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Effect of thermal annealing on microstructure and optical properties of silver-carbon nanocomposite thin films

A. Sakli ^{a,b,*}, A. Lahmar ^a, D. Gamra ^b, M. Clin ^a, H. Bouchriha ^b, M. Lejeune ^a

^a Laboratoire de Physique de la Matière condensée (LPMC), Université de Picardie Jules Verne, Amiens 80039, France. ^b Laboratoire de Matériaux Avancés et Phénomènes Quantiques (LMAPQ), Faculté des Sciences de Tunis 2092, Tunis

Abstract

We reported a novel and versatile processing for the synthesis of Ag-carbon nanocomposites using the combination of the sputtering and PECVD techniques. The influence of the thermal annealing on the surface morphology, the structure and the optical properties of these films was studied. The effective medium model was used to describe the spectrophotometric measurements. Numerical calculations were allowed determining optical constants. The calculated transition gap E_g was found to vary between 1 and 1.5 eV depending on the annealing temperature. These values are lower than those reported for standard Ag-TiO₂ and Ag-ZnO nanocomposites, which is promising for advanced optoelectronic devices.

Keywords: Silver-carbon nanocomposite; optical property; band gap energy.

**Corresponding author:* Akram SAKLI *E-mail address:* akram.sakli@gmail.com

1. Introduction

The last decades have seen a strong interest in nanocomposite thin films, due to their particular properties different to those of their components [1]. Particularly, the noble metal nanocomposites are fascinating for fundamental research and engrossing for technological applications such as nonlinear optics or photocatalysis [2, 3]. It should be notice that these applications rely on the specific optical and electronic properties of the composite material, which depends on the nature of the matrix [4], the size and the morphology of the metallic nanoparticles (NPs) [5-7].

Sine the primary work of Fujishima and Honda about the photocatalytic properties of $TiO_2[8]$, revival interest to this matrix and such related application have been seen [9-14]. Nevertheless, neat TiO_2 suffers from the electrons-holes recombination (e⁻/H⁺) and only a small window of the solar energy spectrum could be used effectively due to its wide band gap (~3.2 eV) [15]. To overcome this drawback, systematic research has been carried out on developing nanocomposites based on titania embedded by metallic NPs such as Ag, Pd, Pt, Au [16-20]. Noting that the heterojunctions in TiO_2 - NPs were reported to extend the light absorption to the visible region. Such a behavior was attributed to surface plasmon resonance effect caused by the interaction between the solar radiation and the nobel metal NPs, which activated also the charges separation [21-23]

Nevertheless, TiO_2 may produces potentially dangerous secondary molecules such as ketones or formaldehyde during its photocatalysis reaction [24-26]. Further, the TiO_2 -NPs present in the catalyst may be released into air, which is harmful for inhalation [27]. Alternatively, amorphous carbon appears an appropriate solution to take advantage from plasmonic performances of NPs, since it endorses a smaller dielectric constant than oxides. Herein, we propose to use the amorphous carbon as matrix to stabilize the Ag-NPs as alternative solution to hazardous Ag- TiO_2 [28, 29]. Then we assess its optical properties experimentally and by using software "CODE" (WTheiss Hard and Software for Optical Spectroscopy) [30], to determine the pertinent optical parameters enhancing the transmission (*T*) and reflection (*R*) spectra.

2. Experimental procedure

20 nm thick Ag films were deposited on glass substrates by direct current (DC) sputtering using an Ag target and a reactive plasma from Cressington[®] sputtering 208HR for 100 seconds as deposition time at 40 mA. Then, the asdeposited Ag film was heat treated at 200°C, 300°C, 400°C, 500°C and 600°C for 90 minutes as dwell time for each temperature under oxygen environment using a programmable tubular furnace (S4R-1700C-TF). Finally, 40 nm thin layer of polyethylene ((C_2H_2)_n), whose precursor is ethylene gas, was deposited by plasma enhanced chemical deposition (PECVD) technique from Plassys[®] company to mechanically stabilize the Ag-NPs in the nanocomposite using a radio frequency (RF) power of 200W, a deposition pressure of 1.6 Pa and an ethylene gas flow of 7 sccm. The flow chart methodology of our experimental procedure is given in Figure 1.

The surface morphology of the obtained films was analyzed using a scanning electron microscopy (SEM). Noting that this technique permitted to have an idea about the size of the formed silver nanoparticles. A room X-ray analysis was performed with four circle high-resolution D8 Discover Bruker diffractometer (Cu K α radiation, λ =1.5418 Å) in grazing incidence mode with $\theta = 2^{\circ}$ as incidence angle and at a scanning rate of 2°/min. Characterization of the optical properties was carried out at room temperature using a UV-Vis-NIR spectrophotometer (Japan, Jasco SLM-468) in wavelength range of 270 – 1800 nm. The different optical parameters were determined by numerical simulation of the transmittance and reflectance spectra using the commercial "CODE" software.



Fig. 1. The used flow chart methodology

3. Results and discussion

3.1. Microstructures

Uniform and crack-free Ag- films were obtained. The surface morphology of the annealed films was analyzed by scanning electron microscopy (SEM). The surface of Ag film without annealing was relatively smooth (Fig. 2(a)) .At 200°C (Fig. 2(b)), shapeless silver NPs began to be formed in the matrix. The increase of the annealing temperature induces a decrease of the Ag-NPs density while the shape of the nanoparticles becomes more spherical and well distributed in the surface (Figs. 2 (c) to (f)). This result is similar to that found by X. Liu and al. [31].

Figure 3 shows the surface distribution of Ag nanoparticles for each annealing temperature of silver films. It is clear that the size of the nanoparticles increases with the annealing temperature and reaches a maximum at 500°C with a size of 340 nm. This behavior is observed in various works such as the work of X. Liu and al [31] and H. R. Abd El-aaty and al. [32] showing an increase in the size of Ag-NPs by increasing the annealing temperature. At 600°C, the Ag-NPs keep their spherical shape but their size decreases. The increase of the temperature induces a constant decrease of the content of the Ag-NPs into the nanocomposite as shown by the variations of the Ag-NPs coverage rate extracted from the SEM measurements.



Fig. 2. SEM micrographs of: (a) Ag thin film before annealing, (b) at 200°C, (c) at 300°C, (d) at 400°C, (e) at 500°C and (f) at 600°C.



Fig. 3. Surface distribution of Ag-NPs depending on the annealing temperature (300, 400, 500 and 600°C).

3.2. X-ray diffractions

Figure 4 shows the X-ray diffraction patterns of the prepared nanocomposites annealed at different temperature in air atmosphere. Only the reflections (111), (200) and (220) associated to metallic Ag were observed which is in accordance with various works carried out [33, 34]. No Clear formation of the silver oxide could be spotted from this diffractogram, in the limit of device detection. It is clearly seen that the formation of the Ag-NPs started around 200°C, which is in good agreement with SEM analysis.



Fig. 4. X-ray diffraction patterns of Ag-C nanocomposites annealed at 200°C, 400°C and 600 °C.

3.3. Optical investigations

Figure 5(a) shows transmission (*T*) and reflection (*R*) spectra of Ag-carbon nanocomposite annealed at various temperatures in the wavelength range 270 - 1800 nm. Both *T* and *R* show an absorption band in the visible region. This band exhibits a red-shift with increasing temperature. Such a behavior is attributed to the coupling effect between the neighboring nanoparticles [21].

It should be noticed that it is difficult to calculate the optical properties without knowing the sizes, shapes, the orientations as well as the positions of Ag-NPs in the matrix [35]. Using the theory of "Effective Medium model", it is possible to provide with an accurate fitting of the experimental reflectance and transmittance curves. Hence, a heterogeneous medium composed of particles having a proper dielectric function (ε_p) embedded into a dielectric matrix (ε_M) can be modeled as homogeneous medium with an effective dielectric function (ε_{eff}).



Fig. 5. (a) Transmittance and reflectance spectra for Ag-C composite annealed at different temperature, (b) Experimental and calculated transmittance and reflectance spectra of Ag-C composite annealed at 300°C.

In our case, the Bruggeman model provides a fine adjustment of the obtained (R, T) experimental spectra, as shown in the Fig. 4(b). This model is expressed by the following equation [36]:

$$(1-f)\frac{\varepsilon_M - \varepsilon_{eff}}{\varepsilon_M + 2\varepsilon_{eff}} + f\frac{\varepsilon - \varepsilon_{eff}}{\varepsilon + 2\varepsilon_{eff}} = 0 \qquad (1)$$

The results of the calculated volume fraction of Ag-NPs and refractive index are gathered in Table 1. One can notice that the increase of the temperature from 300°C to 500°C induces a decrease of the volume fraction of Ag-NPs with an increase of their average size. Further, the temperature seems to favor the NPs coalescence on the surface and their growth as per the Ostwald ripening process [37, 38]. At 600°C the carbon matrix is strongly damaged inducing a loss of nanocomposite properties.

Parameter	300°C	400°C	500°C	600°C
NPs average size (nm) _{SEM}	80	220	300	230
Ag-NPs coverage rate (%) SEM	16	11	10.5	5.5
Ag-NPs volume fraction (%) CODE	18.85	13.65	9.2	6.02
n code	2	1.69	1.58	1.54
<i>n</i> <i>Cauchy</i>	2.03	1.69	1.57	1.53
N Wemple- DiDomenico	2	1.7	1.58	1.54
$E_{g.Tauc \ CODE}(eV)$	1.09	1.18	1.39	1.46
$E_{g.\ M\ Osc\ Eff.}$ Wemple- DiDomenico (eV)	1.06	1.2	1.4	1.42
Deplasma.Drude-Lorentz (×10 ¹⁴ rad.s ⁻¹)	11.64	9.23	8.53	8.38

Table. 1. Values of the average size, volume fraction of the Ag-NPs at different temperature and optoelectronic parameters obtained from different models.

In order to confirm our results, different models for the calculation of optical parameters have been implemented by using "CODE" software.

The static refractive index n calculated using both:

• the Cauchy relationship:

$$n = A + \frac{B}{\lambda^2} \tag{2}$$

Where A and B are the Cauchy parameters.

• the Wemple-DiDomenico single-effective oscillator model expressed by:

$$n^2 - 1 = \frac{E_d E_0}{E_0^2 - E^2} \tag{3}$$

Where *E* is the incident photon energy, *n* the refractive index, E_d is the dispersion energy and E_0 the single-effective oscillator energy.

 \Box_p is the plasma frequency. Indeed, for large wavelengths, the real dielectric constant ε' can be ascribed as [39]:

$$\varepsilon' = \varepsilon_{\infty} - \frac{\varepsilon_{\infty} \omega_p^2}{\omega^2} = \varepsilon_{\infty} - \frac{\varepsilon_{\infty} \omega_p^2}{4 \pi^2 c^2} \lambda^2 = \varepsilon_{\infty} \left(1 - a\lambda^2\right)$$
(4)

Where ε_{∞} is the limiting value of the high frequency dielectric constant with c the speed of light. The plot of ε' vs. λ^2 in (1600 – 1800 nm) spectral region is depicted in Fig. 6. As it can be seen from the plot, a linear dependence is obtained, permitting to determine the values of the lattice dielectric constant ε_{∞} and the plasma frequency \Box_p .



Fig. 6. Variation of real dielectric constant versus λ^2 showing a linear behavior. The lines are just guide for eyes.

The optical transition energy has been calculated using both:

- the single effective oscillator according to the relationship: $E_0 \approx 2 E_g$ (5)
- the Tauc relation for direct band gap semiconductor:

$$(\alpha hv)^2 = C(hv - E_a) \qquad (6)$$

Where α is the optical absorption, *h* is the Plank constant, *v* is the frequency of the incident light, *C* is a characteristic constant of the material and E_g is the band gap. The plot of $(\alpha hv)^2$ versus photon energy is shown in Fig. 7, E_g was evaluated by the extrapolation of the linear part.



Fig. 7. Variation of $(\alpha h \nu)^2$ versus photon energy (eV) for the Ag-C composite at different temperature. The linear extrapolation leads to determination of band gap.

All the used model led to comparable values of the optical transition and refractive index (Table 1). The decrease of the refractive index with increasing annealing temperature is linked to the decrease of the thin film's density. Indeed, there is a good correlation between the decrease of the refractive index and the decrease of the volume fraction of Ag-NPs. Furthermore, the value of plasma frequency a_p decreased with annealing temperature and it is in the order of 10^{14} rad.s⁻¹. Similar order results were reported in some semiconductor-based material [40]. Such decrease can be related to the decrease of charge carriers. In fact, with increasing the temperature, the Ag-NPs density is lower leading to larger free space interparticles, thus the charge carriers may be trapped in the insulating matrix (Ag-NPs). E_g is found to vary from 1 eV to 1.4 eV at 600°C, likewise a_p . The obtained values of E_g are similar to the reported ones for Ag-NPs imbedded in the TiO₂ where E_g decreased to 1.4 eV for high concentration, attributed to a progressive metallization of samples [41]. Concerning the optical properties of silver oxide thin films, Nwanya et al. [42] obtained values between 1.64 eV and 1.70 eV, depending on annealing duration. A smaller value is reported also by Raju et *al.* [43] in the range of 1.01–0.93 eV.

4. Conclusion

In summary, Ag-C nanocomposites were fabricated on glass substrates by a combination of DC sputtering and PECVD techniques. The evolution of the microstructure, the refractive index and the optical transition energy as a function of the annealing temperature of the silver films are studied. Improved conducting properties is observed in Ag-C composite comparing to the usual matrix such Ag-TiO₂ or Ag-ZnO, with a band gap energy in the range of 1.05 eV to 1.45 eV.

The low cost and versatile Ag-C composite with small optical band gaps, investigated in the present work, may be beneficial for numerous advanced optoelectronic devices.

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This manuscript is dedicated to the memory of Pr. Kacem ZELLAMA

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