

Nanostructured Ag/ZnO multilayer plasmonic composites

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We investigated pulsed laser deposited and laser annealed multilayer nanostructures of Ag and ZnO. The laser induced surface modification was applied for decomposition of the silver layer into nanoparticles. The morphology of the Ag nanoparticles is of critical importance in what concerns the surface plasmon resonance (SPR) properties of such multilayer structures. The combined study of the optical transmission and photoluminescence (PL) properties of the Ag/ZnO structures showed that the surface-plasmon-mediated emission is determined by both the Ag particles size and density. The study of the correlation between the structure of Ag nanoparticles array and its optical properties provides information on the three-dimensional reconstruction of nanocomposites from a two-dimensional structure. The PL peak in the ultraviolet (UV) spectral region does not change substantially, while the shape and position of the visible (VIS) emission spectrum is changed and shifted towards the shorter wavelengths after the laser nanostructuring.

(Received February 2, 2013; accepted January 22, 2014)

Keywords: PLD, Laser annealing, Ag nanoparticles, Nanocomposites, Photoluminescence, Surface plasmon resonance

1. Introduction

The development of novel materials and the improvement of their properties by combining two functional phases make semiconductor-based materials promising for a large variety of applications. In this respect, the coupling of surface plasmons (SPs) in Ag with ZnO excitons and donor-acceptor pairs (DAPs) for spectral control has attracted particular attention [1]. The interface morphology plays a key role in determining the coupling of SPs to light, and the roughness is considered to be an important factor in the emission modulation [1, 2]. The SP coupling to light is determined by both the metal particles' size and density. Several techniques have been recently developed to recover the energy trapped in SP modes, e.g. by introducing grating structures with appropriate periodicity or interface roughness, thus enabling the SPs to couple with light [3]. This work is focused on the investigation of Ag-ZnO nanocomposite photoluminescence as a function of surface plasmon resonance of Ag nanoparticles (NPs) and multilayer (ML) structures.

2. Experimental

Nanocomposite structures were successfully formed on a quartz substrates using the third harmonic of a Nd:YAG laser ($\lambda = 355$ nm, pulse duration $\tau = 18$ ns). Silver films with thickness of about 150 nm were deposited by laser ablation in a vacuum chamber at a pulse repetition rate of 10 Hz. The vacuum chamber was pumped down to 3.5×10^{-4} Torr. Laser annealing in air was applied for nanostructuring the silver layers at a fluence of 1 J/cm^2 at a fixed number of laser pulses ($N = 10$). The as-prepared silver nanoparticles were covered by a ZnO thin film using pulsed laser deposition (PLD) at room temperature and oxygen pressure of 2.4×10^{-1} Torr. The thickness of ZnO coating is very nonuniform and evaluated previously average film thickness is about 20 nm [4]. Layer-by-layer deposition was carried out by alternating Ag nanoparticles with ZnO films in order to produce a multilayer structure.

The nanostructuring of silver films was conducted above the ablation threshold of the silver, at $F_{th} = 1 \text{ J/cm}^2$. The threshold value varies for nanosecond laser ablation. It is confirmed by the mean NPs size of 70 nm, while the layer thickness is 150 nm before annealing, i.e. the part of material was removed. This is the way to produce by laser nanostructuring large NPs from the film having such

thickness. The mean size is dependent on the initial film thickness. Otherwise (at lower fluences) the film melts only on the surface, because of the absorption depth at this wavelength. At high fluence the film is ablated, leaving a distribution of nanoparticles only formed as the last of the film boils away. Nanostructuring of these films at higher fluences leads to formation of nanoparticles array, compared to the nanostructures obtained at lower laser fluences where a molten film was obtained between the initially formed nanoparticles.

Fig. 1 presents schematically the so-called “double layer” (DL) structure consisting of Ag/ZnO and the Ag/ZnO/Ag/ZnO system, the latter being the “multilayer structure” (ML). These conditionally adopted terms are used throughout the paper. The surface morphology of the Ag NPs was investigated by field emission scanning electron microscopy (FE-SEM) and the mean size of the nanoparticles and their size distribution were estimated. The optical transmission spectrum of the AgNPs and the composite nanostructures were analyzed in the 200-800 nm spectral range. The photoluminescence spectra of the samples were taken using the 325-nm line of a HeCd laser as an excitation source and a 350-mm effective focal length spectrometer equipped by a thermocooled CCD camera as a detection system. The laser light was incident on the sample at an angle of about 45° forming a 1-mm diameter spot; the photoluminescence light induced was collected in backscattering geometry using an achromatic confocal lens system.

3. Results

In view of improving the properties of nanocomposite heterostructures, we studied the possibility of forming multilayer coatings consisting of two to four alternating layers of AgNPs and ZnO.

By extending the DL system by suitable design variations, one can obtain interesting and useful optical properties over a broader spectral range; the properties of such ML systems can be varied through a proper optimization of the processing parameters. The nanostructured silver layers were used with a view of modifying the ZnO PL properties.

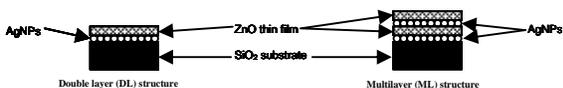


Fig. 1. Schematic of the double and multilayer structures.

Fig. 1 presents schematically the double layer and multilayer structures. The surface morphologies of the Ag nanoparticles before ZnO growth are shown in Fig. 2. The difference in the morphology of the two AgNPs layers is due to these being deposited on different surfaces, albeit under the same deposition conditions. The first silver layer is deposited on pure SiO₂, while the second one is

deposited on a sandwich structure consisting of the SiO₂ substrate covered by Ag nanoparticles (the first annealed layer decomposed into nanoparticles) and a ZnO layer. The silver film decomposition into nanosized droplets during the melting process is due to the pure wetting (dewetting) between the substrate and the liquid phase [5]. The resulting nanoparticles size distribution is influenced by the surface roughness of the initial film and the Rayleigh instability criterion. The thermal conductivity of the substrate is a controlling parameter determining the laser fluence required to melt the film. The first nanostructured silver film shown on Fig. 2 (a) consists of separate nanosized islands of about 90 nm in size having a large interparticle distance. The film is inhomogeneously decomposed and a fine nanoparticles background structure (with a mean grains size of about 25 nm) around the large particles is clearly seen on the magnified image. The large-sized nanoparticles form a porous microstructure of the layer. The upper nanostructured silver layer shows a narrow size distribution with a mean diameter of about 43 nm and a homogeneous structure (Fig. 2 (b)). These results demonstrate that the second silver underlayer in the multilayer structure is helpful in forming a dense nanoparticles array. The close-packed nanoparticles array was observed for the second silver layer.

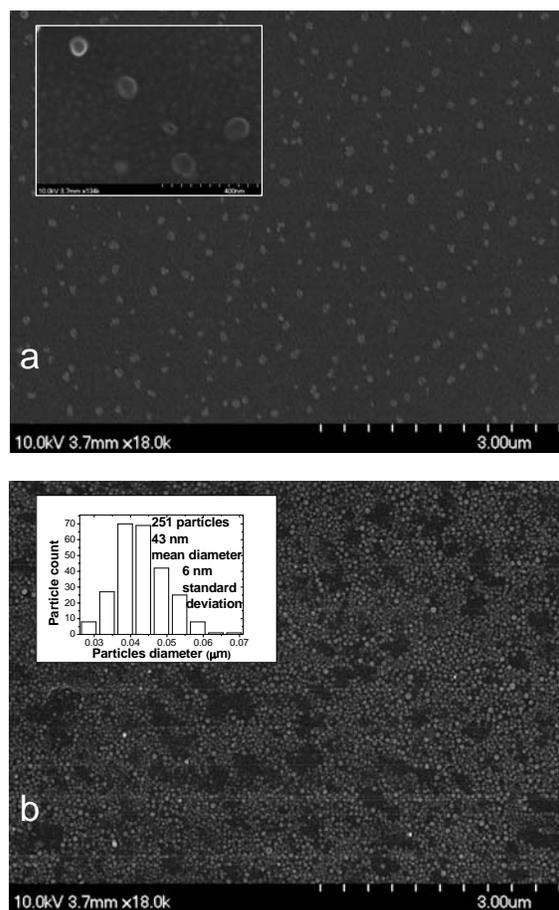


Fig. 2. SEM image of Ag nanoparticles in the DL structure (a) and (b) in the ML structure with an inset of histogram.

The crystal structure of the double and multilayer structures is presented on the XRD patterns (Fig. 3). The formation of a hexagonal wurtzite ZnO structure with *c*-axis preferred orientation along the (002) direction is seen for both samples. The diffraction patterns reveal the Ag (111) and (200) intensities, confirming the face centered cubic (fcc) structure. The intensity of all peaks increases with the number of layers (respectively, the thickness) of the nanocomposites. A comparison among (111) and (200) diffraction intensities indicates that the obtained silver nanoparticles are dominantly ruled by (111) planes. The degree of crystallinity differed in both samples. There is an obvious increase in the diffraction intensity of the (111) peak relative to that of the (200) peak in going from the DL sample to the ML sample.

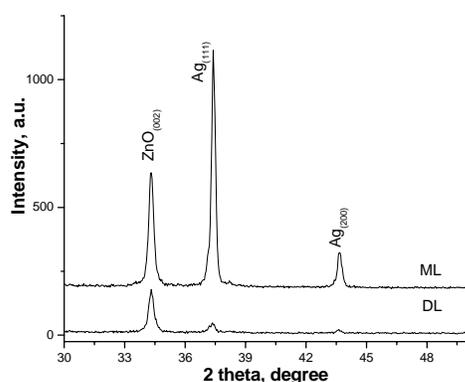


Fig. 3. XRD pattern of Ag/ZnO nanocomposite heterostructures.

Fig. 4 shows the optical transmission spectra of Ag NPs and Ag-Zn nanostructures. Two distinct absorption minima at about 345 nm and 470 nm are observed for Ag/ZnO and Ag/ZnO/Ag/ZnO, respectively, more clearly expressed for the DL structure. The absorption peak at 345 nm is the ZnO layer excitonic absorption, while the one located at 470 nm is the SPR absorption band of Ag [6]. The excitonic absorption peak [7] is blue shifted with respect to the bulk absorption at 371 nm. The presence of distinct features of ZnO and Ag in the optical transmission spectra is evidence for the formation of Ag/ZnO nanojunctions. As the number of layers is increased, the peak absorption position is shifted towards the longer wavelength region of the spectrum. The top ZnO layer significantly modulates the UV absorption spectra, leading to a reduction in the optical transmission. The plasmon excitation resonance wavelength can be controlled by adjusting the size and shape of the nanostructures. The minimal transmission at about 630 nm in the Ag/ZnO/Ag structure could be associated with the presence more absorption states or defect energy bands exist in the samples [8]. The defect structure is probably restored while depositing the second top ZnO film. The composite formation does not affect substantially the SP band of the

metal in other structures and has no impact on the interface effects [9]. However, according to Ref. [10], the absorption in the Ag NPs at both bands could be most probably attributed to dipole LSPRs. The dense microstructure (seen from Fig. 2b) is a prerequisite for the appearance of multiple dipole surface plasmon resonances in Ag nanoparticles, which may be a possible source of the double band spectrum at 470 nm and 630 nm. After coating the NPs by the second ZnO layer, the absorption at 630 nm disappears, so that the plasmon resonance properties of the AgNPs are influenced by the environment with a different dielectric constant.

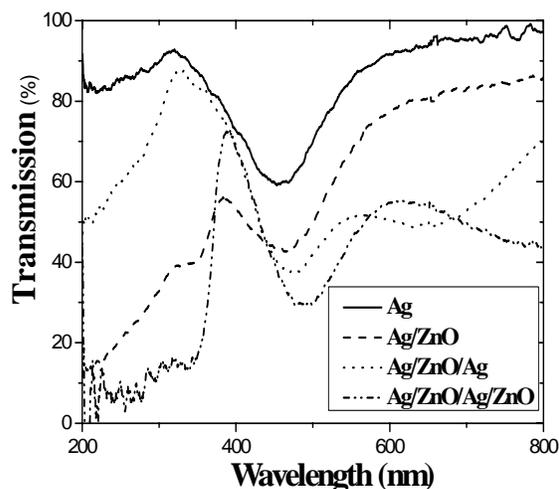


Fig. 4. Transmission spectra of silver nanoparticles and multilayer nanostructures.

The different Ag NPs morphology, which leads to various possibilities of coupling the SPs into light, is responsible for the difference in the optical properties of the composite nanostructures produced. The PL emission of the samples consists of three different spectral contributions, namely, a sharper UV peak at 385 nm and two broader resonance bands in the green and red part of the spectrum at 560 nm and 640 nm, respectively (Fig. 5).

The UV emission spectrum originates from a near band-edge transition of the wide-band-gap ZnO thin films, namely, from the free excitons recombination through an exciton-exciton collision process [11]. The influence of the Ag underlayer on the UV PL enhancement for the DL structure has been investigated previously [4, 12]. Such an effect was not observed for the ML structures. The green emission appears due to oxygen vacancies in a ZnO layer just below the crystalline surface [13]. Various models have been proposed to explain the green emission, including the involvement of O vacancies [14, 15], O interstitial [16], Zn vacancies and Zn interstitials [17]. Band bending at the particle boundaries must be taken into account [18] not only to explain the changes in the ionization state of the oxygen vacancy but also to understand the variations in the green PL intensity. The

green emission disappeared and an orange one appeared after the laser annealing of the second Ag film in the ML structures.

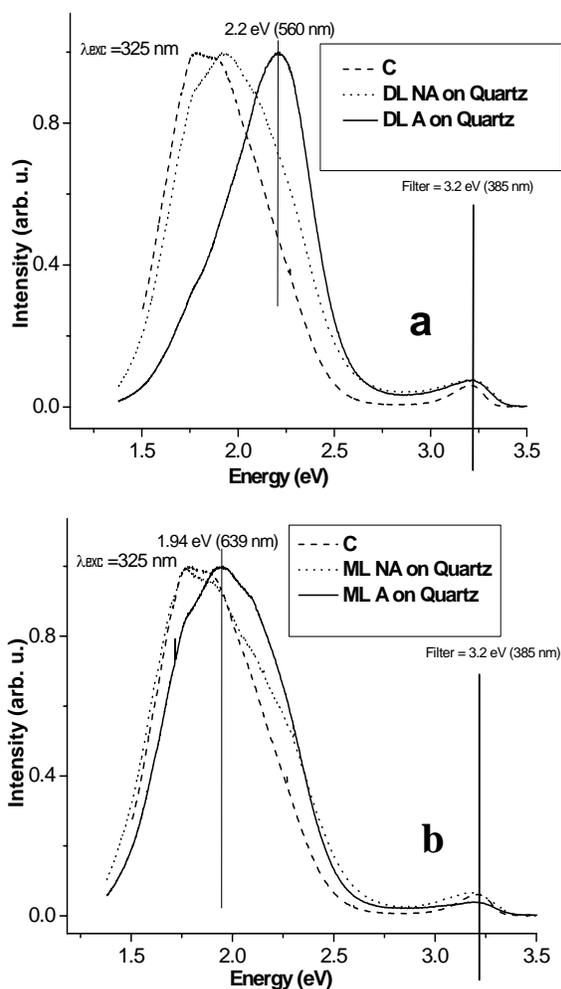


Fig. 5. Peak-normalized PL spectra of annealed (A) and nonannealed (NA): (a) double layer structure and (b) multilayer structure, in comparison with a pure ZnO thin film (curve C).

The samples exhibiting a green photoluminescence emission possess a porous structure of AgNPs; while the samples emitted orange PL light contains a second silver layer with close-packed nanoparticles morphology. This previously established dependence for the ZnO films correlates well with the microstructure of the Ag nanoparticles on the FE - SEM images, as shown in Fig. 2. Upon laser treatment of the nanostructures, the peak position shifted towards the shorter wavelengths (Fig. 5, from nonannealed to annealed). As reported earlier, both the green and the orange PLs are related to the amount of oxygen in the ZnO [13]. The green photoluminescence originates from oxygen deficient samples and the orange, from oxygen enriched samples. The green and orange

emissions were not observed simultaneously. Thus, the photoluminescent emission of the annealed multilayer structures was characterized by the oxygen enrichment. The position of the maximum did not shift substantially towards the peak of nonannealed sample, in contrast to the emission of the DL structure, where after annealing the shift is well expressed. The broad PL feature of the annealed ML sample can be fitted with two peaks, one corresponding to pure ZnO and the other, at about 1.93 eV, related to Ag emission [19]. The red bands with energies lying below 2 eV are related to the presence of Ag nanoparticles [20]. The broadened lineshape and redshift is also associated with the particles size.

The PL spectra are consistent with the results of the analyses of the samples' morphology, structure and transmission, thus confirming that the defect structure is restored when multilayer Ag/ZnO/Ag/ZnO nanocomposite structures are formed.

4. Conclusion

The study of laser-deposited and laser-annealed double layer and multilayer nanostructures of Ag and ZnO showed that the intensity of the X-ray diffraction peaks increases with the number of layers, i.e., with the nanocomposites thickness. The preferential orientation of the Ag nanoparticles along (111) directions was registered. The multilayer nanocomposites of Ag nanoparticles and ZnO exhibit several distinctive optical properties compared to the DL nanocomposites. A red-shifted SPR is observed as the number of the layers is increased, which is associated with the reduction of the interparticle distance. The PL emission properties are affected by the different Ag/ZnO interface morphologies in the double layer and multilayer structures. The investigation of dependence of the photoluminescent emission of the nanocomposite structures on the characteristic parameters of the Ag nanoparticles surface morphology revealed that the photoluminescence is determined by both the Ag particle size and density. The double-layer films showed a poor crystallinity with an inhomogeneous microstructure of the silver underlayer, while the multilayer films showed a higher degree of crystallinity and a close-packed NPs morphology of the second silver layer.

Acknowledgments

This work was supported in part by the Bulgarian National Science Fund at the Ministry of Education, Youth and Science under Contract No. DO02-293/08.

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