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Incorporation of O_2 with Ag/AgO_x nanocomposite thin films

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ABSTRACT

The effect of annealing temperature and time at oxygen atmosphere were detected for Ag films deposited by inert gas condensation (IGC) technique from Ag_2O ingot source. Investigation of the resultant Ag/AgO_x nanocomposite thin films and its incorporation with oxygen were discussed. The structure of deposited films was determined by both grazing incident in plan X-ray diffraction (GIIXD) and high resolution transmission electron microscope (HRTEM). GIIXD patterns showed only the lines of Ag nanocrystalline cubic structure with the probability of acquiring the AgO_x amorphous oxide phase with estimated particle size ranging from 7.96 to 22.2 nm. The HRTEM diffraction patterns indicated that the crystallinity decreased by increasing the annealing temperature and time in oxygen atmosphere. The HRTEM images revealed the surface morphology of crystalline particles at films annealed at 373, 473 K for 2 h and low crystallinity for films annealed at 523 K for 2 h and 5 h. The energy dispersive X-ray analysis (EDAX) data revealed the increase of oxygen percentage in Ag/AgO_x nanocomposite films by increasing the annealing temperature and time. Observed aggregations on the films surfaces increased in size as annealing temperature and time increased as seen by field emission scanning electron microscope (FESEM) images. The electrical resistivity of annealed films in O_2 atmosphere showed abrupt increase at temperature of 450 K for deposited films followed by gradual decrease. The activation energy E_a has the values of 0.86 and 0.88 eV as the annealing temperature increases from 473 to 523 K for 2 h when heated in vacuum. The optical properties showed change in its behavior from metallic to semiconductor for annealed films at temperatures $\geq$473 K. The optical band gap due to direct transition have values in the range of 0.94–1.29 eV for film of thickness 55 nm and 1.42 eV for films of thickness 25 nm. The photoluminescence PL spectra showed for all films under study the lines of silver only at ~400 nm.

1. Introduction

Nanomaterials could be either single or multiphase polycrystalline with a grain size smaller than 100 nm [1,2]. Tailoring the structure of a material down to the nano-scale creates the possibility of preparing materials with novel properties that different from its bulk counterparts [3]. Materials in the nano-range play an important role in variety of industrial

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applications. Among all noble metals, silver has attracted extensive interest due to its optical, electrical and thermal conductivity, unique qualities in terms of plasmonic abilities [4] as well as its economic using especially as thin film samples.

Moreover, the silver-oxygen system exists in several defined compounds, such as AgO, Ag_2O, Ag_2O_3, Ag_3O_4, and Ag_4O_4 [5,6]. These compounds have interesting physiochemical properties such as catalytic [7,8], electronic [8,9], electrochemical and optical properties [8] that arise from various types of crystal structures of silver oxides. This makes silver and silver oxide thin films were extensively attracted by the researchers because of their various and novel applications including photovoltaic cells [10], gas sensors [11], optical memories [12,13], photo diodes, antibacterial coatings [14], solar cells [15,16], plasmon photonic devices [4,17,18], water treatment, bioengineering, medicine and extensive use as an electrode in photography and batteries [12]. Furthermore, silver oxide thin films were employed for surface enhanced Raman spectroscopy as a substrate for molecular level detection [19–21], acts as a mask layer in magneto-optical disks to enhance the magneto optical signals [22–24] and also can be used as the storage material of CD-R [22].

Since the properties of silver nanostructure thin films mainly rely on their size and shape, many techniques have been developed to produce a wide variety of nanostructures with different characteristics [25]. Controlling the deposition and post deposition parameters will influence the structure and consequently the physical properties of nanostructured films.

The growth mechanism of metal thin films has been a little complex since the exhibition of low adhesion energy to most oxides, which is caused by weak chemical bonding. Moreover, the thermal decomposition of silver oxide into silver and oxygen is the unique characteristics which make silver/silver oxide nano-composite thin films in the view of ultra-high density optical storage applications. Silver film is known to show a non-continuous nucleation characterized by formation of islands in the initial stage of the growth [26]. This is because of the difficulty for reaching the Stranski-Kranstanov growth mode which is mandatory for obtaining a continuous thin film.

The structure, degree of crystallinity and physical properties of silver and their oxides thin films could be influenced from the employed of different deposition techniques [25] such as thermal evaporation [6,27], electron beam evaporation [28], electrodeposition [29], pulsed laser deposition [5,30], RF sputtering [31–33], DC sputtering [12,34,35], and thermal oxidation of silver films [22].

In this investigation, the inert gas condensation technique was employed for the preparation of nanostructure Ag thin films from the deposition of pure Ag_2O powder ingot. However, the structure characterization and physical properties of the prepared thin films were investigated using different techniques. A post-deposition heat treatment in oxygen atmosphere of the prepared thin films has been done to allow the detection of introducing the oxygen in silver matrix and its effect on the structure characteristics and physical properties of nanostructured films.

Our aim in the work is detecting the role of oxygen with Ag films. This goal will be achieved through controlling the preparation parameters and investigation of structure, surface morphology, electrical, optical and photoluminescence characterization of Ag/AgO_x nanostructural composite thin films.

2. Experimental

Ag/AgO_x nanocomposite thin films were acquired from films prepared using inert gas condensation (IGC) technique using thermal evaporator Edwards E-306 at Ar gas of constant flow pressure of 10^{-3} Torr and exposed to post deposition thermal treatment in pure Oxygen atmosphere of rate ~12sccm. Films deposited using ingot source Ag_2O of purity 99.99% and were thermally treated at different temperature up to 523 K and annealing times 2 and 5 h. The film thickness was maintained to have 12, 25 and 55 nm as measured by thickness monitor Edwards FTM5 attached to the evaporation deposition chamber. The preparation conditions are listed in Table 1.

The structure analysis is maintained by grazing incident in-plane X-ray diffraction (GIIXD) technique by using Philips X'Pert diffractometer system with CuKα radiation source (1.54 Å). High resolution transmission electron microscope (HRTEM) model (JEM-2100) made by Joel was used to detect the crystallinity, particle size of deposited and treated films. The field emission scanning electron microscope (FESEM) made by Philips model: FEG QUANTA 250 was used to detect the surface morphology of examined films. The evaluation of the elemental compositional analysis of the prepared thin films was evaluated by energy dispersive analysis of X-ray (EDAX) which is attached to the FESEM instrument.

The electrical resistivity 'ρ' of the films was calculated by the following relation

$$\rho = (\mathcal{R} \times L \times d/\mathcal{W}) \quad (1)$$

where $\mathcal{R}$ is the film resistance in ohm, L is the length of the film between 2 electrodes; d is the film thickness in nm and $\mathcal{W}$ is the width of the film. The resistance of annealed films was measured with thermal heating temperature inside an evacuated (10^{-2} Torr) cryostat using Keithley electrometer model 6517B. Thermocouple of k-type was placed close to the sample as a temperature sensor.

The optical measurements of thin films were obtained using optical type double beam UV-VIS-NIR spectrophotometer (JASCO model V-570) at ambient atmosphere. The photoluminescence (PL) spectra of the films is evaluated at room temperature (300 K) using spectrofluorometer made by JASCO model FP-6500 with Xenon arc lamp radiation source of 150 Watt power. The excitation and emission slit band widths are 5 nm. It could be mentioned that all measurements were carried out of the thin films at the same geometrical conditions for comparison.