Broadband optical absorption of amorphous carbon/Ag nanocomposite films and its potential for solar harvesting applications

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ABSTRACT

The emergence of Localized Surface Plasmon Resonance (LSPR) in nanocomposite films consisting of a hydrogen-free amorphous Carbon (a-C) matrix and Ag is considered theoretically and experimentally. While in theory it could be manifested for highly tetrahedral ($>90\%$ sp^3) matrices, Auger electron spectroscopy and neutron reflectivity have shown that the incorporation of Ag into the a-C matrix induces severe graphitization that eliminates the LSPR; nonetheless, the dielectric damping of graphitized a-C, in combination with the $\pi-\pi^*$ electronic transitions of carbon and the defect states introduced by Ag, cumulatively result in a strong broadband optical absorption in the near infrared, visible and UVA/UVB spectral ranges, revealed by optical reflectivity spectra, that coincides with the solar emission spectrum. The incorporation of Ag into a-C at room temperature thus proves to be an energy-efficient pathway for the controlled graphitization and the tailored optical absorption of novel nanocomposite films for solar photothermal applications.

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1. Introduction

Diamond-Like Carbon (DLC) and amorphous Carbon (a-C) are established as very important engineering materials [1] that are suitable for various photonic applications [2,3]. Furthermore, metal-containing a-C films have recently gained special attention [4–13] due to their potential for catalytic [4,5], photonic [10,11], solar [12–15] and biomedical [9,16,17] applications. Such films are usually grown by magnetron sputtering using hydrocarbon reactive gas and metal cathodes, [4,7,18–20] or dual sputtering from graphite and silver targets [21], resulting in hydrogenated carbon matrices with Ag inclusions. Pulsed Laser Deposition (PLD) has been proven to be a versatile technique, capable of growing tetrahedral a-C (ta-C) films of superior optical transparency and mechanical stability [22–24]; thus, the PLD is increasingly becoming the method of choice for incorporating metal nanoparticles into hydrogen-free amorphous carbon matrices [5,6,8,9,11,25]. However, the optical properties of such carbon-based nanocomposite films are inherently complex and they have not been studied in detail, yet. In particular, the main drawback in gaining solid conclusions on their optical properties is the interplay between the sp^3 content of the matrix and the Ag content in the films [8,26,27]; for example, while an ideally insulating ta-C matrix would be able to sustain a strong Localized Surface Plasmon Resonance (LSPR) in the Ag particles [28], it typically gets severely graphitized upon incorporation of Ag [8,27], which causes a strong quenching of any conduction electron oscillation in the Ag nanoparticle.

In this work, we study the optical response of a-C:Ag nanocomposite films deposited by a modified PLD process at room temperature [8,29] and characterize them by Neutron Reflectivity (NR) and in-situ Auger Electron Spectroscopy (AES). We compare the experimentally obtained optical properties with the effective medium response of hypothetical composites consisting of a pure a-C matrix of varying sp^3 content and Ag inclusions of certain

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Abbreviations: a-C, amorphous carbon; AES, auger electron spectroscopy; BOPP, biaxially-oriented polypropylene; DLC, diamond-like carbon; GIXRD, grazing-incidence X-ray diffraction; HACNT, horizontally aligned carbon nanotubes; HOPG, highly ordered pyrolytic graphite; LSPR, localized surface plasmon resonance; MG-EMA, Maxwell–Garnett effective medium approximation; NR, neutron reflectivity; ORS, optical reflectance spectroscopy; PLD, pulsed laser deposition; PET, poly-ethylene terephthalate; ta-C, tetrahedral a-C; TDDFT, time-dependent density functional theory; TEM, transmission electron microscopy; UHV, ultra high vacuum; UV, ultra violet radiation; VACNT, vertically aligned carbon nanotubes; XRD, X-ray diffraction.

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sizes, as identified by transmission electron microscopy [30]. We provide solid evidence that the graphitization process upon incorporation of Ag, as observed in Ref. [8,26,27], is indeed very strong and it prevents the manifestation of LSPR. By the same token, however, we show that these composites may find an important application as optical absorbers. In particular, the spectral absorption of a-C:Ag, which is dictated predominantly by the π–π* interband transition of carbon and the localized states of Ag [27,30], resembles strongly the solar emission, suggesting that a-C:Ag is a significant candidate for solar selective coatings for photothermal solar harvesting.

2. Experimental

The a-C:Ag films were grown at room temperature on commercial Si{001} prime crystal wafers by PLD in a high-vacuum chamber (base pressure $P_b < 5 \times 10^{-6}$ Pa) as described in detail in Ref. [8]. The rotating target consisted of pure, hot-pressed graphite and sterling Ag plates having the form of two opposing sectors covering part of the graphite area; the fraction of target area covered by Ag was varying in order to vary the Ag content in the produced a-C:Ag films. A constant deposition time of 20 min was used for all samples. The laser beam was either the 2nd harmonic ($\lambda = 532$ nm) or the 3rd harmonic ($\lambda = 355$ nm) of a Nd:YAG laser (Lambda-Physik, pulse duration 4 ns, repetition rate 10 Hz), which provided the means to vary independently the sp^3 content of the a-C matrix. The beam was focused using a lens (focal length $f = 50$ cm) outside the vacuum chamber passing through a fused silica viewport. The pulse energy was 200 mJ and 35 mJ for the 2nd and 3rd harmonic, respectively. The working pressure of the ablated vapor under these conditions was about 1×10^{-3} Pa.

The produced a-C:Ag films were studied by *in-situ* Auger Electron Spectroscopy (AES), Neutron Reflectivity (NR), X-Ray Diffraction (XRD), Transmission Electron Microscopy (TEM) and Optical Reflectance Spectroscopy (ORS). The AES spectra were acquired in an ultra-high vacuum (UHV) chamber ($P_b < 5 \times 10^{-8}$ Pa), which is connected to the PLD through a UHV transfer line, using an electron gun (820–830 eV excitation energy) and a cylindrical mirror analyzer (CMA - Physical Electronics). The NR experiments have been performed in D17 beam-line of Institute Laue-Langevin. A Bruker D8-Advance instrument was used for XRD experiments, which were performed in Bragg-Brentano (θ–2θ) and in grazing-incidence, asymmetric geometry (GIXRD); for the GIXRD experiments we used angle of incidence $\alpha = 0.6°$, in order for α to be wider than the critical angle ($0.4°$–$0.5°$) of these samples.

The optical properties of the films were studied by ORS at normal incidence in the spectral range 250–850 nm (1.46–4.96 eV) using deuterium and halogen light sources and an Al mirror for normalization of the spectroscopic data.

3. Computational and analysis methods

Dielectric function spectra QUOTE of hypothetical a-C:Ag composites were calculated using the Maxwell–Garnett effective medium approximation (MG-EMA), which describes the effective optical response of a composite material consisting of a host (matrix) phase and isolated inclusions of the secondary phase [31]:

$$\frac{\tilde{\varepsilon} - \varepsilon_m}{\tilde{\varepsilon} + 2\varepsilon_m} = f_i \frac{\varepsilon_i - \varepsilon_m}{\varepsilon_i + 2\varepsilon_m}, \qquad (1)$$

where f_V^i is the volume filling ratio of the inclusions, ε_i is the reference dielectric function of the Ag inclusions and ε_m is the reference (bulk) dielectric function of the host (matrix). For ε_m we used various amorphous carbon hosts, namely:

i) ta-C: a hydrogen-free carbon film produced by PLD and having sp^3 content $> 90\%$ and density 3.22 g/cm^3 [3],

ii) intermediate a-C: a hydrogen-free carbon film produced by *rf* biased sputtering and having sp^3 content $\sim 45\%$ and density 2.65 g/cm^3 [32,33],

iii) graphitic a-C: a hydrogen-free carbon film produced by *rf* sputtering and having sp^3 content $\sim 20\%$ and density 1.9 g/cm^3 [22,33],

The bulk dielectric function of the Ag nanoparticle inclusions of varying particle size G, used in MG-EMA, were constructed by fitting the experimental data of Johnson and Christy [34] to a combined Drude-Lorentz model [35], and adjusting the Drude relaxation time τ_D (which is the inverse of the Drude broadening parameter γ_D [35]) in order to take into account the electron scattering at the particle boundaries, according to the formalism of Kreibig [36,37]:

$$\frac{1}{\tau_D^{NP}} = \frac{1}{\tau_D^{bulk}} + \frac{v_F}{G}, \qquad (2)$$

where τ_D^{NP} is the Drude electron relaxation time in the Ag nanoparticles, τ_D^{bulk} is the electron relaxation time in bulk Ag (Ref. [34]), v_F is the Fermi velocity of Ag [38], and G is the Ag particle radius.

The experimental optical reflectance spectra were fitted assuming a homogeneous overlayer on top of a semi-infinite substrate [39]. The dielectric function of the a-C–Ag layer was described by three Lorentz oscillators corresponding to the π–π* and σ–σ* interband transitions of a-C and the optical absorption of Ag.

The experimental film density was determined by analyzing the NR data using Parratt's formalism [40], using a model of two homogeneous layers on top of a Si substrate (a-C:Ag/native SiO$_2$/Si) and considering the coherent nuclear scattering lengths of the constituents: 6.6484 fm (C), 5.922 fm (Ag), 4.15071 fm (Si), and 5.805 fm (O). The Ag content and the sp^3 content in the films were determined from the *in-situ* AES spectra, which exhibit the C_{KLL} Auger peak at kinetic energy 272 eV, which is characteristic of a-C [41,42], and the Ag_{MNN} doublet at 351 and 356 eV [43].

4. Results and discussion

4.1. A. Structural features of a-C:Ag composite films

The incorporation of Ag into a-C has been reported to reduce the a-C's sp^3 content [8,26,27,30,44,45]. Also, the effect of the laser wavelength has been reported to be essential for the growth of pure a-C by PLD, because the ionization process of C differs for varying photon energy of the incoming laser beam [24]. However, the detailed nature of the carbon matrix after the Ag incorporation as well as the effect of the laser wavelength on the microstructure and the distribution of Ag nanoparticles, are issues still unresolved. In an effort to clarify them, we critically compare the variation of density, sp^3 content and Ag distribution in a-C:Ag nanocomposite films deposited by PLD using either a 532 nm or a 355 nm laser beam; the main features of those films are summarized in Table 1.

All the samples were measured by Neutron Reflectivity and by *in situ* AES, in order to identify the variations of the film density and sp^3 fraction independently for varying Ag content, as well as to establish a correlation between density and the sp^3 fraction of the carbonaceous matrix. The mass density ρ of the considered samples were determined by Neutron Reflectivity through the critical angle