International Journal of Nanoelectronics and Materials
Volume 11, No. 3, July 2018 [305-310]

Effect of Annealing Temperature on the Structural and Optical Properties of Silver Oxide Thin Films Prepared by Thermal Evaporation with Subsequent Annealing

Basma Chiyah and Kamal Kayed*

Department of physics, Faculty of Science, University of Damascus, Syria.

Received 26 November 2017; Revised 11 January 2018; Accepted 16 January 2018

ABSTRACT

In this study, silver oxide thin films were deposited on silicon and glass substrates using thermal evaporation techniques without oxygen atmosphere with subsequent annealing in air. The deposited films were annealed in air at 100 and 450 C° respectively. Optical properties show very low transparency at lower oxidation temperature. The transparency increased to an average value of55 % when applying annealing temperature of 450 C°. The optical band gap of Ag_2O thin films increases from 0.92 eV to 1.73 eV as the annealing temperature increases from 100°C to 450°C.

Keywords: Silver Oxide, Thin Film, Thermal Evaporation, Annealing.

1. INTRODUCTION

Silver oxide thin films gained the attention of many research groups in recent years [1-9], mainly because they exhibit significant applications in high density optical storage devices, carbon monoxide and ammonia sensors, catalysts for ethylene and methanol oxidation. Photovoltaic cells, as important components in optical memories, photo diodes, antibacterial coatings, photo catalysts [1] plasmon photonic devices [2], as well as photovoltaic materials and, as active cathode materials in silver oxide/zinc alkaline batteries[3].

The binary Ag–O system, has various phases like Ag_2O, Ag_3O4 ,AgO, Ag_4O_3 and Ag_2O_3 [4,5]. Among these different compounds, Ag_2O is the most stable [6].

.

Silver oxide thin film form is a semiconductor with a band gap ranging from 1.2 to 3.4 eV due to the deviation in the stoichiometry, structure and crystallinity phases and physical properties arising from the employed deposition technique [7]. AgO_x is a thermodynamically unstable material. It decomposes into Ag_2O at 220°C and to metallic Ag and O_2 at around 410°C.[8].

There are various methods for preparing thin films of silver oxide. One of the most common methods include that 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 [6].

*Corresponding Author: *khmk2000@gmail.com*

Thermal evaporation technique is one of the oldest techniques used for depositing thin films, which is still widely used in the laboratories and in industries for depositing metals and metal alloys. The thermal evaporation process is widely used because it is an accurate method, where the preparative conditions (evaporation rate, film thickness, surface morphology and the structural state) can be controlled. This technique has already been used for preparation of the thin films of semiconducting compounds and alloys.

Valence electrons in any conductor act like free electrons, where the collision among the electrons is similar to that one that occurs among gas molecules that is described in the kinetic theory of gases [9]. Optical properties of metals are produced because of the interaction between the fallen photons on the surface and the electronic cloud [9-12]. Optical reflectivity is considered the most important physical property of the metal layers, which generally relates to the interaction between the light and the free electrons which could be expressed by the equation of dispersion as follows [9,12]:

$$\varepsilon_f = 1 - \omega_p^2/(\omega^2 - i\omega/\tau) \tag{1}$$

Where ω_p is the plasma edge, it is a unique feature of metals expressing plasma-resonance frequency of a free electron, τ is the relaxing time, ω is the light frequency. Both electrons density and effective mass affect the plasma edge [6] and could be directly determined from the reflecting spectra where dramatic changes of reflectivity occur at the plasma edge as a result of electrons drag difference [6]. Furthermore, shifting of plasma edge towards higher wavelengths means increasing the free charge holders [6].

In this study, silver oxide films are deposited by thermally evaporated silver metal on glass and silicon substrates followed by oxidation process at two different oxidation temperatures. Oxidation processes were performed in the air using an oven. The effect of temperature on the optical and structural properties of the deposited films were studied.

2. MATERIALS AND METHODS

Ag films were deposited onto non-heated polished n-type Si (100)and glass substrates from a high-purity Ag (99.99%) target by thermal evaporation. After attaining the desired vacuum of 10-5 Torr, high current of 225 A is slowly passed across the boat such that silver evaporates and gets deposited on to substrates resulting in Ag thin films. The total duration of deposition is carried out for 15 min. The distance between source and substrate is 25 cm. The prepared thin films were annealed under atmosphere using thermal oven for two hours at 100°C (sample1) and 450°C (sample2) to form silver oxide films..

Fourier-transform infrared (FTIR) spectra were recorded by using FTIR spectrophotometer (JASCO-4200) in the range400–4000 cm^{-1}.with resolutions of 4 cm^{-1}. A silicon substrate indicated as reference. The transmittance and reflectivity measurement was performed by using a UV-Vis spectrophotometer (CARY 5000) with integrating sphere (DRA- 2500) was used to measure the total surface reflectance in the wavelength range from 200 to 800 *nm*.

3. RESULTS AND DISCUSSION

The FTIR spectrum of as grown and annealed films is shown in the Figure 1. The band is observed approximately at 513 cm^{-1} is correspond to the stretching vibration of Ag-O group. The peaks observed at 1050 and 1150 cm^{-1} are assigned to C-O stretching mode, whereas the peak observed at 2400 cm^{-1} is assigned to and C = O stretching mode. The weak band around 3700 cm^{-1} which appear in the sample1 spectrum could be originated from the presence of OH groups. This band disappears in the sample2 spectrum.

The other small peaks that appear in the sample1 spectrum are the result of the interaction between infrared light and surface plasmons. The interaction indicates that the film consists mainly of silver atoms due to the low oxidation rate during the heat treatment process.

The transmittance spectra of the Ag_2O films prepared at two different annealing temperatures, in the wavelengths range of 300–1200 *nm* are shown in Figure2. In the case of the film annealed under100°C we noticed that the films have a metallic behavior because transmittance significantly low. In the case of the film annealed under 450°C we noticed that the transmittance increased significantly due to formation of silver oxide in the film surface. On the other hand, it can be seen that the transmittance spectra shows a resonant increase in transmittance at wavelength of 326*nm* for the two samples, which can be due to the localized surface Plasmons [13].

The curves in Figure2 can be used to calculate the absorption coefficient and the optical energy gap. The optical gap was calculated for all samples using the relation [12]:

$$\alpha h\upsilon = A(h\upsilon - E_g)^2 \qquad (2)$$

Where E is the energy of the incident light, E_g is the estimate of the optical band gap and **A** is a constant. Therefore, E_g can be found by plotting the variation of $(\alpha h v)^2$ against hυ, where the extrapolation of the linear region of the curve with X-axis gives the value of the optical band gap of a thin film. Figure3 shows the method of calculating of the energy band gap in the case of sample 2.

The band gap of the Ag_2O thin film annealed at 100°C was 0.92 eV. This value gradually increased to 1.73 eV as the annealing temperature increased to 450°C.The increase in the band gap is mainly due to the oxidation of silver metal and the formation of silver oxide Ag2O which has been reported to be a P-type semiconductor [6]**.** There are other factors that control the gap such as the deviation in the stoichiometry, structure, crystalline phases, particle grain size, quantization effects, and physical properties arising from the deposition technique employed [6].

Figure4 illustrates the optical reflectivity as function of wavelength. It found that the average reflectivity of the sample1 is about 85% and the reflectivity decreased as the annealing temperature increasing to 450°Cand the decrease varies depending on the wavelength. The reason for this behavior is the decreasing of the non-oxidized metal ratio in the film which leads to decreasing the charge carrier's concentration. Nevertheless, there is a very slight shift to the plasma edge toward the low wavelengths. The reason for this is a radical change in the mechanism of the interaction mechanism between the light and the matter at the surface because the surface layer has oxidized [6].

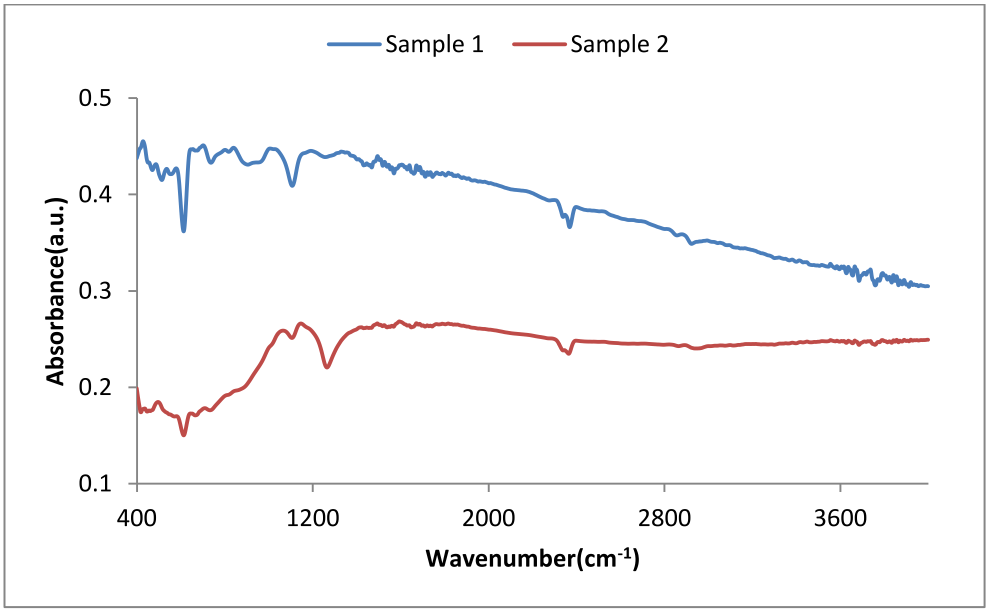

Figure 1.FT-IR spectra for the two samples.

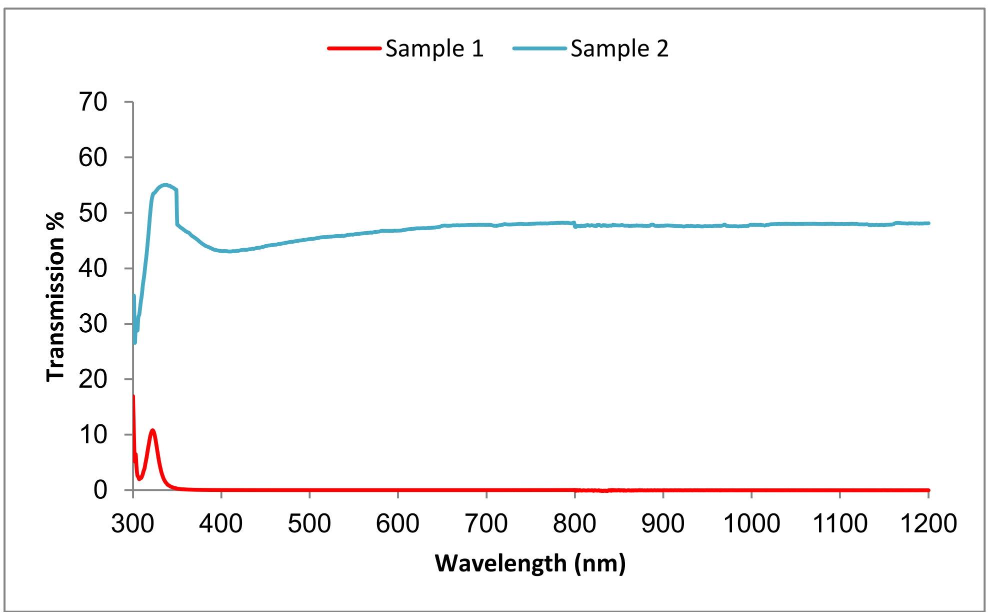

Figure 2. The optical transmissions for the prepared samples.

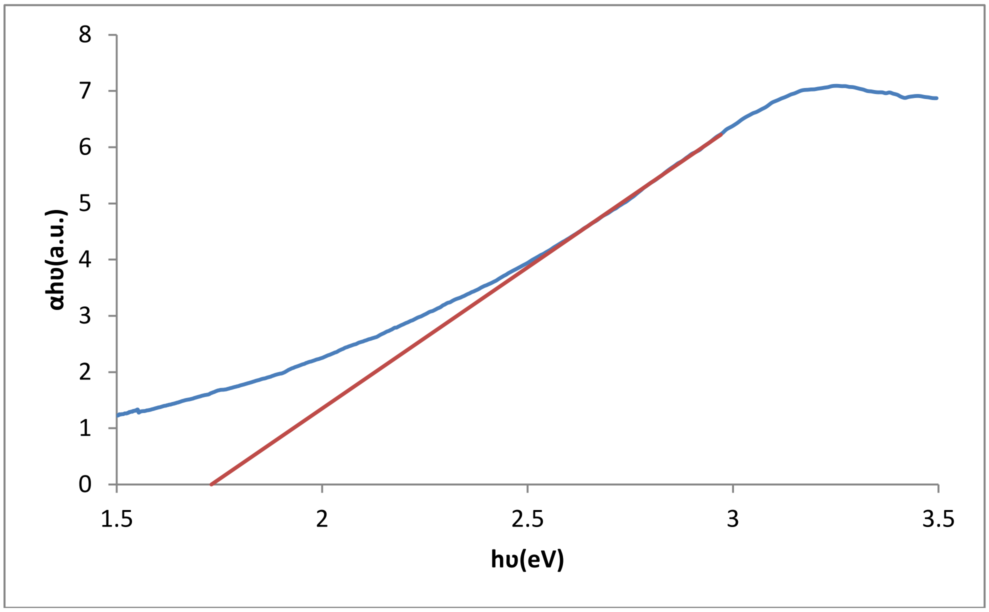

Figure 3. Variation of $(\alpha h\upsilon)^{1/2}$ against hυ for sample 2.

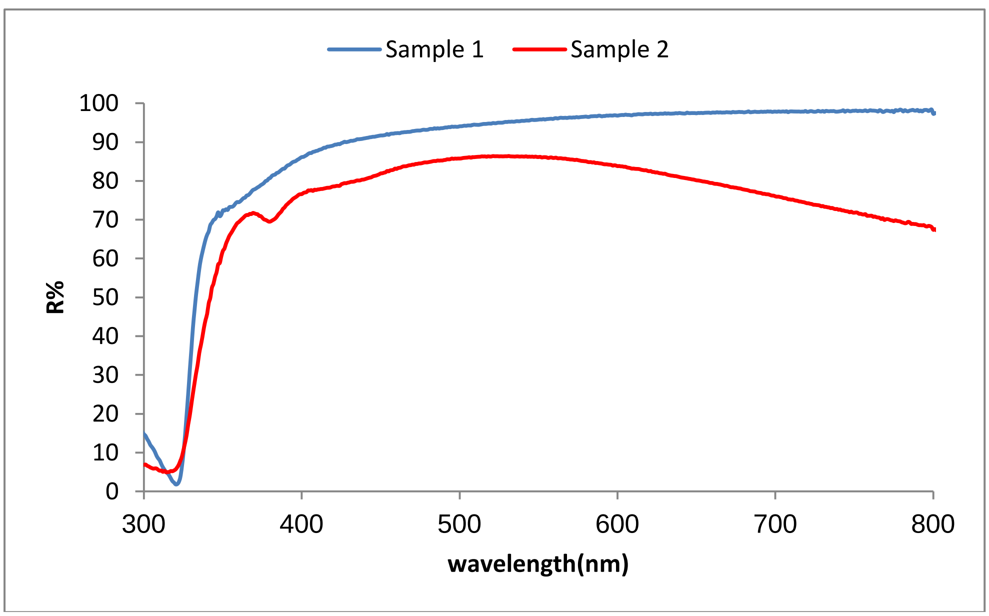

Figure 4. Reflectivity spectra for prepared samples.

4. CONCLUSION

Ag_2O thin films were successfully synthesized on silicon and glass substrates using thermal evaporation techniques with Subsequent annealing in air. The effect of post annealing temperature on the structural, and optical properties of Ag_2O thin films were investigated using FTIR and UV-Vis spectroscopes. Results showed that, the reflectivity and the interaction between infrared light and surface plasmons decreased as the annealing temperatures increased. Also the optical band gap energy of the Ag_2O thin films increased as the annealing temperatures increased.

ACKNOWLEDGMENT

The authors would like to thank Dr. F. Karabet (Department of Chemistry - Faculty of Science - University of Damascus), Dr. M.El-Daher and Mr. T. Fattom (Higher institute for Laser Research and applications), Dr. I. Aljghami, Mr. M. Odeh, and Mr. E. Abdur-Rahman (Department of Physics - Faculty of Science - University of Damascus) for their assistance.

REFERENCES

[1] G. Wang, X. Ma, B. Huang, H. Cheng, Z. Wang, J. Zhan, X. Qin, X. Zhang and Y. Dai, J. Mater. Chem**22** (2012) 21189.
[2] J. Tominaga, journal of Physics: Condensed Matter **15** (2003) 1101.
[3] W. Wei, Xuhui Mao, Luis A. Ortiz and Donald R. Sadoway, J. Mater.Chem. **21** (2011) 432.
[4] B. Standke, M. Jansen, Angew. Chem., Int. Ed. Engl. **25** (1986) 77.
[5] A.N. Mansour, J. Phys. Chem. **94** (1990) 1006.
[6] M. A. Fakhri1, Int. J. Nanoelectronics and Materials **9** (2016) 93.
[7] X.Y. Gao, H.L. Feng, J.M. Ma, Z.Y. Zhang, J.X. Lu, Y.S. Chen, S.E. Yang and J.H. Gu, Physica B, vol. **405** (2010) 1922.
[8] S. Dallek, W. A. West, and B. F. Larrick, J. Electrochem.Soc. **133** (1986) 2451.
[9] M. Born, E. Wolf, Principles of Optics, 6th edition, Cambridge University Press (2005).
[10] S. Canulescu, K. Rechendorff,K, C. Borca, N. Jones, K. Bordo, J. Schou, L. Pleth Nielsen, S. Hoffmann, R. Ambat, Applied physics letters. 1**04** (2014) 121910.
[11] L. Zhang, H C. Jiang, C. Liu, J W. Dong, P. Chow, Journal of Physics D: Applied Physics. **40** (2007) 3707.
[12] K. Kayed, Int. J. Nanoelectronics and Materials XX (2018) XX.
[13] M.F. Al-Kuhaili, J. Phys. D: Appl. Phys. **40** (2007) 2847.