POTENTIAL APPLICATION OF SILVER-DOPED TIN OXIDE THIN FILMS IN CNT GROWTH

Hadjra Ben Haoua[1], Boubaker Benhaoua[2], Lilla Nánai[1]& Klára Hernádi[1]

[1]Institute of Physical Metallurgy, Metal Forming and Nanotechnology, University of Miskolc, Miskolc 3515, Hungary.
[2]Department of Physics, Faculty of Exact Science, University of El-Oued, El-Oued 39000, Algeria.
email: hadjra.ben.haoua@student.uni-miskolc.hu

Abstract

Carbon nanotubes (CNTs) have outstanding electronic, thermal, and mechanical properties that have made them very attractive for applications in the field of energy storage, electronics, water treatment, sensors, and composites and structural materials. However, realizing the controlled CNT growth with the required diameter, density and uniformity remains a great challenge. The support layer, which is located between the substrate and the catalyst, has a critically important role in the regulation of the catalyst nanoparticle stability, diffusion and morphology. Also, it strongly influences the shape and productivity of CNTs. In this paper, undoped and silver-doped tin oxide (SnO_2 and Ag-SnO_2) thin films were fabricated by using spray pyrolysis with the moving nozzle (SPMN) technique. Effects of Ag as doped on the structural, optical, and electrical properties of SnO_2 thin films were studied for new recommendations as a support layer to grow the CNTs. The SnO_2 and Ag-SnO_2 thin films were characterized using XRD, IR, and UV-VIS spectrophotometry analysis, as well as four-point probe measurements. Therefore, their properties to control the catalysts and the growth of CNTs will be undertaken in future studies.

Introduction

Since the discovery of carbon nanotubes (CNTs) by Iijima in 1991 [1] which marked the initiation of extensive research on their unique structural, electronic, and mechanistic properties [2,3]. These characteristics make CNTs valuable in a large variety of applications mainly in the field of electronics, storage of energy, nanotechnologies, and bio-medical devices. Nevertheless, being able to effectively control the CNTs growth in terms of alignment, distribution of diameter, density, and purity is still a key hurdle to large-scale applications [4,5]. Among the existing CNTs fabrication methods, chemical vapor deposition (CVD) seems to be the most suitable one for growing CNTs as it provides better control over growth parameters and predefined locations on an etched substrate such as Si, stainless steel, and quartz [6,7]. A critical element in the outcome of CNTs growth based on CVD is the support layer that performs several basic functions, including prevention of catalyst diffusion in the substrate, prevention of Ostwald ripening and catalyst ripening. Different deposition methods were developed to prepare support layers with exact thickness, uniformity, and precise chemical properties. The materials widely used as support layer to overcome this barrier, a diverse range of oxidized metals (for example: Al_2O_3, SiO_2, MgO, TiO_2, and ZrO_2) [3] and metallic as TiN [3] are used for this purpose. It is worth noting that alumina (Al_2O_3) has been occurred as the most effective one due to its capability to yield high-density, thermally stable, and long-life catalytic nanoparticles. Furthermore, the surface energy of the substrate is the main factor controlling the size of the catalyst particles that form on the surface at a given temperature. The analytical characterization of CNTs using techniques such as SEM, TEM, Raman and XRD is focused on, as careful analyses are crucial not only to understanding its properties but also to

evaluate the potential environmental effects [8]. Although, SnO_2 thin films are extensively investigated in the field of materials science and nanotechnology because of their large band gap (approximately over 3.6 eV) and high transparency in the visible spectrum with excellent electrical conductivity. These properties make SnO_2 films suitable for different uses in conductive transparent electrodes, optoelectronic devices and gas sensors [9]. There is no research on using SnO_2 as a support layer for CNT growth, marking a clear unexplored area. A focus on SnO_2/MWCNTs nanocomposite with its usage in different fields such as gas sensors and photocatalysis, and high-performance Li-ion battery anodes [10]. Thus, behavior of SnO_2 as support layer on growth of the CNTs needs to be investigated as recent subject.

The aim of this paper is to exhibit procedures that were employed to deposit undoped SnO_2 and Ag-SnO_2 silver tin oxide (AgTO) thin films, and the finding results of these refined thin films. The structural, optical, and optoelectrical characteristics of undoped SnO_2 and AgTO, which were characterized using XRD, IR, and UV-VIS spectrophotometry analysis, as well as four-point probe measurements. SPMN deposited thin films are the main emphasis of this part of the present work. To establish the appropriate features that make our films as relevant as possible, effects of silver doping on the properties of AgTO films will be examined.

Experimental

Tin (II) chloride dihydrate ($SnCl_2 \cdot 2H_2O$), a white crystalline solid, was used as the precursor for tin, while silver nitrate ($AgNO_3$) served as the dopant source with Ag/Sn concentrations averaged in (0 – 3) % at. Ag/Sn. Solution of tin precursor was prepared by melting 1.1282 g of $SnCl_2 \cdot 2H_2O$ in 10 mL of a mixture of solvents composed of double-distilled water and methanol in a 2:1 volume ratio. To guarantee complete solubility and clearness, a few drops of hydrochloric acid (HCl) was added. The solution was agitated for 30 minutes at room temperature to produce a transparent and clear solution. This basic solution was utilized directly to deposit SnO_2 thin films without any Ag addition, whereas Ag-doped SnO_2 thin films were achieved by addition to the mother solution the needed quantity of $AgNO_3$ to reach doping rates of 1, 1.5, 2, 2.5, and 3% at. Ag/Sn. Thin films were deposited by spray pyrolysis with a moving nozzle (SPMN) on 485 °C heated glass substrates having the follow characteristics (76.2 × 25.4 × 1–1.2 mm, TICARE). Such substrates were thoroughly cleaned with alcohol and distilled water, and then dried with a nitrogen gas stream in order to remove dust, oils, and other pollutants, to ensure a clean surface for high-quality thin film growth. Before deposition nozzle-substrate distance was fixed at 1.5 cm for all experiments.

Characterization Techniques

Deposited SnO_2 and Ag-doped SnO_2 thin films were systematically characterized. UV-Vis spectroscopy was utilized to assess the mean optical transparency (T) and estimate the optical band gap (Eg) of the films by using the Tauc's relation. The structural properties were investigated by X-ray diffraction (XRD), which gave insight into the crystalline phase, favored direction (Miller indices hkl), the lattice constants (a, b, and c), and the average crystal size (D) computed from the full width at half maximum (FWHM) of diffraction peaks by using the Scherrer equation. Fourier transform infrared spectroscopy (FT-IR) analysis was used both to confirm the chemical composition and identify characteristic absorption bands of Sn-O, O-Sn-O or Ag-O, and to verify any resulting structural modifications caused by silver addition. Lastly, the electrical performance of the films was evaluated using the four-point probe method to measure sheet resistance (R_{sh}), and the figure of merit ($\Phi = T^{10}/ R_{sh}$) was calculated by combining optical and electrical data to assess the suitability of the films as transparent conductive oxides (TCOs).

Results and Discuss of Future Work to Grow CNTs

Impregnating SnO_2 with silver (Ag) doping improves electrical conductivity and optimizes crystallization and increases oxygen vacancy concentration. Such modifications further enhance the functionality of SnO_2 films in various applications [11, 12]. Effect of silver doping (0-3% at. Ag/Sn) on SnO_2 structural, optical, and electrical characteristics was investigated using XRD and IR, UV-VIS spectrophotometry analysis, and four-point probes as seen in Fig 1. Carried out results are as follows:

1. Structural and IR Analysis

- ✓ (0-3% at. Ag/Sn) Ag doped SnO_2 thin films were polycrystalline with a tetragonal rutile structure, according to X-ray diffraction (XRD) patterns. At Ag/Sn doping, a minor additive peak of silver oxide (AgO) was seen at 2θ (29.5 and 31°). The incorporation of silver in the SnO_2 matrix was behaved by a left shift in 2θ degree of the peaks.
- ✓ Grain sizes were estimated to be between 16.071-27.304 nm on average.
- ✓ Before and after silver doped, FT-IR spectra of SnO_2 products revealed a novel Ag-O vibration mode with the well-known Sn-O vibrations which were observed at about 406-495 cm^{-1}.

2. Optical Analysis

- ✓ In the visible spectrum of 0-3% at. Ag/Sn doped SnO_2 thin films demonstrated remarkable transparency of over 70% for all silver doping concentrations, including 1.0, 1.5, 2.0, 2.5, and 3.0% at. Ag/Sn.
- ✓ Optical band gap (E_g) shows a significant drop, going from 3.76 eV for pure SnO_2 to about 3.06 eV for doped ones.

3. Electrical properties

- ✓ According to the electrical analysis, the thin films are n-type electrical conductivity which depends on silver doping concentration. For pure SnO_2 and AgTO with estimated thicknesses of 450 nm, the calculated figure of merit, Φ at λ = 550 nm showed a maximum value of around 1.427×10^{-2} (□/Ω) for 2.5% at. Ag/Sn silver doping concentration in thin films.
- ✓ Due to the high value of Φ and the low barrier for electrons to jump, Eg ~3.06 eV, AgTO may be considered preferred transparent electrodes for solar cells application.

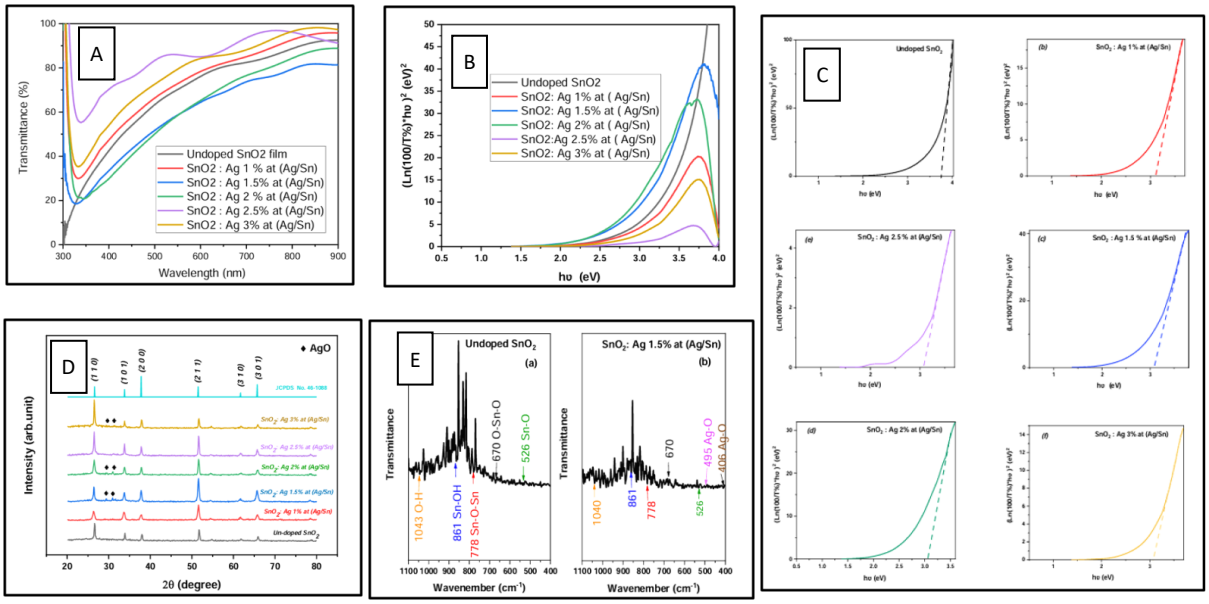

Fig.1: A) Optical transmittance plot of Ag (0–3 % at. Ag/Sn) doped SnO_2 thin films. B) Tauc relation plots gathering the feature of all samples. C) Tauc relation plots for each sample separately: a for undoped sample b, c, d, e, and f for 1, 1.5, 2, 2.5, and 3% at. Ag/Sn respectively. D) XDR patterns of Ag (0-3% at. Ag/Sn) doped SnO_2 thin films. E) FT-IR spectra of undoped and Ag-doped SnO_2 for 1% at. Ag/Sn films.

Conclusions

Growth of high-quality CNTs is strongly linked to the support layer design and geometry. The support layer works as much more than just a passive interface; it also controls the stability, diffusion, and crystallinity of the catalytic nanoparticles, which determines the structural and functional properties of the CNTs. So, clean, high-conductivity thin films made of SnO_2 have been optimized by the addition of Ag. Undoped thin films display an optical transmittance of more than 70% in the visible range, whereas the addition of Ag leads to an increase or a decrease depending on the concentration, with better enhancement at 1, 2.5 and 3% at. Ag/Sn. All the films demonstrate a polycrystalline SnO_2 tetragonal rutile structure with crystallite sizes ranging from 16 to 27 nm. FT-IR analysis verified the presence of Sn-O, O-Sn-O and Ag-O bonds. A minimum sheet resistance of 5.93 (Ω/□)is obtained at 1.5% Ag, and the maximum figure of merit 1.427×10^{-2} Ω^{-1} at 2.5% at. Ag/Sn doping. Thus, these properties of SnO_2 and Ag-SnO_2 will make it more effective and controllable for tailoring CNT growth to specific applications.

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