Int. J. Nanoelectronics and Materials 9 (2016) 93-102

Annealing Effects on Opto-electronic Properties of Ag_2O Films growth using Thermal Evaporation Techniques

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Received 17 Jan. 2015; Revised 5 March 2015; Accepted 29 March 2015

Abstract

High quality transparent conductive silver oxide (Ag_2O) nanocrystals thin films were prepared successfully using thermal evaporation method using pure Ag metal, followed by Oxidation process under two different oxidation temperature. Optical properties show high transparency of about 70% and decrease to 55 % at lower oxidation temperature . Optical band gab of prepared film at optimum condition is about 2.88 and 2.92 eV. Surface morphology measured using AFM give a triangle like structure with average roughness of (2.65 nm). The X-ray diffraction insures the formation of polycrystalline silver oxide nanostructure thin film.

Keywords: Silver Oxide, thin film, optical properties, thermal evaporation, annealing

1. Introduction

Metal oxides in the Ag–O system, including Ag_2O, AgO, Ag_3O_4 and Ag_2O_3, constitute a fascinating group of inorganic materials [4,5]. Ag_xO films can be prepared from Ag and O when a small area is heated by an oxidation furnace under steam to a temperature above a critical value. Ag_2O has been reported to be a P-type semiconductor with a direct band gap ranging from 1.2 to 3.4 eV , due to the deviation in the stoichiometry, structure, crystalline phases and physical properties arising from the deposition technique employed [6,7]. This material has been used extensively in photography and in batteries with the chemical formula Ag_2O. Thin films of silver oxide can be prepared by various techniques , such as thermal oxidation of silver films [8], electron beam evaporation [10], pulsed laser deposition [11-13], chemical vapor deposition [14,15], electro-deposition [16,17], DC sputtering [18,19] , chemical-bath deposition [20,21], exposing the silver films to an atomic oxygen environment[22] and RF sputtering [23-25].

Interest in metal films as contacts in microelectronic devices such as silver, has increased for a wide range of applications including heat-reflecting mirrors [26], the field of flat panel displays [27], anti-reflection coatings [28], organic light-emitting diodes [29,30], gas sensors [31] and as contact electrodes in solar cells [32] .

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The Silver-oxygen system (Ag-O), nanocrystals and thin films have been intensively studied as promising applications in high density optical storage devices, gas sensors for the detection of carbon monoxide and ammonia, catalysts for ethylene and methanol oxidation. Photovoltaic cells, as important components in optical memories, photo diodes, antibacterial coatings, photo catalysts [33] plasmon photonic devices [34] , as well as photovoltaic materials and, as active cathode materials in silver oxide/zinc alkaline batteries[35].

An increase in the number of applications of silver (Ag) thin films have been recognized in recent years due to their unique optical, electrical and mechanical properties compared to those of bulk materials. However the desired properties for silver films which are used as metallization contacts are as follows: 1- Low specific resistivity. 2- Good thermal stability. 3- High uniformity across the flat substrate. 4- Low particle contamination. 5- Good adherence to the substrate. 6- Low manufacturing costs.

N.A.A. Al-Tememee in 2013[36] used spray pyrolysis to prepared CdS nanocrystilline films , followed by structural, optical charechtrization. A.J.M.Al-Jabiry et al in 2014 [37] used spray pyrolysis methods for other nanocrystilline film preparation, after which structural, optical and morphological properties were investigated.

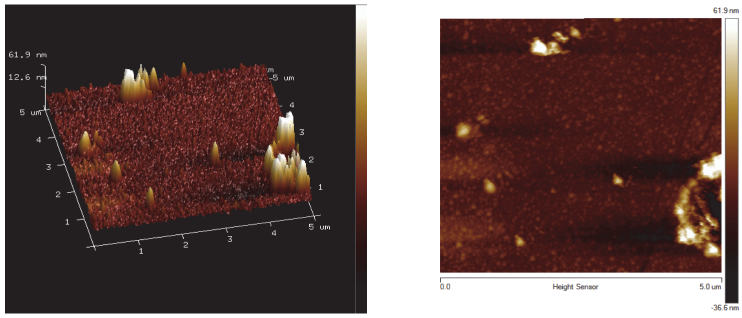
Nanocrystilline Silver oxide thin films were obtained by thermally evaporated silver metal on glass substrate followed by oxidation process at two different oxidation temperatures. The obtaind results proved that the performance of the films is improved by annealing at a temperature of (400 and 500)^{o}C under water steam, simulated to be the operating atmosphere of optoelectronic devices such as solar cells.

2. Experimental

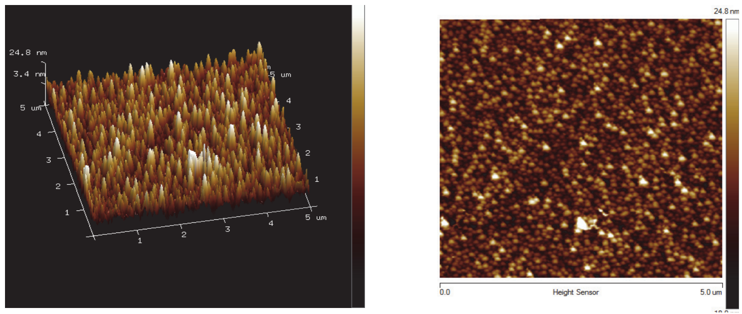
Ag films were deposited on (2.0 × 2.0) cm glass substrates with metal silver (99.99% purity) pellets by thermal evaporation. The substrates were placed in a sample holder and kept at a distance of 25 cm from the evaporation source. The substrate holder was connected to an electric motor to rotate the substrate during the deposition process to achieve uniform film. The electrical current for evaporation was from 120 to 150 A and the deposition pressure was 2.0 × 10^{-5} Torr. The thickness of the all deposited films was 150 nm. The oxidation process was carried out at (400 and 500) C for 2 h under steam and oxygen (oxidation annealing) to form silver oxide films. The crystalline structure prepared films were examined by X-ray diffraction (XRD) , U-V visible and AFM measurements . The structural evolution of the as-prepared thin films was examined using a high-resolution X-ray diffraction (HR-XRD) device , specifically referred to as the X'Pert Pro MRD diffracto - meter (PANalytical Company) system equipped with Cu-K α-radiation (of wavelength λ = 0.15418 nm) at 40 kV and 30 mA . The morphology of the films was studied using an optical microscope. The Atomic Force Microscope of these films was studied using a Shimatzu AAXOO Scanning Probe Microscope . The transmittance of the films was investigated in spectral range (200–1100) nm using UV-VIS Shimatzu double beam spectrophotometer. Optical parameters such as the absorption coefficient (α) and optical energy gap (Eg) of the deposited films were obtained by measuring the transmittance (T) and absorbance (A) spectrum in the range (280-780) nm with a double-beam Ultr-Violet (UV-vis) spectrophotometer (Shimadzu UV-Vis 1800, japan)

3. Result and discussion

The surface morphology of silver oxide thin films prepared at two oxidation temperature (400^{o}C and 500^{o}C) is shown in figure (2 a,b) , respectively .



a



b

Fig 2: AFM graph of silver oxide thin film at a-400^{o}C, b- 500^{o} C

This could be recognized in film morphology due to the substrate being heated up to 500^{o}C Fig 2-b. It is clear that the film is very uniform consisting of large islands distributed on the substrate. The uniformity can be explained by the increase in surface mobility , which is related to an increase in the annealing temperature of the incident atoms, resulting in the atom bung adsorbed on the substrate surface.

Initially, the adsorbed atoms are not in thermal equilibrium with the substrate. In this process, the adsorbed atoms interact with each other and form larger clusters. The next step in the film formation process is coalescence, in which the small particles start coalescing with each other in an attempt to reduce the surface area. This tendency to form larger particles , which is termed agglomeration is enhanced by increasing the surface mobility of the adsorbed atoms. Large particles appear related to the sublimation or particulate phenomena during the annealing process.

Further increases in the oxidation temperature is shown in Fig 2-b . A smaller particle size can sees farther symmetry and homogeneity of the film surface could is recognized in relation to other works [38] .

It was noticed that increasing the oxidation temperature greatly enhanced the surface morphology of the prepared films, and a larger particle size (smaller roughness) was obtained. This could be related to two facts; firstly, it is due to longer growth time , and secondly , due to a high probability of particle aggregation

The UV-VIS transmission spectra of thin film prepared at the two different conditions is shown in figure 3. In general, a slightly increase in the optical transmission as a function of incident light wavelength is connected to an increase in the oxidation temperature, This is related to the slight transformation of the Ag metal thin films to its oxide structure Ag_2O. and, hence , the semiconducting properties of the last one give similar results to those shown in other work [39].

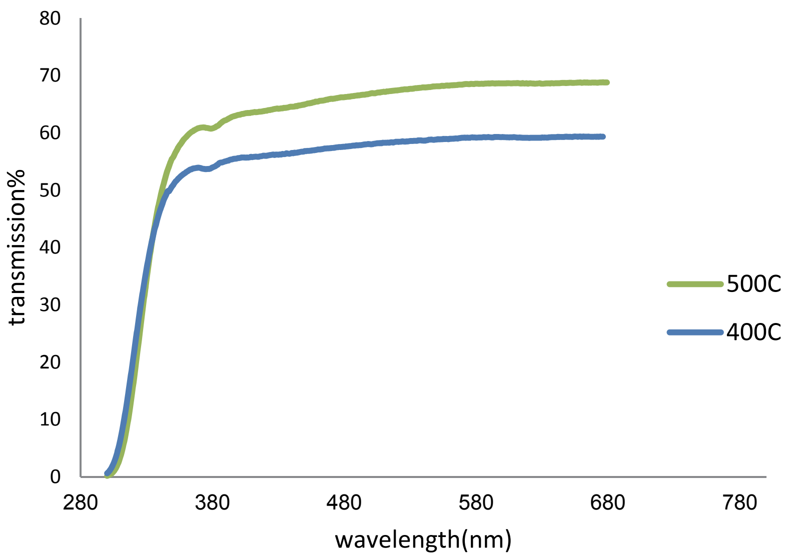


Fig. 3: optical transmission spectra of Ag2O3 at two different annealing temperature

The spectral properties of semiconductors have been shown to vary with quantization effects. The energy band gap (ΔE) is inversely proportional to the particle grain size(d) [40,41].

$$\Delta E=\left(\frac{h}{2\ me*}\right)\left(\frac{\pi^2}{d^2}\right) \qquad (1)$$

Where (ΔE) is the optical band gap shift with respect to bulk band gap (2.88 and 2.92 eV respectively), d is the particle size , h is Planck's constant and me* is the electron reduced mass as a result of a decrease in particle size.

The variation of $(\alpha h\nu)^2$ with photon energy (hν) is shown in fig. 4 . The optical band gap (Eg)of Ag_2O_3 NPs is determinate by extrapolating the linear part of $(\alpha h\nu)^2$ vs (hν) plot on the x-axis. The optical band gap was found to vary from (2.88-2.92)eV depending on the annealing temperature . The incident photon energy (E=hν) was calculated as a function of wavelength (λ) from equation:[42]

$$E_g\ (eV) = 1240 / \lambda(nm) \ldots\ldots\ldots\ldots(2)$$

The energy dependence of the absorption coefficient (α) near the band edge for band to band and excition transition may be described by Tauc formulas:- [43]

$$(\alpha\ h\nu) = B\ (h\nu - E_{gopt})^{r} \ldots\ldots\ldots(3)$$

Where B is a constant, inversely proportional to amorphousity, r is constant and may take values 2,3,1/2,3/2 depending on the material and the type of the optical transition. When the straight portion of the plot of $(\alpha\ h\nu)^{1/r}$ against (hν) is extrapolated to $(\alpha\ h\nu)^{1/r} = 0$, the intercept gives the value of the optical energy gap. The absorption coefficient (α) for each wavelength was calculated from equation: [43].

$\alpha = 2.303 \ (A / t)$ ………………..(4)

The estimated value of the grain size was found to be about 9.94 nm and 5.53nm for 400and 500 ^{o}C oxidation temperatures respectively.

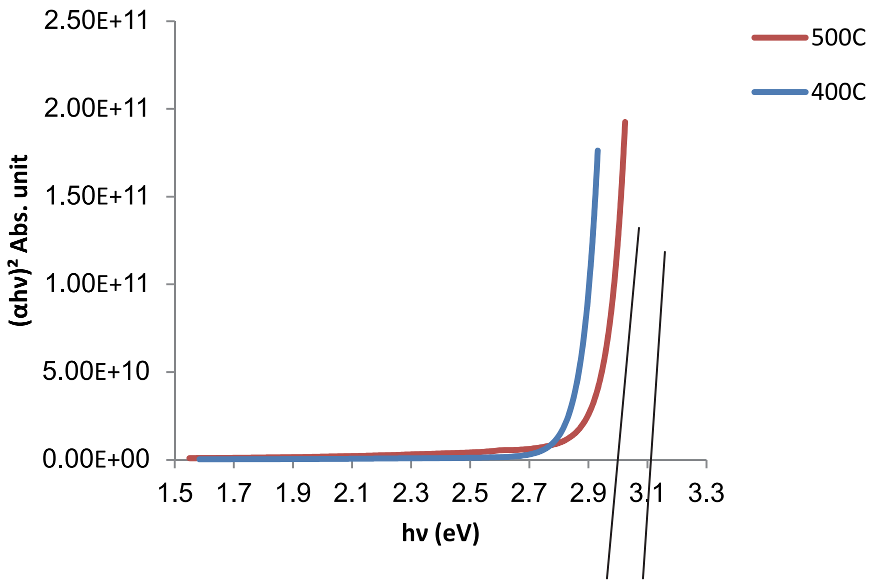


Fig. 4: The optical band gap (E_g)of Ag_2O_3

The X-ray diffraction of the nanostructure Ag_2O_3 can be seen in figure (5). The results ensured the formation of a silver oxide Ag_2O thin film which appears at two main diffraction peaks 200 and 211 as shown in figure 5 obviously; the enchantment in the crystalline structure can be shown due to increase in the oxidation temperature. These results are consistent with the results obtained by G. Saroja, V. Vasu, N. Nagarani [10] , K. T. Sullivan, Ch. Wu et al [44] and G. Wang and X. Ma et al [45].

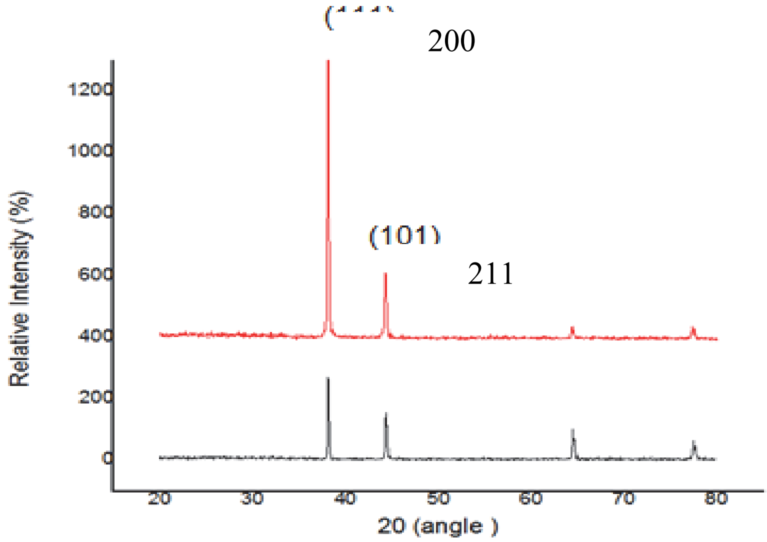


Fig. 5: Ag_2O_3 X-rd diffraction pattern

4. Conclusion

Ag_2O thin films with high optical transmittance were prepared by the thermal evaporation technique and annealing with water steam at different temperatures. The optical energy gap decreased as the film thickness increased, i.e decrease in oxidation temperature. The optical properties of the films could be changed by optimizing the growth parameters, which is an important advance in thin film technology. The crystalline grain size of the prepared film was found to be inversely proportional to the oxidation temperature. An improvement in the crystal structure was obtained by increasing the temperatures in the heat treatment process. The results obtained from this study are important and may be utilized in the field of optoelectronic technology.

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