Silver Oxide Nanostructure: a Study on Physical Properties at Different Chemical Interaction Time

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Abstract
Chemical bath deposition method was employed for the deposition of smooth quantum size Ag2O nanostructure thin film on glass substrate at three different chemical interaction times. The structural properties show the demonstration of Ag2O cubic structure at (002) diffraction plane. Optical properties reflect the dependence of energy gap on the interaction time with moderate band gap energy of about 2.25eV. Other physical properties such as SEM, AFM, was also investigated.

Keywords: Chemical interaction time; physical properties; Ag2O; thin films; Chemical bath deposition

Introduction
Silver Oxide is an important high conductivity p-type semiconductor, it could be found in different phases such as Ag3O4, Ag2O, Ag2O3 and AgO [1-6]. Ag2O, and AgO are the most attractive forms than other phases. Because of its important applications in gas sensors, high density optical storage devices, photovoltaic cells, photo diodes and antibacterial coatings it got attractive attention by researchers [7-12].
Many preparation method were used in the preparation and investigation of silver oxide thin films such as, vapor-liquid-solid process, radio frequency magnetron sputtering, spray pyrolysis method, Pulsed laser deposition, chemical bath deposition, etc [13-18]. the physical properties of Ag2O such as the value of the energy band gap is strongly depends on the preparation method [19-25]. Several works have been done on preparing Ag2O nanomaterial [26-29], in such a work chemical bath deposition was used by A. C. Nwanya et al for Ag2O thin film preparation using glass substrate where AgNO3 precursor, triethanolamienen were depended as a complex agent at different deposition time. Optical constant such as index of refraction and energy gap show an increase in their values with the time of deposition. IA Ezenwa et al. fabricated Ag2O film using chemical bath deposition method at different (TEA) concentration, his results showed a direct relation between complex concentration and film thickness. Effect of deposition temperature was done by Das et. al., they confirmed the effect of temperature on the microstructure of the Ag2O films using CBD; they found that grain size related inversely with temperature, while films porosity were increased. In this work, Ag2O thin films were prepared using a chemical bath deposition method at different chemical interaction time; some of the physical properties have been investigated.

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Experimental
Glass substrates were used for deposited Ag₂O films using CBD method. Before the deposition, the glass slides with (2x1.5) cm dimensions were cleaned using distilled water, methanol, and then dried in air. Silver nitrate (AgNO₃) (0.2 g), 10 ml distilled water and (2.5 ml) triethanolamine (TEA) (C₆H₁₅NO₃) were stirred under constant temperature of (50°C) until the formation of a clear solution [30, 31]. Three different interaction time of (0.5, 1, and 1.5) h were used before the vertical insertion of the glass substrate in the solution. The slide kept in the solution for additional 1h as a deposition time. [32, 33].

After films deposition, the X-ray diffraction was investigated using (Cu-ka x-ray source from Shimadzu 6000) to study the structural properties of the films. The spectrophotometer double beam from (Shimadzu) was used to study the optical characteristics. The properties of the morphological results including AFM using (SPM AA3000, Angstrom advanced, USA) instrument and SEM by employing (scanning electron microscope of AA-3000 type) instrument was investigated also.

Results and Discussions
The first Figure presents the patterns of the XRD, effect of chemical interaction time (0.5h, 1h, and 1.5h) could be shown. The Two peaks diffraction are presented firstly at (200) and secondly at (211) planes of the diffraction belong to the 2Ө= (38.6, 45) angle of diffraction which is linked to the crystals of the Ag₂O also matches the standard cards number (00-001-1041). However, (Ag₂O) silver oxide is the dominant one at (200) diffraction plane. Significant improvement in the crystalline composition of the film at (1h) interaction time can be identifiable, it can be found a similar presented results in other presented works [34-36].

The parameters of the crystal structural that defined of the structure values of the films deposited were estimated by make used the X-ray diffraction results by using the presented following mathematical expressions [37-39]:

\[
D = \frac{K\lambda}{\beta(\cos\theta)}
\]  

\[
\delta = \frac{1}{D^2}
\]  

\[
\varepsilon = \frac{\beta}{4\tan\theta}
\]

\(\beta\): (FWHM) in radius, \(D\): grain size (nm), \(K\): constant (shape factor), \(\theta\): Bragg angle, \(\delta\): density of dislocation, \(\varepsilon\): strain.

In table (1) the obtained value of structural constant could be shown, the average grain sizes found to be constant. As result the values of the structural Strain and the values of the density of structural dislocations show a very little variation with time.

The parameters that characterize the deposited film structure were characterized by an analysis of the X-ray diffraction results using the presented following formulas [40-44]:
Where the value of the $\beta$ refers to the intensity of the (FWHM) (full width at half maximum) in the radius, The value of the $D$ (nm) represents of the crystallite size, the value of $K$ are of constant value and its named of "shape factor" this factor are depended on the used wavelength, the theta angle ($\theta$) are named of "Bragg angle", the value of $\delta$ are of the "dislocation density", $\varepsilon$ are the values of the strain and finally the $\lambda$ refers to the X-ray radiation wavelength. The estimated values of the strain ($\varepsilon$), the crystallite size ($D$), and dislocation density ($\delta$) for the Nano film of the silver oxide deposited have been tabulated and listed in the first table, were found to be almost the same value. As result the calculated values of the ($\varepsilon$) strain and the ($\delta$) dislocation density shows a very little variation with time.

The images of the AFM for deposited silver oxide nano films at different times of interaction could be shown in Figure (2a-c). The films show a uniform surface consists of wide islands on the substrate, the uniform surface can be related to the surface mobility increase with the interaction time of the incident atoms, causing adsorbed of the atom bung on the substrate surface. It has been found that by increasing the interaction time the surface morphology is greatly improved with a clear variation in the particle size of prepared material. The last behavior could be related to increases in the time needed to grow the crystal, and also due to a high particle aggregation probability. The average particle size found to be at the range of quantum dots that is confirming the quantum size effect dominant on the films surface. The obtained results has been presented in Table (2). Similar works could be found elsewhere [34, 45, and 46].

FE-SEM results of the prepared Ag$_2$O samples at different time of interaction 0.5, 1, and 1.5h could be shown in figure (3a-c). It's obvious that the films where smooth, uniform and well substrate covered throughout all the regions on the substrate surface, besides the films are pinhole and cracks free. The bundle of small particles bound together to form a porous structure, this indicates the micro crystalline nature of Ag$_2$O thin films deposited as consistent with other work[30].

The optical transmission of the prepared thin films with the chemical interaction time is present in Figure (4). It is seen from the figure that the transmission of the thin film deposited for (1 h) interaction time is higher than from others. The high transmission in the film can be related to the low thickness and the complete formation of the Ag$_2$O as a good TCOs material, as shown in other work. [47].

Figure (5) presents the coefficient of absorption ($\alpha$) alteration of Ag$_2$O thin films with the wavelength (400- 1100)nm at various interaction time (0.5h, 1h, 1.5h). Using Tauc
equation [48], the energy gap of the deposited film could be estimated depending on the absorption spectrum

\[ \alpha = \frac{A(h\nu - E_g)^n}{h\nu} \]  

(7)

Where \( h \) is the plank’s constant, \( E_g \) is the energy band gap, \( \mu \) is the photon frequency, \( n \) depends on the type of transition For \( n=2 \) indirect or \( n=1/2 \) direct [49]. The results in this figure show that the absorption coefficient decrease at 1.5 hours’ time of interaction after this condition the absorption coefficient starts to increase; this is due to the peaking density increase. 1hr interaction time shows minimum absorption coefficient which is related to the maximum transmission at this condition, this may also due to enhanced in the crystallite structure [50-52].

Figure (6) shows the optical energy gap of the thin films of the silver oxide at the different time of the interaction. The estimated band gap found to range between 1.8 to 2.295 when the time varies from (0.5 to 1.5) hrs. The optical energy gap variation is attributed to the improvement in the crystalline structure quality of the films as shown previously with the x-ray diffraction results [34, 53-55].

Extinction coefficient \( k \) was also estimated depend on the optical properties using the below equation [56-60]

\[ k = \frac{\alpha\lambda}{4\pi} \]

(8)

Extinction coefficient of the Ag\(_2\)O films as a function of interaction times could be shown Figure (7) it value was increases with the optical absorption.

**Conclusion**

1 hour interaction time revealed the formation of smooth and uniform Ag\(_2\)O nanostructure thin film using chemical bath deposition method. A blue shift in the energy gap could be obtained accompanied with decreases in the particle size of prepared material as interaction time increase.

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Table (1): structural parameters of samples prepared at different interaction time.

| Interaction time (h) | 2Θ (deg) | d-spacing (Å) | hkl | FWHM β (deg) | D (nm) | (δ) *10⁻³ (lines/m²) | ε*10⁻³ |
|----------------------|----------|---------------|-----|--------------|--------|----------------------|--------|
| 0.5                  | 38.8     | 2.320 | 200 | 0.578        | 14.57  | 4.70                 | 2.3    |
| 1                    | 38.6     | 2.33  | 200 | 0.584        | 14.42  | 4.8                  | 2.4    |
| 1.5                  | 38.8     | 2.326 | 200 | 0.542        | 14.51  | 4.74                 | 2.3    |
Table (2): The obtained data from analyses the (AFM) of Ag2O nano films at the different times of interaction.

| Reaction Time | Roughness Average (nm) | Root mean square(nm) |
|---------------|------------------------|----------------------|
| 0.5h          | 0.896                  | 1.03                 |
| 1h            | 1.46                   | 1.7                  |
| 1.5h          | 0.831                  | 0.994                |
Figure (1) X-ray diffraction results of Ag₂O film as a function of time of interaction 0.5h, 1h and 1.5h and constant concentration ratio.
Figure (2): 1D, 3D AFM results of Ag₂O films prepared at (a) 0.5h, (b) 1h and (c) 1.5 hrs. Interaction time.
Figure (3a-c) FE-SEM results for Ag$_2$O as a function of chemical interaction time of (a)0.5h (b)1hand (c)1.5h.

Figure (4) optical transmission Vs. Wavelength of Ag$_2$O films at various interaction time.
Figure (5) Ag₂O optical Absorption coefficient as a function of chemical interaction time.
Figure (6) Energy band with time of interaction (a) 0.5h, (b) 1h and (c) 1.5h.
Figure (7) (K<sub>ex</sub>) as a function of chemical interaction time.