Optical properties of Ag/ZnO nanocomposite coatings

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Abstract. In this work, ZnO nanostructures were fabricated on Ag-coated substrates by pulsed laser deposition. Ag was incorporated into ZnO nanostructures during the growth by using a composite, or mosaic, target. The effect was studied of Ag doping on the morphology, structure, composition, and photoluminescence of the ZnO nanostructures. It was found that the increase of the dopant concentration leads to a deterioration of the crystalline structure, as well as to a change of the sample morphology. It was also found that the manner of incorporating Ag into the ZnO matrix affects the photoluminescent performance of the nanocomposite coatings.

1. Introduction
One of the most versatile materials used in nanotechnology is zinc oxide (ZnO), a semiconductor with an exceptional potential for applications in optics, energy conversion, biomedicine, etc. [1]. ZnO exhibits numerous remarkable characteristics, such as functional catalytic and optical properties, electrical, chemical and thermal stability, low dielectric constant, antimicrobial and antibacterial effects, and has formed probably the richest family of nanostructures among all semiconducting materials [2-4]. Modification of the oxide nanostructures through the introduction of appropriate additives is a key factor in optimizing the existing, or developing novel, properties [5,6]. When the additives are in the form of nanoparticles, a new composite structure is obtained, which possesses specific properties defined, on the one hand, by the nanoparticles composition, shape, and size, and, on the other, by the nanosized oxide matrix surface, morphology, and structure. A huge variety of composite materials are being synthesized and investigated for various optical applications ranging from third-order nonlinearity to fabrication of new transparent magnetic materials [7-9]. In this regard, it is essential to clarify the fundamental phenomena and study the optical properties of these nanocomposite materials, as they are expected to form the basis of future technologies.

A wide variety of techniques has been employed to fabricate oxide nanostructures with different morphologies [10]. Among those, pulsed laser deposition (PLD) stands out as a simple, less expensive and more flexible technique for producing well-crystallized structures than many rival gas-surface-

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based growth methods [11]. Furthermore, because laser ablation maintains the stoichiometry of the target material, PLD is especially suitable for obtaining a doped material using pre-doped targets.

The aim of this work was to fabricate Ag/ZnO nanocomposite coatings by PLD. Ag was incorporated into ZnO nanostructures during the growth by using a composite, or mosaic, target. We also studied the effect of Ag doping on the morphological, structural, compositional, and optical properties of the nanostructured ZnO coatings.

2. Experimental
The experiments were performed in a standard on-axis PLD configuration. The third harmonic of a Nd:YAG laser ($\lambda$ = 355 nm and a repetition rate of 10 Hz) was used for ablation of a ceramic target. The laser fluence applied was 0.4 J cm$^{-2}$. Two different targets were used: composite or mosaic. The mosaic target was formed by a ZnO target partly covered by a Ag slide (covering ratio 1/3 Ag:2/3 ZnO). The samples produced by laser ablation of the pure ZnO and the mosaic targets are hereinafter referred to as “sample A” and “sample B”, respectively. Composite targets with three different Ag contents were sintered by using ZnO and AgNO$_3$ powders as initial materials. The samples prepared by ablation of the composite targets with Ag content of 0.5, 1, and 3 at % are referred to as “sample C”, “sample D”, and “sample E”, respectively. The distance between the target and the substrate was kept at 60 mm. All experiments were performed in oxygen atmosphere at a pressure of 5 Pa, a substrate temperature of 600 °C and for a deposition time of 90 min. The substrate was made of (001)-oriented silica (SiO$_2$) covered by a Ag layer. The catalyst layers were produced by laser ablation of a metal target in the same PLD set-up, but under different experimental conditions, namely, at room substrate temperature in vacuum and a target-substrate distance of 35 mm. The average thickness of the covering layers was 100 nm.

The surface morphology of the samples was analyzed using scanning electron microscopy (SEM). X-ray diffraction (XRD) was applied in order to investigate the crystalline structure of the ZnO samples. The elemental composition and chemical state of the sample surfaces were studied using X-ray photoelectron spectroscopy (XPS). The optical absorbance spectra of the samples were determined by a UV-VIS spectrophotometer. The photoluminescent (PL) spectra of the ZnO samples were recorded at room temperature by using an excitation source at $\lambda = 325$ nm.

3. Results and discussion
SEM images of the ZnO samples prepared from the pure and the mosaic targets are presented in figure 1. As seen in figure 1(a), ablating the pure ZnO target under the experimental conditions described above results in the fabrication of nanorods with diameters within 70 – 200 nm and lengths in the 200 – 250 nm range.

![Figure 1](image_url)

**Figure 1.** SEM images of Ag/ZnO samples prepared from: (a) pure – sample A, and (b) mosaic target – sample B.
Ablation of the mosaic target (figure 1(b)) did not lead to a significant change in the samples’ morphology. In the latter case, adding Ag into the ZnO samples during deposition resulted in nanostructures with a larger mean diameter and a wider range of nanorods’ diameters (130 – 250 nm).

SEM images of the ZnO samples produced from composite targets with different Ag concentrations are presented in figure 2. Figure 2(a) shows the SEM image of the sample deposited from the composite target with the smallest Ag content. It is seen that the sample’s morphology (and the particles’ mean diameter as well) did not differ from that of the sample produced from pure ZnO target (figure 1(a)). The increase of the Ag concentration in the target led to the deposition of a denser structure of shorter nanorods with diameters ranging from 150 to 250 nm (figure 2(b)).

Figure 2. SEM images of Ag/ZnO coatings prepared from composite targets: (a) sample C, (b) sample D, and (c) sample E.

Increasing further the Ag content in the composite target changed the morphology of the sample (figure 2(c)). Thus, the sample’s morphology presented a denser grain structure with smaller nanorods diameters in the range of 60 – 120 nm; i.e., increasing the Ag dopant concentration incorporated into the ZnO structure during deposition (by using a composite target) changes the morphology of the samples and impedes the growth of nanostructures.

XRD spectra of the Ag/ZnO nanostructured coatings produced from the mosaic and the composite target are presented in figure 3. The patterns can be indexed to a hexagonal structure of bulk ZnO (ICSD 98-002-6170). All samples were slightly textured along the [002] direction; we should point out that Ag was present in all spectra as a separate phase (ICSD 98-004-4387).

Figure 3. XRD spectra of the Ag/ZnO nanostructures prepared from: (a) mosaic and (b) composite targets.
The XRD spectra of the sample produced from the pure and the mosaic target are compared in figure 3(a). As it is seen, the diffraction peaks intensity for the predominant [002] direction decreased slightly with the use of a mosaic target, i.e. with adding Ag. The average crystallite size, as evaluated for the dominant diffraction peak with (002) symmetry, was about 20 nm. Figure 3(b) presents XRD spectra of the samples produced from composite targets with different Ag content. As seen, the increase of the dopant concentration in the targets led to a substantial decrease of the samples’ crystalline quality. In this case, an intensity decrease was observed for all diffraction peaks. It should be mentioned that both the ZnO and Ag phases were homogeneously distributed in the depth of all samples, independently of the target used for ablation.

The ZnO structures’ physico-chemical composition was studied by XPS analysis of the samples’ surface (not shown). The Zn2p3/2 photoelectron peak located at 1021.4 eV was symmetrical in shape, implying the existence of only one zinc state. On the contrary, the O1s peak outline was asymmetrical and presented an apparent shoulder. The O1s peak was deconvoluted into two components at 530.1 eV and 531.5 eV. The main peak centered at 530.1 eV belongs to the lattice oxygen of the wurtzite structure of ZnO, while the shoulder peak located at 531.5 eV could be associated with O2− ions in the oxygen deficient regions within the ZnO matrix [12,13]. A peak at 367.4 eV was also observed which is due to the binding energy of Ag3d. This result indicated the existence of Ag dopant in the ZnO nanostructures. The XPS analyses showed the presence of oxygen deficient states in the samples; the increase of the Ag content in the targets increased the oxygen deficiency on the samples’ surface. The XPS analyses were also used for quantification of the atomic composition of the samples. According to the experimental XPS peak areas, the Ag/Zn atomic ratio in Ag/ZnO nanostructures deposited from composite targets were approximately: 0.06 % of Ag/Zn in sample C, 0.1 % of Ag/Zn in sample D, and 0.3 % of Ag/Zn in sample E. The Ag/ZnO sample produced from the mosaic target (sample B) had a Ag/Zn ratio of 0.1 % (the same as sample D).

![Figure 4](image1.png)  **Figure 4.** UV-VIS spectra of ZnO samples prepared from pure ZnO and a mosaic target. Inset: optical spectra of samples produced from composite targets.

![Figure 5](image2.png)  **Figure 5.** PL spectra of ZnO samples prepared from pure ZnO and a mosaic target. Inset: PL spectra of the samples produced from composite targets.

The UV-VIS absorbance of the pure ZnO and Ag/ZnO nanostructures (figure 4) were obtained to provide evidence of the presence of Ag nanoparticles in the samples. A well-defined surface plasmon resonance (SPR) band was observed in the Ag/ZnO sample produced from the mosaic target. A broad SPR peak was centered at 460 nm (sample B). The inset in figure 4 illustrates the influence of the Ag content in the ZnO samples on their optical absorbance. As seen, all samples possessed an SPR peak, with a monotonic red shift observed in the SPR resonance with the increase of the Ag content, indicating that Ag was present in the ZnO nanostructured coatings in the form of nanoparticles, independently of the manner of the incorporation.
Figure 5 presents PL spectra of the pure and the Ag-doped ZnO nanostructures. They exhibited a strong UV emission and a broadband visible emission with a peak at ~500 nm. It is well known that the UV emission corresponds to the near band-edge emission, while the green emission peak is commonly referred to as a deep-level or a trap-state emission [14,15]. Incorporating Ag nanoparticles in ZnO nanostructures by using a mosaic target led to a change in the emission spectrum as compared with that of the pure ZnO nanostructure (figure 5). The UV emission kept its intensity, but the full width at half maximum (FWHM) of the peak was substantially narrower. At the same time, the intensity of the green emission increased, while the FWHM of its peak decreased. The inset in figure 5 shows the dependence of the Ag/ZnO samples’ PL performance on the Ag concentration. As seen, increasing the Ag content reduces the intensity of the PL signal from the samples, which is probably due to a decrease in the crystalline quality of the samples. It should be mentioned that, despite the same crystalline quality and Ag/Zn atomic ratio of samples B and D, their PL spectra are different, or the manner of incorporating Ag in the ZnO matrix affects the photoluminescent performance of the nanocomposite samples. Clarifying the effect of incorporating Ag nanoparticles in a ZnO matrix on the PL performance will require further detailed studies of these nanocomposites’ microstructure.

4. Conclusions
Pure ZnO and Ag/ZnO nanocomposite coatings were grown by means of PLD. Ag was incorporated in ZnO nanostructures during the growth by using a composite, or mosaic, target. It was found that the use of a mosaic target for ablation did not change significantly the samples’ morphology. Furthermore, the Ag doping did not change the growth direction of the nanostructures on the samples. Ag was present in the ZnO nanostructure coatings in the form of nanoparticles, which was confirmed by detecting an SPR peak in the absorbance spectra of all nanocomposites. The PL spectra exhibited a strong UV emission and a broadband green emission with a peak at ~500 nm. The manner of incorporating Ag in the ZnO matrix affected the photoluminescent performance of the nanocomposite samples.

Acknowledgements
The authors wish to thank Vladimir Georgiev and Nadya Stoykova for the special equipment provided for registering the optical spectra of the samples. The authors also acknowledge the financial support of the Bilateral Join Research Project “Laser-assisted fabrication of composite nanostructures” between the Bulgarian Academy of Sciences and CNR-SPIN Consiglio Nazionale delle Ricerche.

References
[1] Wang Z 2007 Appl. Phys. A 88 7
[2] Huang M, Mao S, Feick H, Yan H, Wu Y, Kind H, Weber E, Russo R and Yang P 2001 Science 292 1897
[3] Law M, Greene L, Johnson J, Saykally R and Yang P 2005 Nat. Mater. 4 455
[4] Aal N, Al-Hazmi F, Al-Ghamdi F, Al-Ghamdi A, El-Tantawy F and Yakuphanoglu F 2015 Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 135 871
[5] Zhang X, Chen Y, Liu R and Tsai D 2013 Rep. Prog. Phys. 76 046401
[6] Baffou G and Quidant R 2014 Chem. Soc. Rev. 43 3898
[7] Beecroft L and Ober C 1997 Chem. Mater. 9 1302
[8] Khan R, Uthirakumar P, Bae K, Leem S and Lee I 2016 Mater. Lett. 163 8
[9] Lee M, Kim T, Kim W and Sung Y 2008 J. Phys. Chem. C 112 10079
[10] Wang Z 2004 J. Phys.: Cond. Matter. 16 R829
[11] Eason R 2007 Pulsed Laser Deposition of Thin Films: Applications-Led Growth of Functional Materials (Hoboken: Wiley)
[12] Zhang L and Yin Y 2013 Sens. & Act. B 183 110
[13] Xu X, Chen D, Yi Z, Jiang M, Wang L, Zhou Z, Fan X, Wang Y and Hui D 2013 Langmuir 29 5573
[14] Li C, Fang G, Fu Q, Su F, Li G, Wu X and Zhao X 2006 J. Crystal Growth 292 19
[15] Yang P, Yan H, Mao S, Russo R, Johnson J, Saykally R, Morris N, Pham J, He R and Choi H 2002 Adv. Funct. Mater. 12 323