The Effect of Deposition Angle and Thickness on Structural and Optical Properties of Manganese Oxide Thin Films

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Abstract:
Manganese oxide thin films were deposited on glass substrates by resistive evaporation at room temperature. The layers were produced with electron gun evaporation method under ultra-high vacuum condition. Thickness of the layers was measured 60 and 120 nm, by a quartz crystal method. Deposition conditions such as deposition rate, vacuum pressure, incidence of angle and substrate temperature were the same for all layers. After producing pure manganese oxide layers a post-annealing method was used in the presence of a uniform oxygen flow of 300 (sccm) and at 320 °C annealing temperature. Optical reflectance and transmittance of the layers were measured in the wavelength of 350–850 nm by a spectrophotometer. Kramers–Kronig relations were used to calculate the optical constant. The influence of annealing temperature and oxygen flow on optical properties is investigated. It was found that film thickness and deposition angle plays an important role on the nanostructures as well as optical properties of layers and cause significant variations in behavior of thin titanium oxide films. The physical properties of materials were characterized by X-ray diffraction (XRD), FE-SEM, AFM, EDX, and UV-Vis techniques.

Keywords: manganese oxide; optical properties; structural properties; Kramers-Kronig relations; thin films

1. Introduction
Nanostructured transition metal oxide thin films have attracted the attention of researchers and industry due to their unique physical and chemical properties [1-4]. Their special properties are because of the finite size and high surface to volume ratio. Among these nanomaterials, manganese oxide is particularly interested due to its non-toxicity, low prices, and availability [5]. Thin film technology occupy a prominent place in basic research and the use of thin film semiconductors have attracted much interest in an expanding variety of applications in various electronic and optoelectronic devices due to their low production costs[6]. The metal oxide thin
films are an important group of the nanostructured materials. The nanomaterials of thin films can be synthesized and grown by different techniques. Thin films can be deposited upon a substrate by different common techniques such as pulsed laser deposition [7]. Chemical vapor deposition [8,9] reactive magnetron sputtering [10], spray pyrolysis[11] atomic layer deposition [12], chemical bath deposition [13], sol–gel method [14-16] and so on. Manganese oxides with various valence states and crystalline structures are currently under investigation for electrochemical, electronic, catalytic and other applications. [17–21]. Various approaches have been used to fabricate manganese dioxide, such as self-reacting micro emulsion [22], precipitation [23], room-temperature solid reaction [24], so no chemical [25], and hydrothermal methods [26]. Manganese oxide is a transition metal oxide. Cubic Mn$_2$O$_3$, tetragonal Mn$_3$O$_4$ and cubic MNO structures could be obtained from MnO$_2$ by varying the post--annealing conditions. Among these oxides, MnO$_2$ is most stable. Such varieties in their structures and hence in physical and chemical properties make them attractive to study their fundamental physical properties and technological applications [27-28]. The mean object of this research is to improve the knowledge of the relationships between the thin film deposition by physical vapor and the properties of the resulting MnO films. In this work, we discuss the effect of annealing and thickness on the properties of manganese oxide thin films, and its applications. These thin films were prepared by electron gun evaporation method. The film was characterized using UV-Vis spectrophotometer, (AFM), (XRD), FE-SEM

2. Experimental Details

Prior to physical vapor deposition, substrate cleaning is a necessary step. Prior to deposition, all glass substrates were ultrasonically cleaned in heated acetone then ethanol. The substrate holder was a disk of 35 cm in diameter with adjustable height up to 50 cm and also adjustable kippers for placing any kind of substrates. The distance between the center of the evaporation boat and the center of the substrate was 33 cm. Manganese oxide layers on the glass substrates in different thicknesses and deposition angles were made of silver-gold manganese metal target by electron gun method. The purity of manganese oxide metal was 99.97%. Manganese oxide thin films in 60 and 120 nm thicknesses were deposited on glass substrates (20×20×1 mm$^3$ cut from microscope slide) by resistive evaporation from tungsten boats at room temperature. In addition, pure manganese oxide layers in 30 nm and 90 nm thickness were produced at room temperature. After producing pure manganese oxide layers we used the post- annealing method in the presence of a uniform Oxygen flow 300 cm$^3$/s and at 320 °C annealing temperatures. Using an EDWARDS E19 A3 vacuum evaporation system with a pressure 3×10$^{-7}$ torr. The layers were deposited in ultra-high vacuum condition, using an electron gun evaporation method with the deposition rate of 0.8 A/s. Crystal and phase structure of the deposited manganese oxide layers were identified an using X- ray Pattern radiation (Cu K$_\alpha$ radiation, $\lambda=0.15406$nm), a complete 2Θ scan was made between 20 to 85. Thickness of layers was determined by quartz crystal technique (SIGMA INSTRUMENTS SQM-160-USA). To view the surface image and cross section of the samples were investigated by FE- SEM (S-4100, Hitachi, Japan). Surface physical morphology
was obtained by means of AFM. Reflectance and Transmittance of the layers was determined with UV-VIS spectrophotometer (STELLER-USA) instrument. Other deposition conditions such as deposition rate, vacuum pressure, incidence of angle and substrate temperature were same for other layers. The spectra of layers were in the range of 350–850 nm wave length. Kramers-Kronig relations were derived to calculate optical properties as R, T, n, k, ε₁, ε₂, and optical band gap energy.

3. Result and discussion

3.1. Structural properties of manganese oxide nano layers

3.1.1. X-Ray Diffraction analysis

Figure 1 shows the variation in XRD patterns of manganese oxide layers in different thicknesses and deposition angles. The results show that the samples annealed at 320°C has diffraction peaks at different angles. In figure 4(a) the crystalline phase Mn₃O₄ at an angle of 2θ=32.495 with miller's index (103) having tetragonal structure. This result is in good accordance with JCPDS Card number (00-008-0017). By increasing the deposition angle in figure 4(b) the phase transfer to Mn₂O₃ at an angle of 2θ=32.851 with miller's index (222) having cubic structure. This result is in good accordance with JCPDS Card number (00-041-1442) and phase Mn₃O₄ at an angles of 2θ=50.211 and 2θ=58.445 with miller's indexes (105) and (321) having tetragonal structures respectively. These results are in good accordance with JCPDS Card number (00-008-0017).

Figure 1: XRD images of manganese oxide layers with different thicknesses of 30 and 90 nm and vertical and 40° deposition angles with a annealing temperature of 500°C Kelvin made on the glass substrate by electron gun method with annealing temperature of 500 ° Kelvin
By increasing the thickness to 120 nm in figure 4(c) and 4(d) the crystalline phases of manganese oxide on the layer have been increased. In figure 4(c) crystalline phases Mn$_2$O$_3$ at an angle of $2\Theta=32.856$ with miller's index (222) having cubic structure. This result is in good accordance with JCPDS Card number (00-041-1442) and MnO at an angles of $2\Theta=34.34.165$, $2\Theta=40.482$, $2\Theta=58.541$, $2\Theta=70.112$ and $2\Theta=73.51$ with miller's indexes (111), (200), (220), (311) and (222) having cubic structure respectively. These results are in good accordance with JCPDS Card number (00-041-1442). By increasing the deposition angle in figure 4(d) crystalline phases of Mn$_3$O$_4$ at angles of $2\Theta=28.810$, $2\Theta=32.306$ with, $2\Theta=39.841$, $2\Theta=50.682$, $2\Theta=58.501$ with miller's indexes (112), (103), (004), (105), (321) having tetragonal structures respectively. These results are in good accordance with JCPDS Card number (00-008-0017). In general, it can be concluded that in figure 1(a-d) Increasing the annealing temperature has had a great effect on the crystallization of the layers.

3.1.2. Energy dispersive X-ray spectroscopy

Figure 2 shows EDAX diagrams of manganese oxide layers made on glass substrate at different deposition angles (vertical and 40°) and different thicknesses (60 and 120 nm) with annealing temperatures of 600 ° Kelvin.

Figure 2: EDAX images of manganese oxide thin layers produced by PVD method at vertical deposition angle and thickness 60 nm (a), deposition angle of 40° and thickness 60 nm(b), vertical deposition angle and thickness 120 nm (c), deposition angle of 40° and thickness 120 nm(d), with annealing temperature of 600 ° Kelvin
As we can see in figure 2, in general, by increasing the thickness plus the annealing temperature, the absorption rate of manganese atoms on the layer is a significant increase. Annealing temperature is one of the most important parameters for layer growth, which increases activation energy and increases the depth of oxygen penetration into the layer. By increasing the thickness under the same accumulation conditions in figures 2 (a and b) the amount and fraction of manganese atoms in the layer increased and itself absorbed more oxygen atoms in thicker layers, by increasing the deposition angle to 40° and deviation from the optimum deposition conditions in addition to less absorption of manganese atoms on the layer, the amount of oxygen impurities due to the increase of cavities and the absorption of impurities (oxygen) increased completely adapt to AFM images. As we see in general between 4 layers, in lower thicknesses, the deposition angle has less effect on growth, but with increasing thickness, the fraction of manganese atoms increases and the effect of deposition angle increases. Also, with increasing the angle of accumulation, the oxygen in the layer increases, which itself acts as an impurity factor in the growth of grains and causes the grains to become smaller.

3.1.3. Field Emission Scanning Electron Microscopy analysis

Figures 3(a-d) show images of scanning electron microscopy of field emission. As can be seen, by increasing thickness, large grains are formed on the substrate. In low thicknesses (60 nm), nucleation is observed in a smaller form. By increasing the thickness to (120 nm) growth, annexation and integration in addition to re-nucleation is observed. By increasing the deposition angle in low thicknesses (60 nm) the nucleation is observed in a smaller form. By increasing the deposition angle in high thicknesses (120 nm), growth, annexation and integration and re-nucleation with smaller grain sizes have occurred. By increasing the deposition angle in accordance with atomic force microscope images, smaller grains are formed due to the greater penetration of oxygen gas into the grains.

3.1.4. Atomic Force Microscopy analysis

In general, figure 4 shows the topography of the manganese oxide layers made on the glass substrate at different thickness (60 and 120 nm) and deposition angle (0 and 40°) and annealing temperature a 600° of Kelvin by electron gun method. Figure 4 (a), shows two-dimensional image of the atomic force microscope of the layer with a thickness of 60 nm and deposition angle of 40° and an annealing temperature of 600° Kelvin by electron gun method. As we can see, the size of the grains has increased due to the increase in thickness and the increase in the annealing temperature in this layer, coarse grains and interconnected tiny grains are quite evident. As we know, increasing the thickness cause to increases the size of the grains and increases the annealing temperature, cause to increases the activation energy of the grains and therefore causes to the surface and volumetric distribution of grains and their accession and integration. The grain size in this layer is 0.213 μm. Figure 4(b) shows the topography of the manganese oxide layer made on the glass substrate with a thickness of 60 nm and deposition
Figure 3: Field Emission Scanning Electron Microscopy of manganese oxide thin layers produced by PVD method at vertical deposition angle and thickness 60 nm (a), deposition angle of 40° and thickness 60 nm (b), vertical deposition angle and thickness 120 nm (c), deposition angle of 40° and thickness 120 nm (d), with annealing temperature of 600° Kelvin angle of 40° and an annealing temperature of 600° Kelvin by electron gun method. As is evident in figure 4 (b) of the two-dimensional image of the atomic force microscope of this layer, by increasing the deposition angle, the empty spaces between the grains are increased, and in addition, the grains are smaller and in some places larger. The grain size in this layer is 0.193 μm. Figure 4(c) shows two-dimensional image of the atomic force microscope of the layer with thickness of 120 nm and with vertical deposition angle and an annealing temperature of 600° Kelvin by electron gun method. As shown in figure 4(c) with increasing thickness, the grains grow and the surface is filled with coarse grains and due to the annealing temperature of 600° Kelvin, the accession and integration of the grains can be seen. Empty spaces are visible in the layer. The grain size in this layer is 0.230 μm. Figure 4(d) shows two-dimensional image of the atomic force microscope of the manganese oxide layer made on the glass substrate with a thickness of 120 nm and deposition angle of 40° and an annealing temperature of 600° Kelvin by
electron gun method. As can be seen, the surface is filled with coarse grains, but compared to figure 4 (c) it is smaller and the empty spaces have increased. The grain size in this layer is 0.225 μm. Increasing the accumulation angle, causing the seeds to become smaller and increasing the holes and empty spaces in the layer. Figure 5(a) shows the 3D image of the atomic force microscope of the desired layer. As can be seen, the surface is filled with interconnected duchy-shaped grains (annexation and integration) and in some places dome-shaped grains that are perfectly matched with two-dimensional images. There is an empty space between the layers. The average hardness is 6.0107 nm and the average height is 24.752 nm. Figure 5(b) shows the 3D image of the atomic force microscope of the desired layer. As can be seen, the layer becomes non-homogeneous and the surface is full of tiny grains and in some places it is coarse dome-shaped. The average hardness of the surface is 6.238 nm and the average grain size is 20.5738 nm. Figure 5(c) shows the 3D image of the atomic force microscope of the desired layer. As is evident, the surface is filled with saw-tooth and coarse grains and the empty space has been reduced. Grains have been accession and integration as a result of increased activation energy both surface and volumetric and saw-tooth grains were formed. The average hardness of the surface is 11.711 nm and the average height of the grains is 46.4536 nm. Figure 5(d) shows the 3D image of the atomic force microscope of the desired layer. As can be seen, the surface is filled with domed grains and we see less than of the saw-tooth grains seen in figure 5 (c). The average hardness of the surface has dropped dramatically to 6.3449 nm. The average height of the grains was approximately halved and reached 25.1822 nm. As we can see, in each thickness, the angle of deposition and its changes clearly shows itself and also the annealing temperature also shows its effect on the growth, size of the grains, and the formation or filling of empty spaces on the layer.

Figure 4: 2D AFM images of manganese oxide layers produced by PVD method at different deposition angles (0 and 40°) and different thickness (60 and 120 nm) with annealing temperature of 600° Kelvin
3.2. Optical properties and Kramers-Kronig relations

In this work Kramers-Kronig relations were used to calculate the phase angle $\theta(E)$ that we have explained in Kangarlou and et al. works [29, 30] extensively.

$$\theta(E) = -\frac{E}{\pi} \int_0^{E_2} \frac{\ln R(E) - \ln R(E_0)}{E^2 - E_0^2} dE + \frac{1}{2\pi} \ln \left[ \frac{R(E)}{R(E_2)} \right] \ln \frac{E_2 + E}{|E_2 - E|} + \frac{1}{\pi} \sum_{n=0}^{\infty} \left[ 4\left( \frac{E}{E_2} \right)^{2n+1} \right] (2n + 1), \quad (1)$$

Where $E$ denotes the photon energy, $E_2$ the asymptotic limitation of the free-electron energy, and $R(E)$ the reflectance. Hence, the $\theta(E)$ can be calculated. Then the real and imaginary parts of the refractive index were calculated, from which other parameters were obtained.

The results of optical properties are as follows:

Figures 6(a-b) shows the reflectance and transmittance curves of manganese oxide layers produced in this work. By increasing thickness in the vertical deposition angle, due to the completion of the layers and the disappearance of the cavities, the reflection increases and so, with the disappearance of the cavities due to the formation of the layer, the transmittance decreases. Due to the increase of the deposition angle to $40^\circ$ with increasing thickness due to the increase of depositional grains on the substrate, the reflectance has increased and due to the reduction of cavities, the transmittance has decreased. In general, according to atomic force microscopy images, the grains are broken and smaller by increasing the deposition angle. This is due to the penetration of oxygen into the depth and surface of the grains, As a result, the layer is filled with small grains, which itself increases reflection and decreases the transmittance (due to the reduction of cavities). In figure 6(c), we depict the real part of refractive index ($n$) for manganese oxide layers with different deposition angles and Thicknesses. In general at the
vertical accumulation angle, the real part of the refractive index increases due to the denser formation of the layers. By increasing the deposition angle to 40° and forming fractal layers and forming non-homogeneous layers, the real part of the refractive index has increased. In Figure 6(d) displays the extinction coefficient (k) of the layers produced in this work. In general, at vertical deposition angle, with increasing thickness and formation of complete layers by manganese oxide grains and of the much disappearance of the cavities, the imaginary part of the refractive index decreases. In addition, due to increasing the deposition angle and creating more cavities on the layer and in fact the formation of non-homogeneous layers, the imaginary part of the refractive index increases. Figures 7(a-b) shows the Real and imaginary part of dielectric constant for layers produced in this work. The real part of the dielectric constant in the vertical deposition angle increases with increasing thickness due to the formation of semiconductor complete layers of manganese oxide. That is, dielectric properties have increased. With increasing deposition angle, in addition to the formation of layers by manganese oxide semiconductor grains, empty spaces (cavities) show their effect more. As a result, the actual part of the dielectric constant increases. In general, at the vertical deposition angle, by increasing the thickness and formation of complete layers by manganese oxide grains, And from the much disappearance of the cavities, the absorption or imaginary part of dielectric constant is reduced. Also, due to increasing the deposition angle and creating more cavities on the layer and in fact, the formation of non-homogeneous layers of the imaginary part of the dielectric constant increases, so that the optical band gap ($E_g$) of the layers can be calculated with the following relationship [31]:

$$(ahv)^2 = (hv - E_g),$$

Where $hν$ is photon energy and Experimental absorption coefficient is given as:

$$\alpha = \frac{2E}{nc} k(E)$$

Where $c$ is the velocity of light and $k(E)$ is the imaginary part of refractive index. We depict the band gap energy for layers produced in this work in figure 8. Table I shows the values of band energy for the layers produced in this work. The band gap energy is generally enhanced by increasing thickness, which is also in full compliance with the dielectric properties of the layers according to previous analyses, which formed the semiconductor layers of full manganese oxide. In general, by increasing the deposition angle due to the loss of ideal deposition conditions (vertical deposition angle) and the formation of more empty spaces on the layers, the band gap energy has decreased, which is in full accordance with the analysis and dielectric constant.
Figure 6: Reflectance (a), Transmittance (b), Real part of refractive index (c) and Imaginary part of refractive index (d), curves for manganese oxide thin layers produced by PVD method at different deposition angles (0 and 40°) and different thickness (60 and 120 nm) with annealing temperature of 600° Kelvin.
Figure 7: Diagram of changes in the real part (a) and imaginary part (b) of the dielectric constant at different deposition angles (vertical and 40 °) and in thicknesses (60 and 120 nm) at a refill temperature of 600 ° Kelvin.

Figure 8: Diagram of band gap energy changes at different deposition angles (vertical and 40 °) and in thicknesses (60 and 120 nm) and at annealing temperature of 600 ° Kelvin.
Table I: Band gap energy values of manganese oxide thin layers

| Samples Name | band gap energy (eV) |
|--------------|---------------------|
| 60 nm 0°     | 3.2                 |
| 60 nm 40°    | 3                   |
| 120 nm 0°    | 3.7                 |
| 120 nm 40°   | 3.62                |

Conclusion

In conclusion, the results of the study are summarized as follows:

In this work, manganese oxide thin film was grown on the glass substrates by physical vapor deposition method and was annealed at 320°C. We studied variations in the optical and structural properties of these thin films that resulted from changing the thickness and deposition angle. In general, in atomic force microscope analysis, increasing thickness causes the layers to crystallize as much as possible and increasing the deposition angle causes phases transfers in the layers. As we can see in general between 4 layers, in lower thicknesses, the deposition angle has less effect on growth, but with increasing thickness, the fraction of manganese atoms increases and the effect of deposition angle increases. In FE-SEM analysis we can see that by increasing the deposition angle in accordance with atomic force microscope images, smaller grains are formed due to the greater penetration of oxygen gas into the grains. The optical reflectance and transmittance of the thin films at angles of deposition of (0° and 40°) and annealing temperature of 320°C, with increasing thickness, the reflection increases and the transmittance decreases. Depending on the thickness, in vertical deposition angle, extinction coefficient \((k)\) decreased and refractive index \((n)\) increased. On the other hand, extinction coefficient \((k)\) and refractive index \((n)\) increase with increasing deposition angle. The band gap energy is generally enhanced by increasing thickness, which is also in full compliance with the dielectric properties of the layers according to previous analyses. The calculated energy band gaps from optical data in this study are in good agreement with the value of other works [32-39].

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