Structural and photoluminescent properties of Ag/ZnO nanocomposite heterostructures

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Abstract. We describe the preparation of Ag nanoparticles covered by ZnO and investigation of the Ag/ZnO nanocomposite heterostructures. The silver nanoparticles were produced by pulsed laser deposition (PLD) on quartz substrates in a vacuum chamber and were post-deposition annealed by a Nd:YAG laser for surface nanostructuring. The morphology and optical properties of Ag nanoparticles were studied and the mean particles diameter and size distribution were estimated. Laser ablation was used for the subsequent deposition of ZnO. In order to study the Ag nanoparticles influence on ZnO, X-ray diffraction (XRD) and photoluminescent (PL) spectra were obtained and analyzed. It was found that the band-gap emission of ZnO grown on Ag nanoparticles can be enhanced by about a factor of five compared to the emission of ZnO film without Ag undercoating. The silver nanoparticles are also responsible for the UV shift in the PL emission.

1. Introduction

It is well-known that an electric dipole placed in the proximity of a metal surface may transfer energy to surface plasmons (SP), which results in modification of its spontaneous emission decay rate [1]. This effect has been used to enhance the photoluminescence (PL) of light emitters, further aiming to raise the emission efficiency of light emission diodes (LEDs) [2, 3]. The metal films morphology has been found to be of paramount importance for SP-mediated emission enhancement [2], because after radiation energy is transferred to SPs, the coupled SP energy can only be transferred to free space radiation by scattering which bridges the momentum gap. Thus, metal films with periodic grating or random corrugation have been typically used to realize light emission enhancement.

Several methods have been applied in view of improving the light emitting efficiency of the optoelectronic devices based on ZnO, such as hydrogen doping, annealing or metal doping [4-7]. In all these methods, the underlying mechanisms for the improvement were attributed to the passivation of defects by doping atoms, or to carrier transfer. Newly devised ZnO/Ag nanocomposites have been based on another mechanism of combined effect of surface modification, namely, band alignment and charge transfer between Ag and ZnO in the nanostructure.
2. Experimental

Silver films with thickness of 180 nm were deposited on 1×1 cm quartz substrates by laser ablation in a vacuum chamber at a base pressure of 3.9×10^{-4} Torr and fluence of 2.6 J/cm². The substrate to target distance was 3.5 cm. Laser annealing in air at a fluence of 1 J/cm² was applied for nanostructuring the silver layers by a fixed number of laser pulses \( N_p = 10 \). The as-prepared silver nanoparticles were covered by a ZnO thin film using pulsed laser deposition at room temperature. A reference sample without Ag nanoparticles was also prepared at the same deposition conditions for PL comparison. Since a good quality crystalline and stoichiometric ZnO films were produced also at low oxygen pressures [8, 9], our depositions were carried out at 3 Pa of oxygen flow for 10 min. The laser deposition of Ag and ZnO films and the laser annealing were performed by using a third harmonic Nd:YAG laser (Lotis LS-2147, \( \lambda = 355 \) nm, pulse duration \( \tau = 18 \) nm) operating at a repetition rate of 10 Hz for the laser deposition. The morphology of the thin films, nanoparticles and nanocomposites was characterized by scanning electron microscopy (SEM) (Dual beam system SEM/FIB, Lyra/Tescan) and the mean size of the nanoparticles was estimated. The crystalline nature of the films was confirmed by XRD with Cu-K\( \alpha \) radiation (1.54 Å). The transmission spectrum of the Ag nanoparticles was analyzed using a VIS OTS spectrometer (Ocean Optics Inc.) in the range of 380 – 780 nm. The PL measurements were made using a Fluorolog spectrofluorometer (HORIBA Jobin Yvon) under excitation at 320 nm.

3. Results

Laser annealing of silver films at 1 J/cm² leads to melting and fragmentation of the material into nanosized droplets. Except on the laser fluence, the particles density and size distribution depend also on the film thickness and the other deposition conditions [10]. The morphology of the Ag nanostructured film and nanocomposite heterostructures of ZnO/Ag are presented in figure 1 (a and b). A mean particles diameter of 70 nm was estimated for the silver nanoparticles in the range of 30 – 110 nm (figure 1a). Figure 1b shows the ZnO/Ag nanocluster formation, where the nanoparticles formed are also spherical and have a mean diameter of 90 nm in the range of 40 – 130 nm. Therefore, the silver nanoparticles are covered by approximately 20-nm ZnO shell. The deposition of ZnO on a quartz substrate at room temperature and oxygen ambient leads to the formation of a continuous film having a flat surface, as presented on figure 1c.

![Figure 1](image)

**Figure 1.** SEM images and size histograms of (a) Ag nanoparticles (b) ZnO/Ag nanocomposite heterostructures and (c) ZnO thin film.

The transmission spectrum of Ag nanoparticles is given in figure 2. A transmission minimum is observed at 450 nm, which is due to the excitation of surface plasmons by narrow-size-controlled Ag nanoparticles. The small interparticle distances, visible on figure 1a, lead to interaction between the particles, such as plasmon coupling and multiscattering effects.
Crystalline ZnO films were successfully deposited at room temperature in oxygen ambient on quartz substrates. Figure 3 shows XRD patterns of ZnO thin films fabricated with and without a Ag nanostructured layer. The results confirm the single-phase structure of ZnO with a (002) preferred orientation. The peaks obtained are indexed to wurtzite ZnO with high crystallinity. The ZnO film and the ZnO/Ag nanocomposite film exhibit the same XRD spectra, the only difference being the diffraction intensity which depends on the metal undercoating. The presence of Ag nanoparticles is found to induce a reduction in the diffraction intensity due to the Ag nanoparticles role of impurities induced defects in the ZnO matrix. No characteristic peaks of other phases were observed in the samples.

![Figure 2](image1.png)

**Figure 2.** Transmission spectra of silver nanoparticles produced from the film with thickness of 180 nm annealed at 1 J/cm².

A broad photoluminescent peak centered at 420 nm is observed for the pure ZnO thin film on quartz. The photoluminescence is strongly enhanced after ZnO is grown onto the silver nanoparticles. The separation from the substrate by a nanostructured plasmonic silver film with thickness of 180 nm also leads to a shift in the PL peak position from the violet towards the near UV spectrum. The PL enhancement in these heterostructures is attributed to hot electron transfer to the conduction band edge [11]. The origin of the hot electrons can be understood in terms of excitation of local surface plasmons (LSPs) in the metal nanoparticles. The LSP resonances depend on the particular geometry of the individual nanoparticles and on the dielectric environment [12].

![Figure 3](image2.png)

**Figure 3.** XRD patterns of (a) ZnO and (b) ZnO/Ag on SiO₂ substrates.

![Figure 4](image3.png)

**Figure 4.** PL spectra of (a) pure ZnO on SiO₂ and (b) ZnO/Ag on SiO₂ substrate.

Conclusions
Silver nanoparticles having a spherical shape with size in the range of 30 – 110 nm and mean diameter about 70 nm were prepared from a 180-nm silver layer by laser annealing in air. Silver films were produced by pulsed laser deposition using a third-harmonic Nd:YAG laser. ZnO films with a flat surface and single crystalline phase structure were deposited on SiO₂ substrates at room temperature. Transformation of the ZnO thin film to a discontinuous structure consisting of small particles was
observed when the deposition was performed onto a silver nanostructured surface. Spherical nanocomposite particles with mean diameter of 90 nm and a relatively narrow size distribution were observed. The characteristic silver plasmon minimum was observed in the optical transmission spectrum at 450 nm. A broad peak in the visible band of the PL spectrum was detected for pure ZnO. Utilizing an Ag underlayer, the light emitting efficiency of the ZnO layer was improved considerably. The interfacial charge transfer between metal Ag and ZnO is also responsible for the emission shift from the VIS to the UV spectrum.

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