The structural effects on silver nanoparticles plasma edges in optical reflectance spectra of Ag/Ag2O composites synthesized by oxygen plasma treatment of silver thin films

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Research Article

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Abstract

In this work, we present the results of a unique study that aims to detect the structural effects on the plasma edges in optical reflectance spectra of Ag/Ag$_2$O composites synthesized by treating silver thin films manufactured by thermal evaporation method with oxygen plasma afterglow. The results showed that, each of the optical reflectance spectra contains two plasma edges, the first ($\lambda_I$) belongs to the surface plasmons of the individual silver nanoparticles, and the second ($\lambda_L$) belongs to the larger silver nanoparticles. In addition, we found that the positions of the plasma edges are linearly related to the positions of the optical absorption peaks, except for high and low oxidation rates cases. On the other hand, taking into account previous work, we obtained indications that, the ratio $N_I/N_L$ may be a measure of the film's effectiveness in inhibiting bacteria.

1. Introduction

The increased interest of many research groups around the world in the synthesis and characterization of Ag/Ag$_2$O composites [1-13] is due to the unique modifications to the optical properties of silver oxide caused by the silver nanoparticles that are mainly related to the surface plasmon resonance (SPR) of silver nanoparticles [8]. The resonance effect occurs due to the interaction of the incident light with the electron density surrounding AgNPs [8].

In our previous work [14], we used oxygen plasma afterglow to treat silver thin films for the preparation of high quality Ag$_2$O thin films. The optical and structural properties of the prepared samples were investigated. The obtained results showed that, exposing silver thin films to oxygen plasma leads to a monocrystalline structure of cubic-Ag$_2$O phase. We found that, the silver oxide content increases with increasing of the plasma power in the region from 250 W to 1000 W. Otherwise, the treatment with plasma power of 1250 W leads to a decrease in the intensity of this peak. We also found that, the plasma power has significant effects on the characteristics of all plasmon resonance peaks (intensity, position and spectral width). On the other hand, a slight degradation of the individual silver nanoparticles plasmon peaks was recorded. It has been suggested that this decomposition occurs because of the mutual interaction between the individual silver nanoparticles located near Ag$_2$O grain shell and the larger Ag nanoparticles located in the neighboring grains. The results also showed that the degradation is degree related to the silver oxide grain size.

Optical reflectivity is considered one of the important physical property of the metal layers and metal/semiconductor composites, which relates to the interaction between the light photons and the free electrons which could be expressed by the equation [15,16]:

$$\omega_p = \sqrt{\frac{4\pi Ne^2}{\epsilon_\infty m^*}}$$

(1)
Where $\omega_p$ is the plasma edge, $(N)$ is the conducting electrons concentration, $(e)$ the electron charge, $(\varepsilon_\infty)$ dielectric constant and $(m^*)$ the effective mass of the electron. The plasma edge is related to electrons concentration and electron effective mass [15], and could be determined from the optical reflecting spectra, where a dramatic increase in reflectivity happen at the wavelength of the plasma edge as a result of the photons reflection from the conduction band of the electron plasma oscillations [16]. Furthermore, equation 1 indicates that, when charge carrier concentration, the plasma edge shifts to high frequencies (shorter wavelengths) [16]. In this paper, we are interested in identifying the factors affecting the plasma edges formed in the optical reflectance spectra of Ag/Ag$_2$O composites synthesized by oxygen plasma treatment of silver thin films.

2. Experimental

2.1. Sample preparation

Pure silver metal thin films were deposited onto thoroughly cleaned n-type Si (100) and glass substrates from a high-purity Ag target by using thermal evaporation system (JSM200) at room temperature. The substrate placed above the target in the direction of the vapor flux. Table 1 contains the deposition parameters.

| Deposition pressure | Deposition time | Target current | Deposition temperature | Target purity | The silver film thickness |
|--------------------|----------------|----------------|------------------------|---------------|--------------------------|
| $5 \times 10^{-4}$ Pa | 15 min         | 225 A          | 25°C                   | 99.99%        | 316 nm                   |

The oxidation process was done by placing each silver film in an evacuated Pyrex tube and exposing it to a stream of oxygen plasma afterglow at a specific plasma power. The oxygen plasma stream was generated by using Microwave SAIREM GMP 20 KEDS. More details about the plasma generation system are available in previous works [17–18]. Table 2 contains The conditions of oxygen plasma exposure for each sample.
Table 2
The conditions of oxygen plasma (afterglow) exposure for each sample.

| Sample name | Plasma power | The film - discharge center distance | Plasma power | Oxygen plasmapressure | Processing time |
|-------------|--------------|-------------------------------------|--------------|-----------------------|-----------------|
| A           | 250 W        | 0.25 m                               | 250 W        | 300 Pa                | 30 min          |
| B           | 500 W        | 0.25 m                               | 500 W        | 300 Pa                | 30 min          |
| C           | 750 W        | 0.25 m                               | 750 W        | 300 Pa                | 30 min          |
| D           | 1000 W       | 0.25 m                               | 1000 W       | 300 Pa                | 30 min          |
| E           | 1250 W       | 0.25 m                               | 1250 W       | 300 Pa                | 30 min          |

2.2. Sample characterization

The crystallite structure of the prepared thin films was determined using (Stoe StadiP) transmission X-ray diffractometer employing a Cu Kα1 source (λ = 1.54060 Å). The Raman spectra of silver oxide films were recorded using Micro Raman Jobin-Yvon (LabRAM HR) equipped with a laser source having an excitation wavelength of 514.5 nm. Scanning Electron Microscopy (TSCAN, Vega\XMU) with SEM HV of 20 kV was performed to determine the thickness and the surface morphology of the prepared thin films. The optical absorption spectra was recorded by using a UV–Vis spectrophotometer (Cary 5000). The photoluminescence (PL) spectra were recorded at room temperature using a He–Cd laser with an excitation wavelength of 325 nm. A grating monochromator (1200 groves/mm) and cooled photomultiplier tube PMT, was also used to measure PL spectra. All PL spectra were fitted into two Gaussian–Lorentzian peaks to identify their position, spectral width and relative intensities.

3. Results And Discussion

The reflectance spectra of the oxygen plasma treated silver thin films are shown in Fig. 1.

We notice that, the reflectivity is at a maximum for the sample A that treated at 250 W, and when power of 500 W is applied (sample B), it decreases dramatically and then increases again as the plasma power increases. In this figure, it appears that the samples with low oxygen content have the highest values of reflectivity and that the spectra of the rest of the samples are within a narrow reflectivity range. These results demonstrate the diversity of mechanisms that control the optical reflection of the prepared samples. In the case of the samples A and E, high reflectivity is obtained due to the metallic nature of these samples that have a low content of oxygen [14]. As for the rest of the samples, the surface plasmon formation controls the overall optical properties, not just the optical reflectivity, and this is what we have seen in our previous works [14, 19–20]. The surface plasmons absorb or scatter the incident light. It seems that in the case of the sample B the absorption of light by the surface plasmons is dominant because the reflectivity near the edge of the plasma is low compared to the rest of the samples. As the plasma power increases (samples C and D), the reflectivity increases at the expense of the optical absorption.
In Fig. 1, it can be seen that there are two plasma edges in each spectrum, the first ($\lambda_i$) is located in the range 347-363 nm and belongs to the surface plasmons of the individual silver nanoparticles, and the second ($\lambda_L$) is located in the range 366-586 nm and it belongs to the larger silver nanoparticles. We previously obtained a similar case of plasma edge duality when studying the optical properties of aluminum oxide thin films prepared by thermal oxidation of aluminum films [21]. Table 3 contains the values of plasma edges for all samples.

| Sample label | $\lambda_i$ (nm) | $\lambda_L$ (nm) |
|--------------|------------------|------------------|
| A            | 347              | 366              |
| B            | 352              | 413              |
| C            | 362              | 468              |
| D            | 363              | 586              |
| E            | 348              | 364              |

The effect of the oxygen plasma power on the plasma edge is shown in Fig. 2. We notice that, for the two edges of the plasma, when the plasma power increases, the plasma edge increases exponentially until it reaches its maxima at $p=1000W$, and then decreases dramatically at $p=1250W$. This behavior is quite similar to that of the silver oxide content of the sample as a function of the plasma power, which we studied in previous work [14]. We also notice that, the response of the $\lambda_i$ edge to power changes is very small compared to the response of the $\lambda_L$ edge.

Fig. 3 illustrates the plasma edge as a function of Ag$_2$O grain size. In this figure, one observes that the grain size increases with grain size. The effect of grain size on the (I) edge position is very small, while in the case of the (L) edge, the effect becomes obvious for sizes larger than 30 nm. Similar behavior is obtained when investigating the relationship between the edge position and silver oxide XRD peak intensity (the XRD spectra of the prepared samples were studied in detail in a previous work [14]). These results can be explained based on the fact that, the increase in the film's oxygen content (which is associated with the increase in the size of the silver oxide grains [14]) leads to a decrease in the concentration of charge carriers and thus the shift of the plasma edge towards higher wavelengths (red-shift) as predicted by Equation 1.
In our previous work [14], we found that the optical absorption spectra of the prepared samples contain two main characteristic peaks: the peak (I), which belongs to the individual silver nanoparticles, and the peak (L), which belongs to the larger silver nanoparticles. It is important to investigate the relationship between the positions of these peaks and the positions of the plasma edges (I and L) inferred from optical reflectivity spectra. Fig. 5 represents the relationship between the positions of the absorption peaks and the positions of the plasma edges. An interesting result can be deduced from this figure, as we notice that the points of the two series are organized in a uniform linear relationship, except for two points in series L that represent the samples A and B. The point A of the L series does not belong to the straight line in Fig. 5 due to the dipole-dipole interactions that occur because this sample contains a high concentration of large Ag nanoparticles [14]. On the other hand, sample D contains a relatively high oxygen content as a result of the oxidation of silver atoms. This results in polarized chemical bonds [20] and the polarization in turn affects the positions of both the absorption peaks and the plasma edges causing point D to move away from the straight line in Fig. 5.

Equation 1 describes both \( \lambda_I \) and \( \lambda_L \) plasma edges and can be used to calculate the ratio \( N_I/N_L \). Where \( N_I \) is the charge carrier density for individual silver nanoparticles and \( N_L \) is the charge carrier density for larger silver nanoparticles. Fig. 6 shows the \( N_I/N_L \) ratio as a function of oxygen plasma power.

We notice that, the ratio \( N_I/N_L \) behaves similarly to the two edges of the plasma in Fig. 2, where when the plasma power increases, the ratio \( N_I/N_L \) increases exponentially until it reaches its maxima at \( p= 1000W \), and then decreases dramatically at \( p= 1250W \). This behavior is quite similar to that of the silver oxide content of the sample as a function of the plasma power, which we studied in previous work [14]. Based on this, we conclude that the ratio \( N_I/N_L \) increases with the increase in the concentration of Ag\(_2\)O oxide in the sample, (see the curve in Fig. 7, which shows the ratio \( N_I/N_L \) as functions of silver oxide XRD peak intensity). In other words, these results confirm that while the film content of large nanoparticles decreases due to oxide formation [14], the concentration of charge carriers in individual silver nanoparticles increases compared to the concentration of charge carriers in larger silver nanoparticles. We believe that the ratio \( N_I/N_L \), which has a maximum value in sample D, is what gives this sample the highest activity to inhibit bacteria [22], and this supported by our previous findings that individual silver nanoparticles are a major factor in bacterial inhibition [22].

Finally, Figure 8 shows the ratio \( N_I/N_L \) as a function of particle size, as we notice that the ratio \( N_I/N_L \) increases with increasing particle size. The ratio \( N_I/N_L \) starts to increase significantly starting from a particle size of 30nm.

4. Conclusions

In this work, we are interested in investigating the structural effects on the plasma edges observed in the optical reflectivity spectra of Ag/Ag\(_2\)O composites synthesized by oxygen plasma treatment of silver thin films. We obtained unique results summarized in the following points:
1. Two types of plasma edges were observed in the reflectivity spectra of Ag/Ag$_2$O composites, the first (\(\lambda_I\)) belongs to the surface plasmons of the individual silver nanoparticles, and the second (\(\lambda_L\)) belongs to the larger silver nanoparticles.

2. Oxygen plasma power has a large effect on the silver nanoparticles edge plasma edge (\(\lambda_L\)) compared to its effect on the individual silver nanoparticles plasma edge (\(\lambda_I\)).

3. The increase in both the particle size and the film's oxygen content causes the plasma edges to shift towards higher wavelengths.

4. The positions of the plasma edges are linearly related to the positions of the optical absorption peaks, except for high and low oxidation rates cases.

5. Silver oxidation leads to a decrease in the concentration of charge carriers in the nanoparticles configurations, but at the same time leads to an increase in the ratio \(N_I/N_L\).

6. The ratio \(N_I/N_L\) may be a measure of the film's effectiveness in inhibiting bacteria.

**Declarations**

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Not applicable

**Code availability**

Not applicable

**Ethical Approval**

This is an observational study. No ethical approval is required.

**Consent to Participate**

Not applicable
Consent to Publish

Not applicable

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**Figures**
Figure 1

The reflectance spectra of the prepared Ag2O thin films.
Figure 2

The two plasma edges as functions of plasma power.

Figure 3

The grain size of the material as functions of plasma power.
The two plasma edges as functions of grain size.

*Figure 4*

The two plasma edges as functions of silver oxide XRD peak intensity.
Figure 5

The plasma edge as functions of absorption peak position.

\[ y = 0.8534x + 55.002 \]

\[ R^2 = 0.2943 \]
Figure 6

The ratio $N_I/N_L$ as functions of plasma power.

Figure 7

The ratio $N_I/N_L$ as functions of silver oxide XRD peak intensity.
Figure 8

The ratio $N_I/N_L$ as functions of grain size.