Effects of Annealing on the Structural and Optical Properties of Silver Thin Films

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ABSTRACT: Silver thin films were prepared on glass substrates using chemical bath method. The thin films were annealed at different temperatures of 100 and 200°C for 1 hour. The samples, as-prepared and annealed were characterized using X-ray diffractometer (XRD) and UV-Vis spectrophotometer. XRD results revealed that silver films present a cubic phase with (111) preferred orientation. The XRD result and analysis also revealed that the intensity of the peaks and the crystallite size increase with increase in annealing temperature. All the films showed very low transmittance within the visible region with the 200°C annealed film having the highest at 1.4%. Reflectance was found to reduce from 65% for the as-deposited film to as low as 17% for the 200°C annealed film within the visible region of the wavelength. The reflectance reduces with increase in annealing temperature. The films also showed low percentage absorbance within the UV region of the wavelength with the 200°C annealed film having the highest absorbance of 2.79%.

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Interest in metal films as contacts in microelectronic devices such as aluminium and silver, has increased for a wide range of applications including heat-reflecting mirrors (Volkonen and Karlsson, 1987), the field of flat panel displays (Meiss et al, 2009), antireflection coatings (Bouhafs et al, 1998), organic light-emitting diodes (Hofmann et al, 2011), gas sensors (Xu et al, 2000) and as contact electrodes in solar cells (Yang et al, 2011). The ability to deposit thin films of various materials is important for the fabrication of modern microelectronic devices and for enabling a variety of investigations of fundamental physical principles (Zakia et al., 2014). The advantages of the Ag thin film application on microelectronic devices 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 substrate, (6) Low manufacturing costs (Chia-Ching and Chia-Hsuanua, 2016).

Silver thin films have been studied widely because of their extensive applications in different industries and medical science. Also they are good candidate as interconnectors in electronic devices and electrical contacts in high temperature superconductor (HTSC) thin film devices (Winau et al., 1992). They can achieve unique optical and electrical properties and can have better performance relative to other metal films in optical applications. Silver layers are ideal reflecting and conducting electrodes for thin film solar cells (Hajakbari and Ensandoust, 2016). Ag thin films had been prepared by several techniques including thermal evaporation (Mohammed et. al, 2018), DC magnetron sputtering (Hajakbari and Ensandoust, 2015). In the present investigation, Chemical bath deposition was employed to prepare Ag films and the effect of annealing on the structural and optical properties of Ag films at different temperatures were investigated.

MATERIALS AND METHODS

Substrate Cleaning: Commercially available glass slides of dimension 75 mm x 25 mm x 2 mm were used as substrates for the deposition of Ag thin films. Using ultrasonic cleaning, the glass slides were successively rinsed in chromic acid, acetone and distilled water.

Silver thin films preparation: For the deposition of Ag thin films, Silver nitrate (AgNO₃), and triethanolamine (TEA) purchased from Merck were used without further purification. Silver nitrate (AgNO₃) and triethanolamine (TEA) were used as source material for Ag⁺ ion and complexing agent respectively.

0.25 g of silver nitrate (AgNO₃) solid was dissolved in 5 ml of distilled water in a 100 ml beaker. There after triethanolamine (TEA) solution was added drop wise
with constant stirring using magnetic stirrer until the initially formed precipitate was dissolved. Distilled water was added to make a total volume of 80 ml. The pH value of the bath was maintained as 8.0. The well cleaned glass substrates were slowly immersed vertically into the bath and the bath was brought to and kept at 50°C under continuous stirring.

After a period of 50 mins, the coated slides were removed from the bath, thoroughly rinsed with distilled water, and air dried. Two samples were annealed at different temperatures of 100°C and 200°C while one sample was kept as-prepared.

Structural analysis of the samples was determined using X-ray diffraction (XRD) (model ANCHOR analytical Expert PRO X-ray diffraction) using Cu Kα radiation (λ=1.5406 Å) operated at voltage of 45 kV and current of 40 mA. The optical properties of the films were examined using UV-Visible spectrophotometer in the wavelength range of 300 nm-900 nm

RESULTS AND DISCUSSION

**Structural Properties:** Figures 1-3 show the XRD pattern for the as-prepared and annealed Ag thin films deposited at 50 mins. It is inferred from the figures that all the spectra exhibit peak at 2θ equal to 37.89° corresponding to the orientation along (111) direction. In addition, weak diffraction peaks also appear at 2θ equal to 44.08° and 64.25° which correspond to orientation along (200) and (220) plane respectively, thus confirming the presence of cubic Ag phase. The results are in good agreement with the results observed by Hajakbari and Ensandoust (2015). The high intensity and sharp peaks in XRD patterns confirm the highly oriented and polycrystalline nature of the Ag films prepared in this study. It is also observed that the intensity of the peaks increases with increase of the annealing temperature.

The average crystallite size is estimated using Debye-Sherrer’s formula (Cullity, 1978)

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

Where D is the crystallite size, λ is the wavelength of CuKα radiation (λ=1.5406 Å), k = 0.9 is the shape factor, θ is the Bragg angle and β is the experimental full-width at half maximum on the respective diffraction peak. It was observed that an increase in the annealing temperature of the films introduces variations in the crystallite sizes and FWHM. These variations are shown in Table 1 for the (111) plane of the films. The table shows that increasing the annealing temperature results in Ag films with higher crystallite size and lower width of the diffraction peak (FWHM). The maximum Crystallite size is 36.97 nm when the annealing temperature is 200°C. Decrease in the width of the diffraction peaks suggests that annealing at higher temperature produces better quality crystal (Ezema Nwankwo, 2010). There is no significant change in the peaks position with annealing.
**Table 1:** Variation of the (111) Plane Crystallite Size and Full Width at Half Maximum (FWHM) of Ag thin films with Annealing Temperature.

| Annealing Temp (°C) | 2θ (degree) | Crystallite size (nm) | FWHM (degree) | Intensity (counts) | D-spac (nm) |
|---------------------|-------------|-----------------------|--------------|-------------------|-------------|
| As-prepared         | 37.89       | 26.88                 | 0.1791       | 5234.32           | 2.3         |
| 100                 | 37.90       | 36.93                 | 0.1279       | 5411.33           | 2.5         |
| 200                 | 37.91       | 36.97                 | 0.1278       | 6262.49           | 2.5         |

**Optical Properties:** Fig 4 shows the transmittance spectra for the as-prepared and annealed Ag thin films. From the figure, it can be observed that all the films, as-deposited and annealed exhibit a metallic behavior with almost zero transmittance, with the film annealed at 200°C having the highest transmittance of about 1.4% within the UV region. Also, the transmittance spectra show a resonant increase in transmittance at wavelength of about 320 nm for all films, which can be due to the localized surface Plasmons (Al-Kuhaili, 2007). Similar result was reported by Hajakbari and Ensandoust (2016).

Figure 5 shows the reflectance spectral for as-deposited and annealed Ag thin films. From the figure, it can be observed that all the films exhibit an increase in reflectance as the wavelength increases. It is also observed that the reflectance reduces as the annealing temperature increases. This is in agreement with the finding of Chia-Ching and Chia-Hsuanhsua (2016). The as-deposited film have a maximum reflectance of 65% within the UV region and 73% at the near infrared region, as compared to 200°C annealed film with 17% and 20% respectively.

**Conclusion:** The role of annealing temperature on silver thin films prepared by chemical bath deposition method has been investigated. XRD study shows that the thin films are polycrystalline in nature. It was deduced that as the annealing temperature increase, the peak of the preferred orientation and the crystallite size increases. Optical study shows that annealing increases the transmission and reduces the reflectance of the films within the visible region of the wavelength. The results showed that the material can be applied in optoelectronic devices, where it can serve as a reflection coatings.

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