Structural and Optical Properties for Nanostructure (Ag$_2$O/Si & Psi) Films for Photodetector Applications

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Abstract:
Ag$_2$O (Silver Oxide) is an important p-type (in chasm to most oxides which were n-type), with a high conductivity semiconductor. From the optical absorbance data, the energy gap value of the Ag$_2$O thin films was 1.93 eV, where this value substantially depends on the production method, vacuum evaporation of silver, and optical properties of Ag$_2$O thin films are also affected by the precipitation conditions. The n-type and p-type silicon substrates were used with porous silicon wafers to precipitate ±125 nm, as thick Ag$_2$O thin film by thermal evaporation techniques in vacuum and via rapid thermal oxidation of 400°C and oxidation time 95 s, then characterized by measurement of XRD, optical properties and scanning electron microscopy properties (SEM). Maximum value of photo response obtained from p-Ag$_2$O/p-PS/Si photodetector results revealed two peak sat 600 nm and 800 nm. According to the x-ray diffraction four peaks appear, (111), (200), (110) and (311) Ag, respectively, (polycrystalline film) and lattice constant of (4.077 Å). Also the results showed a sharp increasing in the absorption-wave length plot of Ag$_2$O film at UV and IR regions. The accumulation of the stars-like are semi-regular of the Ag$_2$O nanocrystals on the surface of p-type PS and the other diffuse inside the pores in a nearly uniform distribution with a different grain size on the surface. The results of the dislocation density and strain are decreased with the grain size increasing.

Key words: Ag$_2$O, Porous silicon, Structural study, Spectral Responsivity, Thermal evaporation system in vacuum.

Introduction:
Silver being diverse forms and various phases like Ag$_2$O, AgO, Ag$_3$O$_4$ and Ag$_2$O$_3$, belong to a group of inorganic materials (1-4). Experimentally, the workers found that Ag$_2$O and AgO are the most important forms in observable phases than silver oxide multivalent (Ag$_3$O$_4$, Ag$_2$O$_3$) and exhibited a high specific capacity (2,3). Several authors (5,6) have examined the preparation and properties of silver and silver oxide thin films using a variety of techniques such as radio frequency magnetron sputtering, vapor-liquid-solid process, and a spray pyrolysis method, etc. (the value of the optical band gap of Ag$_2$O strongly depends on the preparation method).

The objective of this work is to produce the nanocrystalline silver oxide films by means of thermal evaporation techniques in vacuum and via rapid thermal oxidation of 400°C and oxidation time 95 s, for Ag precipitated film on n-type and p-type wafers Si and porous Si(where the porous silicon is an affective material in optoelectronics filed due to its high absorption coefficient, low cost, simple synthesis technique and good anti-reflection coating (7,8), prepared by electrochemical etching and characterized via of XRD, SEM and optical measurement towards its application as photo detectors, physical and chemical properties of silver and silver oxide are illustrated in Table1.

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Table 1. physical and chemical properties of (Ag) and (Ag$_2$O) (9) .

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Crystal structure</th>
<th>Color</th>
<th>Melting point °C</th>
<th>Density kg/m$^3$</th>
<th>Molecular weight kg/mol</th>
<th>Lattice constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>FCC</td>
<td>Silver</td>
<td>1234.93</td>
<td>7220</td>
<td>0.107</td>
<td>4.077</td>
</tr>
<tr>
<td>Ag$_2$O</td>
<td>Pyramid-like</td>
<td>Brown-black</td>
<td>460</td>
<td>7220</td>
<td>0.231</td>
<td>4.736</td>
</tr>
</tbody>
</table>

Materials and Methods:

Silver thin films were deposited using thermal evaporation system, high purity (99.9%) silver on a clean glass slide substrate (2x2cm) at (+125nm) measured by electric balance as a thickness and crystalline wafer of p and n-type at room temperature with resistivity of (0.2-2) Ω.cm, under low pressure (~10$^{-6}$ torr), thickness about (507 μm) prepared using a rectangles wire-cut machine with areas of (1.7×1.7) cm$^2$. P-type Ag$_2$O thin film highly (111) oriented was prepared using rapid thermal oxidation system (RTO) with oxidation time 95 s, as shown in Fig. 1-a. Electrochemical etching, (anodization etching, in dark) for p-type Si wafer, while n-type was etched by using (PECE), with halogen lamp (100 W) to produce porous Si (PSi) layers, performed at room temperature with HF (40%) and high purity Ethanol in (1:1) mixture using Au electrode with 23mA/cm$^2$ applied current density for 15min for the nano size formation process where the etched area was (0.805 cm$^2$), the previously procedure is shown in the Fig.1-b. After that, thickness of 0.1 μm of Al layers were deposited on the backsides of the Ag$_2$O films using the evaporation technique which deposited on Si and Psi wafers. Photovoltaic measurements of hetero junctions were estimated. Ag$_2$O thin films were characterized by the measurement of XRD(LabX XRD 6000 SHIMADZU X-Ray diffractometer with Cu Kα radiation, wavelength 1.54059 Å, voltage 30 kV, current 15 mA, scanning speed = 4°/min), optical properties and scanning electron microscopy properties SEM (carried out by VEGA TESCAN-SEM at 20–30 kV).

Results and Discussion:

Structural Characterization of Ag$_2$O Thin Film:

The structure and lattice parameters of Ag thin films Fig. 2-a and Ag$_2$O nanostructure films Fig.2-b were analyzed by X-Ray diffractometer which contains main peaks at diffraction angle of 32.784° and 38.6156° corresponds to (111) and (101) planes with lattice constant 4.736Å. The two diffraction peaks are indexed to the pyramid-like structure and there is no trace of cubic face, which has a well matching with standard peaks (JCPDS No. 77-2307) (11,12). The sharpness of the peak appears at (111) plane mention that the crystal characteristic of the Ag$_2$O thin film amelioration with raising the oxidation temperature as shown in Fig. 2-b and listed in Table 2. Also, the crystalline quality of Ag$_2$O is greatly enhanced with smaller width of the peaks (13) and a strong diffraction planes have been taken from the same table accounts, four peaks has been appeared.

The film is polycrystalline according to the ASTM standards where (111), (200), (110) and (311) Ag, respectively, with lattice constant of 4.077 Å could be recognized. This was related to the formation of Ag thin film and such result indicates that no formation of the oxide film occurred on glass substrate (14).The crystallite size D in nm for a known X- ray wavelength $\lambda$ at the diffraction angle $\theta$ of Ag and Ag$_2$O nanostructures was calculated by using Scherrer formula(1)

$$D = \frac{K\lambda}{\beta \cos \theta}.$$
Where: $\beta$ is a full width half maximum to this wavelength and from eqs. 2, 3 a strain value ‘$\eta$’ and dislocation density ‘$\delta$’ of Ag and Ag$_2$O nanostructures films can be evaluated and listed in Table 2 (15,16).

$$\eta = \frac{\beta \cos \theta}{4}$$ ............................................. 2

$$\delta = \frac{1}{D^2}$$ ......................................... 3

These values were varied from $2.601 \times 10^{-4}$ lines$^{-2}$ m$^{-2}$ and $3.55-2.38 \times 10^{-4}$ lines$^{-2}$ m$^{-2}$ respectively, while the dislocation density of the same films were varied from $(3.136$ to $3.652) \times 10^{14}$ line m$^{-2}$ and $2.356-2.649 \times 10^{14}$ line m$^{-2}$. The results revealed that the strain and dislocation density are decreased with the increasing of the grain size (16).

Table 2. The XRD results of Ag thin films and Ag$_2$O nanostructured films.

<table>
<thead>
<tr>
<th>Thin films prepared</th>
<th>(20) degree</th>
<th>$\eta^*$ Line$^{-1}$ m$^{-2}$</th>
<th>$\delta^*$ Line$^{-1}$ m$^{-2}$</th>
<th>d (Å)</th>
<th>ASTM (h k l) plane</th>
<th>FWHM (2Ө)</th>
<th>D(nm)</th>
<th>(20) ASTM</th>
<th>d (Å) ASTM</th>
<th>Type</th>
<th>Card number</th>
</tr>
</thead>
<tbody>
<tr>
<td>at room temperature</td>
<td>38.0689</td>
<td>2.601</td>
<td>3.136</td>
<td>2.361</td>
<td>(111)</td>
<td>0.38630</td>
<td>21.6552</td>
<td>38.116</td>
<td>2.3590</td>
<td>Ag</td>
<td>04-0783</td>
</tr>
<tr>
<td></td>
<td>44.2318</td>
<td>3.520</td>
<td>6.282</td>
<td>2.046</td>
<td>(200)</td>
<td>0.62020</td>
<td>13.7593</td>
<td>44.277</td>
<td>2.0440</td>
<td>Ag</td>
<td>04-0783</td>
</tr>
<tr>
<td></td>
<td>64.4079</td>
<td>2.805</td>
<td>3.652</td>
<td>1.445</td>
<td>(220)</td>
<td>0.48640</td>
<td>19.3071</td>
<td>64.426</td>
<td>1.4450</td>
<td>Ag</td>
<td>04-0783</td>
</tr>
<tr>
<td>T=400°C, 125 nm and 95 s.</td>
<td>32.7824</td>
<td>3.553</td>
<td>2.356</td>
<td>2.691</td>
<td>(111)</td>
<td>0.30341</td>
<td>27.1466</td>
<td>32.790</td>
<td>2.7290</td>
<td>Ag$_2$O</td>
<td>41.1104</td>
</tr>
<tr>
<td></td>
<td>38.6156</td>
<td>2.383</td>
<td>2.649</td>
<td>2.283</td>
<td>(101)</td>
<td>0.33431</td>
<td>24.6223</td>
<td>38.609</td>
<td>2.3300</td>
<td>Ag$_2$O</td>
<td>19-1155</td>
</tr>
</tbody>
</table>

Optical Studies of Ag$_2$O Thin Film

As observed in other works (17, 18), the deposited structure of Ag film on glass substrate without oxygen pressure represents a purely metal film that has high reflectivities in the visible region. The film conversion from metal to diaphanous oxide due to the optical quality and crystallinity after treatment oxygen pressure can be greatly improved. As shown in Fig. 3-a which displays the absorption as a function of the wavelength (200-1000) nm, it is known that the sharp increasing of in absorption of Ag$_2$O film in UV and IR regions is due to the fundamental light absorption and by free-carrier absorption, consecutive this result is conditional with many other works (19, 20).

To date, the spectra of the optical absorption coefficient can be tested by using the next eqs. (11):

$$\alpha h\nu = A(h\nu- E_g) m$$ for $h\nu > E_g$

$$\alpha h\nu = 0$$ for $h\nu < E_g$

Where $\alpha$ is the absorption coefficient, $A$ is a constant depending on specifics of the band structure, $h\nu$ is the photon energy, $E_g$ is the absorption band gap, $m = 2$ mentions an allowed indirect transition and $m = 1/2$ mentions an allowed direct transition. The direct optical band gap was predestined by extrapolating the straight line of $(\alpha h\nu)^{1/2}$ contra the photon energy as shown in Fig.3-b and it is found to be 1.93 eV and this agrees with the result in a similar work(11).
Morphology Studies of Ag₂O Nanocrystals
Figure 4 depicts the SEM images of 125nm as a thick of Ag₂O nanocrystals deposited on n-type, p-type and PS (porous silicon), respectively. Figure 4-b shows that the accumulation of the stars-like are semi-regular of the Ag₂O nanocrystals on the surface of p-type PS and the other diffuse inside the pores in a nearly uniform distribution with a different grain size on the surface and the particles which have size less than the pore size diffuse inside the pores. This accumulation in p-type PS may be attributed to the flow current where charge carriers regularly make much better etching process than disordered matrix surrounding the nanocrystals of n-type PS as shown in Fig.4-a. Thus, the average quantum efficiency of a p-type PS layer results from a statistical distribution of high quantum efficiency nanocrystals (21).

Spectral Responsivity
Figure 5 shows the responsivity (Rₐ) variation with the wavelength of (p-Ag₂O/n-Si), (p-Ag₂O/p-Si), (p-Ag₂O/PS/n-Si) and (p-Ag₂O/PS/p-Si) Photo detectors respectively, synthesized at 15 min as an etching time and 23 mA/cm² as a current density. It can be observed from the Figure that the maximum responsivity exists at visible region and the other at the NIR region, the spectral responsivity detour of these photo detector consists of two response peaks; the first located at 560 nm due to the absorption verge of (Ag₂O/PS) Photo detector pertain. This pertain is very close to the surface and it can reveal short wavelengths (<600 nm). The second peak is located at (750 and 800 nm) due to absorption edge of (n-PS/Si), (p-PS/Si) hetero junctions respectively to reveal the NIR wavelengths (absorption of Si). From Fig. 5 it is evident that the value of responsivity has increased characteristically after the drilling process of p-type (Si) and the maximum value obtained after etching current density of 23 mA/cm² was nearly (0.17 A/W) at (λ =800 nm). While the responsivity rate of (n-PSi/Si)
photo detector reaches to about (0.15 A/W). The improvement of responsivity of Ag$_2$O/p-PS/Si photo detectors can be justified as a result of the partial dissolution of silicon which causes i) the performance of small Si nano crystals in the PS material,( ii) an increased light extraction efficiency from PS,( iii) decreasing the dark current (iii) increasing the depletion width iiiii) increasing the light absorption(22).

Figure 5. Spectral Responsivity plots for a) p-Ag$_2$O/n-Si, b) p-Ag$_2$O/p-Si, c) p-Ag$_2$O/n-PS/Si and d) p-Ag$_2$O/p-PS/Si, photodetectors.

Specific Detectivity

Figure 6 shows the specific detectivity (D*) versus the wavelength for (p-Ag$_2$O/n-Si), (p-Ag$_2$O/p-Si), (p-Ag$_2$O/n-PS/Si) and (p-Ag$_2$O/p-PS/Si) photo detectors, respectively, prepared at the same etching current density, specific detectivity depending directly on responsivity. The maximum detectivity was $5.7 \times 10^{11}$ W$^{-1}$ cm Hz$^{1/2}$ at $\lambda = 825$ nm and this value increased to $10 \times 10^{11}$ W$^{-1}$ cm Hz$^{1/2}$ after the drilling process for n-PS and the maximum D for p-Si was $8 \times 10^{11}$ W$^{-1}$ cm Hz$^{1/2}$ at $\lambda = 775$ nm and this value increased to $9.1 \times 10^{11}$ W$^{-1}$ cm Hz$^{1/2}$ for p-PS (23), this Figure is very important for IR detection since the noise current is very significant.
Figure 6. Detectivity depicts of (a) p-Ag\(_2\)O/n-Si, (b) p-Ag\(_2\)O/p-Si, (c) p-Ag\(_2\)O/n-PS/Si and (d) p-Ag\(_2\)O/p-PS/Si, photodetectors.

Conclusions:
Silver oxide thin film (high purity oxide) was formed by Thermal Oxidation and the optical properties revealed that the direct band gap of 1.93eV measured by optical absorption experiments for Ag\(_2\)O thin film was predestined and indicated to the effect of quantum size. X-ray diffraction measurement disclosed that the Ag\(_2\)O film at (400°C) and (95 s) condition has apyramid-like crystal structure and the reflection was from (111). Scanning electron microscopy (SEM) demonstrated that the Ag\(_2\)O/PS nanocrystals prepared by electrochemical etching and photo electrochemical etching processes that can give us advantageous properties of PS and that they are so important to give suspensions photodetector characteristics after deposition of Ag\(_2\)O nanostructure. The spectral response (R\(_s\)) and the specific detectivity (D') of our photodetectors has been synthesized by the absorption edge of Ag\(_2\)O and silicon, respectively.

Conflicts of Interest: None.

References:
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1. الاسماء و$r_n$ خليل 

2. السنة 

3. المراجع 

التوصيلية عالية وفجوة طاقة بصرية مباشرة قيمتها $1.93eV$. علاماً أن فجوة الطاقة $E_g = 1.93eV$. 

الخلاصة

1. ظهر نموذج القابل (p-type) لحالة توصيلية عالية وفجوة طاقة بصرية مباشرة قيمتها $1.93eV$. 

2. المراجع 

3. المفتاحية: ستارك، و톤، موسكو، ستارك، ولون