

Effect of the plasmon-exciton coupling on the optical response of a ZnO/Ag/ZnO nanocomposite

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Abstract. The study presented is focused on the optical properties of ZnO/AgNPs/ZnO multilayer nanocomposites. The optical properties of the nanostructures depend on the silver layer thickness. The optical spectral characteristics of Ag nanoparticles (AgNPs) nanostructured by laser irradiation in a ZnO medium were investigated theoretically and experimentally. The extinction spectrum was determined as a function of the nanoparticles size distribution and of the surrounding medium. The extinction efficiency calculated is red-shifted and broadened when the AgNPs are introduced in a ZnO environment. This result is in agreement with the experimental measurements, where the plasmon resonance peak position of the ZnO/AgNPs/ZnO composite is red-shifted, compared to the AgNPs/ZnO sample. Raising the thickness of the Ag layer increases the resonance extinction. We also propose a method for controlling and tuning the SPR-based sensing of Ag nanoparticles in a ZnO medium.

1. Introduction

Metal-semiconductor nanocomposites are of great interest because of their potential applications in various nanodevices that cannot be designed based on single individual components [1, 2]. Hybrid nanomaterials composed of plasmonic metal nanostructures and semiconductor thin films provide the unique combination of a highly-localized and enhanced electromagnetic field in, e.g., Ag nanoparticles (NPs) with the wide bandgap and large exciton binding energy of a semiconductor, such as ZnO [3, 4]. Zinc oxide is an important material used in solar cells as transparent conductive contacts, in thin film transistors and in optoelectronic components. One of the approaches to developing novel materials and improving their functions is to combine two or more functional phases. The research efforts have been focused on determining the influence of the coupling mechanism attributed to the combined effects of surface modification, band alignment and charge transfer on the optical response in composite heterostructures. The theoretical and experimental studies of the properties of noble metal nanoparticles have shown that they could be modified by varying the plasmon resonant frequency through varying the size, the shape, the interparticle distance and the dielectric properties of the surrounding environment [5-7]. The AgNPs behavior in a ZnO ambient has in recent years attracted a great interest [8-10]. By analyzing composites containing metal nanoparticles, one could explore the possibilities of fabricating sensors based on surface plasmon resonance (SPR) that operate in various spectral ranges. The interpretation of the results could be further extended to other semiconductors and

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be useful for creating a variety of nanocomposite materials with novel optical properties. In this paper, we describe the formation of a ZnO/AgNPs/ZnO nanocomposite by laser deposition and laser annealing and a study of the morphology and plasmon resonance properties.

2. Theoretical model

The simulation model considered an ideal array, where all Ag nanoparticles have the same diameter of 60 nm and the medium is ZnO. Nanoparticles array with the mean diameter of 60 nm and a size distribution in the range of 30 nm – 90 nm was also the object of the theoretical investigations. For comparison, calculations for the case of an air ambient were also performed. The theoretically estimated optical properties were compared with the experimentally measured ones. The optical efficiencies, (Q_{ext} , Q_{sca} and Q_{abs}) were calculated by applying the generalized multiparticle Mie (GMM) method [11]. Each simulated system consisted of 27 nanoparticles.

3. Experimental

A ZnO sintered target was ablated for ten minutes in a vacuum chamber at an oxygen pressure of 2.4×10^{-1} Torr. The chamber was evacuated down to 3.9×10^{-4} Torr before introducing the oxygen. The ZnO thin film was deposited on a SiO₂ (100) substrate. A third-harmonic Nd:YAG laser (Lotis LS-2147, $\lambda = 355$ nm, pulse duration $\tau = 18$ ns) was used at a repetition rate of 10 Hz and a fluence of 1.7 J/cm^2 . The ZnO layers thus formed on two substrates were covered by a Ag thin film for deposition times of two and three minutes. The thickness of the silver films was 120 nm and 180 nm as determined in previous experiments [12]. The silver layer was decomposed into nanoparticles by laser annealing in air by ten laser pulses of high fluence (1 J/cm^2) incident normally to the surface. The NPs morphology was observed by scanning electron microscopy (SEM) (dual beam system SEM/FIB, Lyra\Tescan). The AgNPs mean diameter and size distribution were calculated. The optical transmission spectra of the fabricated samples in the range from 200 nm to 800 nm were obtained by an Ocean Optics HR 4000 spectrophotometer.

4. Results

Laser annealing leads to a decomposition of the thin silver film into a layer of nanoparticles. Figure 1a presents a SEM image of AgNPs formed as described above on a ZnO layer. The laser annealing results in well-formed NPs in the case of the thicker layer (figure 1b), while the thinner film shown in figure 1a does not exhibit a well-defined nanoparticles structure. Most probably, the laser annealing leads to embedding of silver in the ZnO matrix. Figure 1c shows the histogram of the size distribution of the AgNPs, which is in the 30 nm – 90 nm range. The silver nanoparticles's mean diameter for the thicker layer is 60 nm.

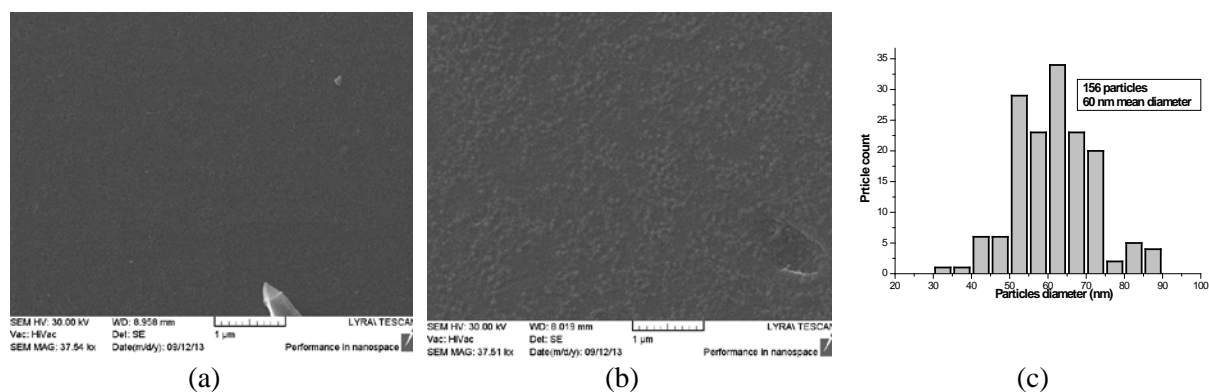


Figure 1. SEM images of AgNPs on a ZnO film: (a) deposited for 2 min; (b) deposited for 3 min; (c) size histogram of the AgNPs layer deposited for 3 min.

The strong optical extinction band associated with the SPR of AgNPs was registered for all samples after laser annealing (figure 2). Resonance extinction was registered also for the sample with the thinner AgNPs layer (figure 2a, curve 2), where the SEM image does not show a good nanoparticles' morphology. Obviously, interaction with silver nanoclusters embedded in ZnO provokes a resonance response with a lower intensity compared to the signal arising from the other sample shown in figure 2b (curves 2 and 3). Figure 2 presents the transmission spectra of Ag layers of different thicknesses and a fixed thickness of the upper and lower ZnO layers. The spectrum shows a resonance extinction in the Ag/ZnO sample before laser annealing, when the silver layer is thinner (figure 2a, curve 1). The sample having a thicker silver

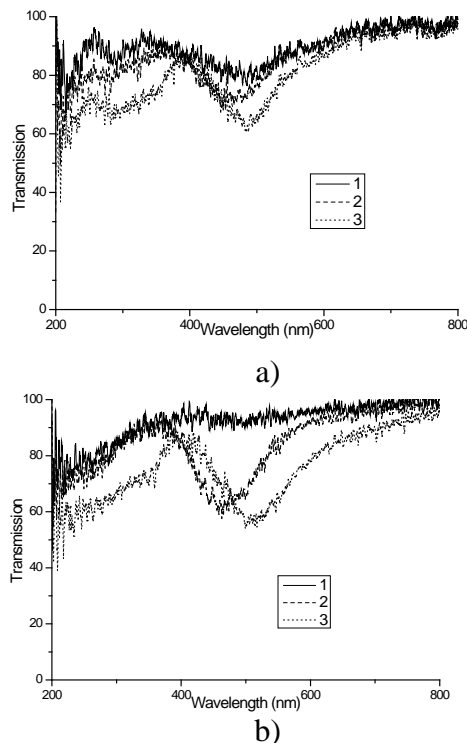


Figure 2. Transmission spectra of nanocomposites containing AgNPs produced by laser annealing of a silver layer (a) deposited for 2 min.; (b) deposited for 3 min.; curve 1 – Ag film/ZnO on SiO₂ (100); 2 – AgNPs/ZnO on SiO₂ (100); 3 – ZnO/AgNPs/ZnO on SiO₂ (100).

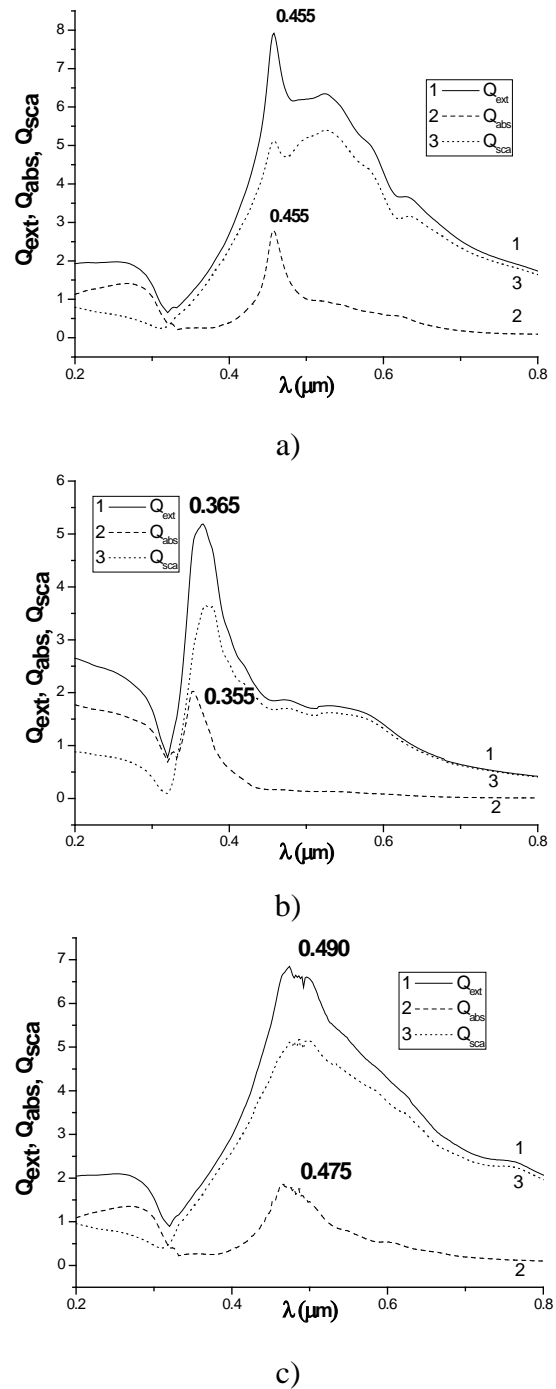


Figure 3. Extinction, absorption and scattering efficiency spectra of AgNPs arrays composed of 27 nanoparticles, where (a) all AgNPs in ZnO environment have the same diameter of 60 nm (an ideal system); (b) AgNPs with mean diameter of 60 nm in air environment; (c) AgNPs with mean diameter of 60 nm in ZnO environment.

layer does not exhibit any resonance band before annealing (figure 2b, curve 1). This result is associated with a rough surface formation in the case of two-minute Ag deposition and a discontinuous (island-like) structure of the silver layer. The surface plasmon resonance response in the ZnO/AgNPs/ZnO nanostructure is obtained at about 490 nm – 500 nm. A higher value was measured for the sample with the thicker silver layer. The excitonic band of ZnO at about 300 nm in figure 2a is detected for the sample where the silver layer is thinner. This band disappears when the silver film thickness is increased in the multilayer structure, as demonstrated in figure 2b.

The nanocomposite heterostructure under consideration consists of Ag nanoparticles (figure 1b) with a mean NPs diameter of 60 nm arranged between two ZnO layers. In all spectra calculated and presented in figure 3, the scattering maximum dominates over the absorption one by a factor of more than two; also, the maximum of the scattering spectra is red-shifted with respect to the absorption one. The scattering dominates the optical spectra and provides the main contribution to the overall extinction for the nanoparticles array with a diameter of about 60 nm. The extinction calculated corresponds to the plasmon resonance extinction measured of the fabricated nanostructures. The NPs size distribution has a strong impact on the overall extinction. This multiparticle system consists of peaks related to excitation of different plasmon modes in a single particle within the array, as well as to collective excitation. Figure 3a presents the extinction efficiencies for the ideal system of NPs with a diameter of 60 nm, to be compared to the real NPs array system (size distribution in the 30 nm – 90 nm range) in figure 3b. The extinction calculated of the real system in figure 3c exhibits one broad peak due to the overlapping of the individual peaks.

The change from an air environment (figure 3b) to ZnO leads to a broadening of the extinction peaks (figure 3c). The calculation results show a red-shift of the extinction efficiency in a ZnO environment. This shift is accompanied by an increased intensity, as was also demonstrated by the SPR results in figure 2. The maximal extinction efficiency shown in figure 3c and the maximal resonance extinction of AgNPs in a ZnO medium in figure 2b were located at about 490 nm.

5. Conclusions

Multilayer composite structures of ZnO/AgNPs/ZnO were fabricated by pulsed laser deposition and laser annealing. The nanocomposites produced with AgNPs of 60-nm mean diameter and size distribution in the 30 nm – 90 nm showed strong plasmon resonance properties. The experimental results were validated by the simulation conducted. The optical properties of the nanostructures explored depend on the AgNPs mean diameter, their size distribution and the surrounding environment. The ZnO medium causes a SPR shift to the higher wavelengths in the VIS spectrum to about 490 nm and broadens the bandwidth. Resonance wavelength tuning could be performed by varying the AgNPs size distribution in an ZnO environment. The results may contribute to the development for SPR-based sensors covering various spectral regions.

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