Superlattices and Microstructures 69 (2014) 175–186

Contents lists available at ScienceDirect

Superlattices and Microstructures

journal homepage: www.elsevier.com/locate/superlattices

Synthesis and characterization of Mo doped SnO_2 thin films with spray pyrolysis

Güven Turgut *, Erdal Sönmez

Department of Physics Education, Kazim Karabekir Education Faculty, Atatürk University, Erzurum 25240, Turkey
Department of Nanoscience & Nanoengineering, Graduate School of Natural and Applied Sciences, Atatürk University, Erzurum 25240, Turkey

ARTICLE INFO

Article history:
Received 4 February 2014
Accepted 18 February 2014
Available online 1 March 2014

Keywords:
Mo doping
SnO_2
Urbach energy
Spray pyrolysis

ABSTRACT

Tin oxide thin films doped with different Mo content were successfully grown by spray pyrolysis and they were characterized as a function of Mo content, changed from 0 to 3.5 at.% with 0.5 at.% step. The XRD studies showed that the films had SnO_2 cassiterite structure with (2 1 1) preferential orientation and the best crystal properties was observed for 2 at.% Mo doped sample. The SEM images indicated the films were made up of nanosized grains and it was observed pyramidal, polyhedron shaped grains on the deposited films' surfaces. From electrical and optical studies, although 2 at.% Mo doped SnO_2 film exhibited the lowest sheet resistance (39.81 Ω) and the highest IR reflective (81.77%), 1 at.% Mo doped film has the highest optical band gap (4.011 eV). The lowest Urbach energy (293 meV) and the highest figure of merit ($1.80 \times 10^{-3}\ \Omega^{-1}$) values were observed for 0.5 at.% Mo doped sample between all films. The results found in present study showed that Mo doped SnO_2 thin films is a good candidate for solar cells, IR coating and other optoelectronic and technological applications.

1. Introduction

Recently, there is a growing effort on wide band gap oxide semiconductors owing to their excellent optical, electrical, chemical, mechanical properties [1], abundance in nature, non-toxicity, low-cost

* Corresponding author at: Department of Physics Education, Kazim Karabekir Education Faculty, Atatürk University, Erzurum 25240, Turkey. Tel.: +90 442 231 40 11; fax: +90 442 236 09 55.
E-mail addresses: guventurgut@atauni.edu.tr, guventrgt@gmail.com (G. Turgut).

http://dx.doi.org/10.1016/j.spmi.2014.02.009
0749-6036/

and easy fabrication [2,3]. One of these oxide semiconductors, tin oxide-TO–SnO_2, has wide range of application areas such as gas sensing devices, transparent conducting electrodes, liquid crystal displays [4,5], window layers, heat reflectors in solar cells [6], optoelectronic devices and photo-catalysts [7]. In order to increase efficiency of SnO_2 in technological applications, many studies on fabrication of SnO_2 thin films have been made up to the present with several thin film deposition technique. The spray pyrolysis is one of the most effective methods at growing of SnO_2 thin films. It has many advantages such as inexpensive and simple experimental setup [8], easy control of chemical specimens, reproducibility and uniform and large area coating [9].

In spray pyrolysis process of SnO_2, the features of SnO_2 depend on the spraying parameters; substrate temperature, spray duration and flow rate of carrier gas, nozzle-substrate distance, ambient atmosphere, spray solution content (solvent type, doping element, chemical salt type, etc.), substrate type, etc. [10–13]. The doping with foreign atoms greatly affects the properties of SnO_2 thin films. The doping of SnO_2 structure can be achieved by replacing X^{m+} cations and Y^{n-} anions with Sn^{4+} and O^{2-} ions [14]. If $m > 4$ and $n < 2$, X and Y ions give extra free electrons to SnO_2 structure and they cause to increasing electrical conductivity and optical transparency and reflectance. The doping elements can also improve microstructural, morphological and mechanical features of SnO_2.

In literature, numerous works have been carried out on doping cation Sb and anion F into SnO_2 [15–21], and it found that Sb and F elements improved some properties of tin oxide structures. However, nowadays, SnO_2 structure have been doping with Nb, V, Mo, W elements as alternative cations and their effect on SnO_2 have been investigated. Molybdenum (Mo) has many oxidation states up to Mo^{6+} like tungsten (W) [22], and it is expected that electrical conductivity, optical transparency and reflectance of SnO_2 increase with Mo doping because of giving two extra free electrons to SnO_2 lattice. A great number of detailed studies on spray deposited Mo doped SnO_2 thin films should be made in order to investigate Mo doping effect on properties of SnO_2, because, in earlier studies, there are a few studies have been made on Mo doped SnO_2 thin films [23–33], and to our best knowledge, there is no study about Mo doped SnO_2 thin films with spray pyrolysis. Thus, we aimed to deposit Mo doped SnO_2 thin films on glass substrates with spray pyrolysis and to investigate Mo doping effect on microstructural, morphological, optical and electrical properties.

2. Experimental details

SnO_2 thin films doped with different Mo content from 0 at.% to 4 at.% with step of 0.5 at.% were prepared by an economic spray pyrolysis method. The essential amounts of $SnCl_2{\cdot}2H_2O$ and $MoCl_6$ salts were dissolved in propane-2-ol solvent contained of a few drops of HCl in order to prepare undoped (TO), 0.5 at.% Mo doped (MTO-0.5), 1 at.% Mo doped (MTO-1), 1.5 at.% Mo doped (MTO-1.5), 2 at.% Mo doped (MTO-2), 2.5 at.% Mo doped (MTO-2.5), 3 at.% Mo doped (MTO-3), 3.5 at.% Mo doped (MTO-3.5), 4 at.% Mo doped (MTO-4) spray solutions. After these solutions were prepared, they were stirred for two hours for obtaining more homogenous solution then they were sprayed onto preheated hot glass substrates, which were cleaned with acetone, methanol and deionized water in ten-minute periods. The substrate temperature (500 °C), nozzle-substrate distance (40 cm), the flow rate of filtered carrier air (1.5 ml/min.), spray solutions quantity (25 ml) were kept constant. After the substrates were deposited, they were characterized with Scanning Electron Microscope (FEI inspect S50 SEM), X-ray Diffraction (XRD) using Rigaku Miniflex II Diffractometer, four point electrical measurements, UV–VIS spectrophotometer (Perkin-Elmer, Lambda 35). All measurement were taken at room temperature.

3. Results and discussion

3.1. Microstructural characterization

The microstructural characterization of the films are made with X-ray diffraction spectra (XRD). Fig. 1 shows the XRD curves of undoped and Mo doped SnO_2 thin films. It is seen that all peaks belong to SnO_2 tetragonal cassiterite structure (JCPDS 41-1445). SnO, Sn_2O_3 and any peak belonging to Mo are