The relationship between tunable optical absorption and SERS activity of Ag/ZnO nanocomposites

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Abstract. The optical characteristics of Ag/ZnO composite nanostructures have long been of particular interest and, thus, the subject of broad experimental and theoretical studies. This work is focused on the synthesis and properties of Ag/ZnO nanocomposites and demonstrates the possibility of their application as active substrates for surface-enhanced Raman spectroscopy (SERS) in detection of pesticides. The samples were synthesized by pulsed laser deposition (PLD) of ZnO thin films, followed by Ag\textsuperscript{+}-ion implantation in the ZnO matrix and by laser annealing of the heterostructures produced. The morphology and properties of the samples were studied with respect to the processing parameters. The optical absorption studies revealed the existence of tunable surface plasmon resonance of silver nanoparticles in the ZnO matrix.

Theoretical calculations of the optical properties, as extinction, absorption and scattering efficiencies, were performed based on a generalized multi-particle Mie (GMM) approach. The simulated system assumed in this comparative study consists of a surface-embedded ensemble of silver nanoparticles in a ZnO surrounding media and in air. The simulated structures were reproduced from the corresponding SEM images after laser annealing at 355 nm and 532 nm.

1. Introduction
Recently, great attention has been paid to the contribution of metal structures encapsulated in semiconductors and dielectrics to their optical response [1]. The nature of surface plasmons determines the noble metal nanostructures as promising materials for the development of high-resolution sensing methods based on plasmon resonance properties [2, 3]. The possibility to tune the properties of some materials over a large range of values extends the range of materials investigated and of the fabrication methods used. The laser annealing offers distinct advantages over thermal annealing in processing implanted materials [4]. Light strongly absorbed in a thin surface layer produces a very high temperature in the implanted region, which is necessary for annealing the lattice damage. Laser annealing could be carried out in air since the introduction of impurities from the atmosphere is minimal and a highly localized annealing is possible [5].

The detection of pesticides is an important step in regulating and monitoring their level in the environment. Recent technological advances have brought to the fore techniques, such as SERS, that provide additional advantages compared to the standard techniques. Fungicides are widely used in...
agricultural farming to enhance yield and the quality of fruits and vegetables. Thiophanate-methyl (TM) is a benzimidazole fungicide applied pre- and post-harvest to control diseases caused by fungal pathogens in vegetables [6]. However, TM is unstable in plants and can be converted to carbenzazim (methyl benzimidazol-2-ylcarbamate) that causes endocrine disruption and embryotoxic and teratogenic effects [7, 8]. Therefore, the TM fungicide and residues of its metabolite carbenzazim in agricultural products constitute a significant health risk.

This work presents an experimental and theoretical study on the optical properties of Ag/ZnO composite nanostructures for SERS substrates. The efforts are focused on applying laser-based techniques and ion implantation to designing appropriate structures that can increase the efficiency of the SERS detection of pesticides at low concentrations making use of the local electromagnetic field enhancement in the vicinity of a structured surface.

2. Experimental

The Ag/ZnO nanostructures were prepared by combining laser and ion-implantation techniques. Laser deposition was used to grow ZnO thin films by means of a Nd:YAG laser at a fluence of 2 J/cm² and a pulse repetition rate of 10 Hz. Before deposition, the vacuum chamber was evacuated to a base pressure of \(\sim 3\times10^{-4}\) Torr. The films were grown at a substrate temperature of 500 °C and oxygen pressure of 150 mTorr. The films were slowly cooled down to room temperature in an oxygen environment and then implanted with Ag⁺-ions by an ILU-3 ion accelerator at room temperature with a current density of 5 μA/cm², energy of 30 keV and irradiation dose of \(10^{17}\) ion/cm². The implanted samples were laser annealed at the wavelengths of 355 nm and 532 nm with different number of laser pulses, namely \(N_p = 2, 5, 8\). The laser annealing fluence was kept at 800 J/cm².

The morphology of the samples was observed by high-resolution scanning electron microscopy (HRSEM) (Merlin, Carl Zeiss). The transmission spectra were recorded in the spectral range 210 – 800 nm by an HR 4000 UV–VIS spectrometer (Ocean Optics). A comparative study was performed for the SERS activity of the samples at different concentration of pesticides. A water solution of thiopanate-methyl (the active substance of the Topsis fungicide) was investigated as the analyte at the two concentration levels of 0.05 % and 0.1 %, marked as L (low concentration) and H (high concentration), respectively. The TM solution was loaded by dropping to the annealed points on the surface of the samples. After the TM solution dried at room temperature, the samples were prepared for SERS measurements. The Raman spectra were obtained using a LabRAM HR 800 (Horiba Jobin-Yvon) Raman spectrometer at 633 nm, with a laser spot size of 1 μm and a laser power of 0.05 mW to avoid overheating.

3. Results

The samples’ morphology was studied by SEM analyses. The SEM images (figure 1) show the presence of silver with sphere-like shape on the ZnO surface. The laser annealing of films at 355 nm leads to the ZnO layer fragmentation due to the higher absorption in the UV range (figure 1 (a)). Irradiation by nanosecond laser pulses results in melting and reshaping of the composite layer with the formation of a porous surface ZnO microstructure with distributed Ag NPs. A denser ZnO microstructure was obtained after annealing at 532 nm, as shown on figure 1 (b). It is due to the lower level of ZnO layer absorption in the VIS range. The sample annealed at 355 nm, where ZnO has a higher absorption, exhibits a more uniform size distribution of silver nanoparticles compared to the sample annealed at 532 nm, where a wide AgNPs’ size distribution is seen. In the latter sample (figure 1 (b)), particles with a maximal size of 45 nm were registered, unlike the sample in figure 1 (a), where the largest NPs are 24 nm in size.
Figure 1. SEM images of Ag⁺-ion implanted ZnO nanostructures after laser annealing by five laser pulses at 355 nm (a) and at 532 nm (b).

Figure 2. Transmission spectra of Ag/ZnO nanocomposites laser annealed at the wavelengths of (I) 355 nm and (II) 532 nm as a function of the number of laser pulses: a – \( N_p = 2 \), b – \( N_p = 5 \), c – \( N_p = 8 \) and d – before annealing.

Figure 2 presents the optical transmission spectra of the produced nanostructures annealed by various numbers of laser pulses. As the number of pulses increases, the resonance absorption band is red-shifted. The samples annealed by five pulses (figure 2, curves b) tended to absorb strongly within about 467 – 470 nm. In particular, the sample with a uniform Ag NPs size distribution annealed at 355 nm demonstrates the highest absorption after five pulses. Increasing the number of pulses to \( N_p = 8 \) results in attenuation of the absorption.

In order to analyze the dependences observed of the optical properties of the samples, a theoretical model was employed. It is based on the generalized multi-particle Mie (GMM) approach described in Refs. [9-12] and can be used for obtaining the optical spectra of nanoparticle ensembles with arbitrary configurations. The system under consideration is an ensemble of spherical Ag NPs embedded into a medium with a refractive index in the range 1.5÷2. These values are chosen because they roughly describe two media – one of ZnO (\( n = 2 \)) and the other, a boundary between ZnO and air (\( n = 1.5 \)), thus simulating two different degrees of incorporation of AgNPs into the medium of ZnO. Figure 3 presents the theoretically calculated extinction cross-section spectra of spherical AgNPs in two different media with \( n=1.5 \) (a) and \( n=2 \) (b).
Figure 3. Theoretically calculated extinction cross-section spectra of spherical Ag NPs with different sizes embedded into a media of air/ZnO with a refractive index of 1.5 (a) and ZnO with a refractive index of 2 (b). The configuration of the Ag NPs is shown in (c) and corresponds to a sample annealed by five pulses at the wavelength of 355 nm (I) and 532 nm (II).

The results of the SERS measurements presented in figure 4 are promising. The most intensive characteristic peaks of TM were seen in the Raman spectra at 783 cm\(^{-1}\), 1044 cm\(^{-1}\) and 1160 cm\(^{-1}\). The intensities of the Raman peaks of the samples annealed at 355 nm (figure 4 (a)) are about twice as strong as those annealed at 532 nm (figure 4 (b)). One should note the differences in the range of the y-axes. The SERS signal of the low TM concentration (L) for the sample annealed by five pulses is about tenfold stronger than the lowest registered signal of the sample annealed by eight pulses. The samples annealed by two and eight pulses demonstrate a weak Raman enhancement for the L concentration. The SERS activity depends on whether the silver nanoparticles were formed mostly in the volume of the matrix or on the surface.

Figure 4. SERS spectra of thiophanate-methyl (TM) fungicide at two concentration levels (L and H) on the surface of Ag/ZnO nanostructures annealed at (a) 355 nm and (b) 532 nm as a function of the number of laser pulses: \(N_p = 0, 2, 5\) and 8.
4. Conclusion

The results demonstrate that the combined technique of shallow implantation of Ag dopant in PLD-grown ZnO films followed by laser annealing leads to the preparation of effective SERS substrates for detection of pesticides. The laser annealing in the UV and VIS spectrum affects differently the ZnO absorption and, consequently, the metal NPs diffusion in the ZnO matrix. The results also demonstrate that the nanoparticles are partially embedded in the ZnO matrix and the number of pulses for annealing has a significant impact on the red shift of the resonance absorption band. The shift is associated with the Ag NPs size distribution and how deeply the NPs are embedded into the ZnO matrix. The measured optical spectra of the samples exhibit a good correlation with the theoretical calculations, particularly for the samples laser-annealed at 355 nm. The UV modification of the samples results in a higher surface-to-volume ratio of the ZnO matrix and a more uniform distribution of Ag NPs. The samples modified at 532 nm with a wider NPs’ size distribution demonstrate a similar resonance bands with close intensities for annealing at different laser pulses. The laser-produced nanostructures exhibit promising results for SERS detection of thiophanate-methyl fungicide with low concentrations, particularly the samples modified by UV irradiation. The laser annealing with five pulses exhibits the most promising SERS results associated with the most intensive resonance bands. The combined method proposed for synthesis of Ag/ZnO nanostructures contributes to the development of SERS as a sensitive and reliable method for monitoring fungicide residues in vegetables to guarantee food safety and quality.

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