1.5 cm × 1.5 cm were used to be substrate. The substrate temperature (500 °C), nozzle–substrate distance (40 cm), the flow rate of filtered carrier air (1.5 ml/min.), and spray solutions quantity (30 ml) are constant spray pyrolysis deposition parameters. The undoped, 1 at%, 2 at%, 3 at%, 4 at% and 5 at% Nd doped SnO_2 films were named to be NdTO-0, NdTO-1, NdTO-2, NdTO-3, NdTO-4 and NdTO-5, respectively.

2.2. Characterization of NdTO thin films

The micro-structural investigations of films were made by X-ray diffraction (XRD) measurement at room temperature by using a Rigaku/Smart Lab diffractometer with CuKα radiation ($\lambda = 0.154059$ nm) operated at 40 kV and 30 mA. The measurements were taken in geometry of coupled θ–2θ varied between 20° and 80° with step of 0.02°. The surface morphology of thin films was investigated with a scanning electron microscope (FEI inspect S50 SEM). The thickness of Nd doped SnO_2 thin films is measured to be about 750 nm. The optical properties of undoped and Nd doped thin films grown on glass substrates were investigated with a UV–vis spectrophotometer (PerkinElmer, Lambda 35). When the optical transmittance data were taken, a glass substrate was used as a reference. Thus, transmittance values of glass substrate without a film were extracted from the values obtained for the deposited film grown on a substrate at the same wavelengths. The electrical properties were examined with Hall measurements by using van der Pauw configuration.

3. Results and discussions

3.1. Microstructural investigation of NdTO thin films

The structural properties of NdTO films were investigated by X-ray diffraction analysis. The SnO_2 tetragonal cassiterite structure (JCPDS 41-1445) is observed from XRD graph given in Fig. 1. As seen from these spectra, non-becoming peaks of oxide phases of Sn (SnO, Sn_2O_3) and Nd indicate that Nd ions homogenously disperse in SnO_2 structure. For each peak, the inter plane distance values are calculated by Bragg's law. The matching calculated and standard values (see Table 1) obtained from JCPDS card no: 41-1445 also show that films have tetragonal cassiterite SnO_2 structure. The peak intensities of undoped SnO_2 film slightly increase with Nd doping until 3 at% Nd dopant level and then they gradually decrease with more Nd content. The texture coefficient ($TC_{(hkl)}$) value of each peak is calculated with formula [31]

$$TC_{(hkl)} = \frac{I_{(hkl)}/I_0}{(1/N)\sum I_{(hkl)}/I_0} \quad (1)$$

where $I_{(hkl)}$ and I_0 are the peak intensities from XRD graph and JCPDS card no 41-1445, respectively, and N is reflection number in XRD. Fig. 2 and Table 2 show TC values of films. TC values of (200), (210), (211), (310), (202), and (321) peaks for undoped sample are higher than one, which indicates more crystal grains than one grow at those plane [25,31]. Although TC value of (211) peak

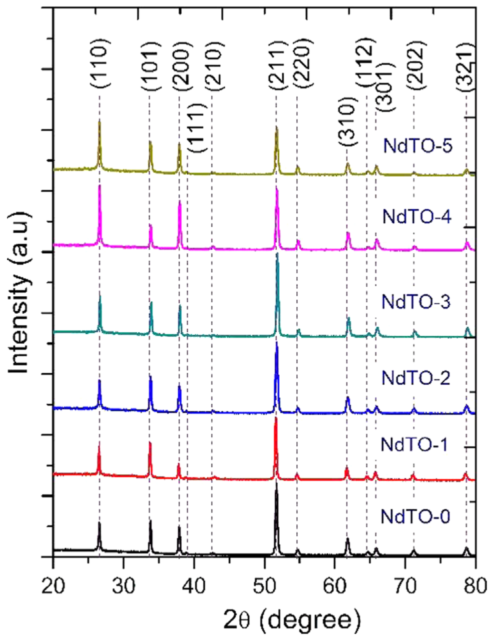

Fig. 1. The XRD spectra of NdTO thin films.