Hybrid Ag/ZnO nanostructures for SERS detection of ammonium nitrate

M E Koleva\textsuperscript{1,4}, N N Nedyalkov\textsuperscript{1}, Ru G Nikov\textsuperscript{1}, Ro G Nikov\textsuperscript{1}, V I Nuzhdin\textsuperscript{2}, V F Valeev\textsuperscript{2}, A M Rogov\textsuperscript{2,3} and A L Stepanov\textsuperscript{2}

\textsuperscript{1}Acad. E. Djakov Institute of Electronics, Bulgarian Academy of Sciences, 72 Tzarigradsko Chaussee, Sofia 1784, Bulgaria
\textsuperscript{2}Kazan Physical-Technical Institute, Russian Academy of Sciences, 420029, Kazan, Russia
\textsuperscript{3}Kazan Federal University, 420081, Kazan, Russia

E-mail: mihaela_ek@yahoo.com

Abstract. Ag/ZnO composite nanostructures are produced by combined laser and ion implantation techniques. The ZnO layers are grown on SiO\textsubscript{2} (001) and Al\textsubscript{2}O\textsubscript{3} (r-cut) substrates by pulsed laser deposition (PLD) in vacuum and in oxygen ambient using a third-harmonic Nd:YAG laser. The ion implantation allows the introduction of Ag nanoparticles (NPs) in the surface of the ZnO matrix. These NPs are incorporated into the ZnO matrices to fabricate metal-semiconductor nanocomposites with the aim of manipulating their functionalities, exploiting the characteristics of both the matrix and the metal NPs. The composite samples are modified by laser annealing at 355 nm and 532 nm. The changes are investigated in the plasmon resonance absorption of the nanostructures before and after the annealing. The influence is explored of the different substrates used and the deposition conditions of ZnO growth on the properties of Ag/ZnO. The nanostructures obtained are efficient as SERS substrates for detection of ammonium nitrate under laser excitation at 633 nm. The SERS enhancement is attributed to the synergistic interactions between the plasmonic coupling among the surface embedded AgNPs and the enhanced charge transfer properties of the ZnO.

1. Introduction

The study of the collective effects arising in the interaction of an electromagnetic field with composite materials consisting of semiconductors functionalized by noble metal NPs is related to the development of efficient methods for fabrication of nanostructures with desirable optical parameters and their application in surface enhanced Raman spectroscopy (SERS) [1]. The latter is of interest for use in detection of substances with high social impact, such as nitrates, in food and water. Zinc oxide has received much attention because of its numerous technological applications [2]. The incorporation of noble metals as NPs in ZnO thin films is a very attractive way of enhancing their structural and optical properties [3, 4]. The noble metals, in the form of nanoparticles, exhibit a selective surface plasmon resonance (SPR) band. The presence of plasmon-active nanoparticles in a matrix offers new optical properties for different plasmonic applications [5, 6]. The nanocomposites consisting of metal

\textsuperscript{4} To whom any correspondence should be addressed.
NPs embedded in a matrix have attracted considerable attention for fundamental and applied research [7, 8]. The interest in ion implantation as a method for synthesizing metal NPs in matrices is due to the use of composites in designing elements with unique optical properties [9]. Since the optical properties of metal nanoparticles are directly related to their size, one may control the optical performance of a composite as a whole by controllably varying the metal NP’s size and size distribution by laser annealing [10]. These heterostructured nanocomposites with AgNPs arrays hold a great potential for SERS applications [11]. In this work, we describe a combined laser and ion implantation method for synthesis of hybrid Ag/ZnO nanostructures for SERS substrates.

2. Experimental
The ZnO layers are grown on SiO$_2$ (001) and Al$_2$O$_3$ (r-cut) substrates by pulsed laser deposition (PLD) utilizing a third-harmonic Nd:YAG laser. The depositions are carried out in vacuum and in oxygen ambient at a pressure of 20 Pa. Shallow implantation of Ag$^+$ in the ZnO matrix is performed by an ILU-3 ion accelerator at room temperature with an energy of 30 keV, an irradiation dose of 10$^{17}$ ion/cm$^2$ and a current density of 5 µA/cm$^2$.

The morphology of the samples and surface roughness are monitored before and after the ion implantation by a FastScan (Bruker) atomic force microscope (AFM). After the implantation, the samples are laser-annealed at two different wavelengths – 355 nm and 532 nm, using 5 pulses at a laser fluence of 800 mJ/cm$^2$ and 750 mJ/cm$^2$, respectively.

The transmission spectra are recorded in the spectral range 200 – 800 nm by an HR 4000 UV-VIS spectrometer (Ocean Optics) to explore the plasmonic properties of Ag nanoparticles in ZnO environment before and after the laser modification by UV or VIS irradiation, respectively, 355 nm and 532 nm.

The SERS sensitivity of the nanostructures for ammonium nitrate (AN) is studied under excitation at 633 nm. The AN molecules are loaded by dropping a water solution on the surface of nanostructures; once the solution dries up, the Raman signal is collected. The samples are exposed to an AN concentration of 50 mg/l, this value being the drinking water exit standard at waterworks [12].

3. Results
The surface analyses of the samples’ morphology performed by the AFM are shown in figure 1. The surface topography of the ZnO thin films on Al$_2$O$_3$ and SiO$_2$ substrates is observed before and after the Ag$^+$ ion implantation. The fabricated ZnO layers demonstrate a relatively rough surface with columnar growth and an average size of the grains in the range 5 – 60 nm depending on the substrate used (figure 1 a and d). The films are crystalline and have a dense microstructure. The ion implantation results in the formation of AgNPs embedded on the surface as shown on figure 1 (b and e). The films deposited on sapphire substrates are characterized by the formation of smaller NPs and more uniform surface microstructure. The NPs mean size is about 13 nm with a narrow size distribution in the range 6 – 20 nm. In comparison, the silver ion implantation in ZnO on a sapphire substrate leads to the formation of larger nanoparticles with a mean size of 35 nm and a size distribution in the range 10 – 60 nm. The laser annealing of the nanostructures at 355 nm transforms the nanoparticles in the Ag/ZnO composites on the Al$_2$O$_3$ substrate into a nanoporous microstructure, namely, clusters of nanoparticles with a broader size distribution of the AgNPs, as shown in figure 1c. The surface morphology for the Ag/ZnO samples on SiO$_2$ substrates after the annealing at 355 nm is completely different. The image in figure 1 f demonstrates a more uniform microstructure with a narrow size distribution of the NPs.

The AgNPs synthesized in a ZnO matrix by ion implantation demonstrate a characteristic absorption line associated with the surface plasmon resonance effect (figure 2). The plasmon resonance band of the samples on a SiO$_2$ substrate is at about 390 nm (figure 2 – I and II), while the implanted samples on an Al$_2$O$_3$ substrate show resonance absorption about 460 nm (figure 2 – III and IV).
The results demonstrate that the substrate used has a considerable influence on the ZnO growth and, respectively, the crystal structure of the deposited ZnO has a strong impact on the SPR properties of AgNPs in a ZnO matrix. Generally, the laser annealing leads to a red shift of the SPR band position, except in the case of the sample grown in oxygen on an Al$_2$O$_3$ substrate. The samples on quartz exhibit red-shifted resonance absorption, which increases noticeably after the laser annealing at 355 nm, while the sample deposited in oxygen possesses a narrower resonance band (Figure 2-II). This could be

**Figure 1.** Plane view AFM images of the surface topography of a pristine ZnO film on: (a) Al$_2$O$_3$ and (d) SiO$_2$ substrates; Ag$^+$-ion implanted ZnO film, (b) Al$_2$O$_3$ and (e) SiO$_2$ substrates and corresponding laser-annealed samples at 355 nm, (c) Al$_2$O$_3$ and (f) SiO$_2$. The insets show histograms with the size distribution of AgNPs after the ion implantation.

**Figure 2.** Transmission spectra of Ag/ZnO nanostructures. I – ZnO/SiO$_2$ in vacuum, II – ZnO/SiO$_2$ in oxygen, III – ZnO/Al$_2$O$_3$ in vacuum, IV – ZnO/Al$_2$O$_3$ in oxygen.
associated with the more uniform morphology and the narrower size distribution of the small NPs for the samples deposited on SiO$_2$ (figure 1f).

The samples with the ZnO grown in vacuum do not exhibit any noticeable SERS enhancement after the annealing procedures. It is expressed slightly for the sample on sapphire for both annealing wavelengths of 355 nm and 532 nm. The nanostructures with ZnO grown in oxygen show an enhanced SERS signal. Intense signal is observed for the sample on Al$_2$O$_3$ after the implantation and before annealing (figure 3-IV). Attenuation of the signal is found after the annealing, despite the same resonance absorption curves form figure 2-IV. Most probably it is due to a near-field energy redistribution by the NPs, which has no impact on the properties registered in far field. Another possible explanation is that the change in the NPs size is compensated by the change in the interparticle distances after annealing, so the curves in figure 2 are similar. Thus, the most intense Raman signals from AN are registered for two nanostructures of Ag/ZnO (figure 3-II and IV). One is the implanted sample deposited on sapphire in oxygen before the annealing. The other is the sample with ZnO grown on quartz in oxygen and annealed at 355 nm. This SERS enhancement could be associated with the plasmon contribution together with the enhanced charge transfer properties of ZnO after the annealing in the UV spectrum, where ZnO absorbs strongly.

![Figure 3. Raman spectra for ammonium nitrate of Ag/ZnO nanostructures as SERS substrates: I – ZnO/SiO$_2$ in vacuum, II – ZnO/SiO$_2$ in oxygen, III – ZnO/Al$_2$O$_3$ in vacuum, IV – ZnO/Al$_2$O$_3$ in oxygen.](image)

4. Conclusions
A fabrication strategy is experimentally demonstrated whereby plasmonic AgNPs are embedded and modified in ZnO layers. The results show that the proposed approach based on laser and ion implantation techniques can be adapted to produce hybrid substrates for SERS applications. The effects are investigated of ion implantation and post-implantation laser annealing on the structural and optical properties of ZnO films deposited on different substrates and in different surrounding media. The surface morphology changes significantly after ion implantation, while the size of the AgNPs depends on the substrate used for growing the ZnO layer used as a matrix for implantation. The AgNPs produced after implantation in a ZnO layer grown on SiO$_2$ in oxygen ambient have a smaller size. These samples exhibit a narrow NP size distribution and a strong SERS enhancement after laser annealing at 355 nm. The sample grown in oxygen on sapphire shows a high SERS signal before the annealing. The composite nanostructures with ZnO deposited in oxygen ambient are the most
promising candidates for SERS-active substrate for detection of AN. Also, the SERS enhancement is stronger before or after the laser annealing procedures depending on the substrates used.

Acknowledgements
This work is supported in part by the Bulgarian National Science Fund under the Russian-Bulgarian bilateral project DNTS/Russia 02/3 – 14.06.2018 “Combined laser and ion implantation techniques for nanostructuring of Ag/ZnO composites for SERS applications”; in Russia - RFBR grant No. 18-58-18001.

References
[1] Zhou J et al. 2019 Nanoscale 11/24 11782-8
[2] Gupta T K 1990 J. Am. Ceram. Soc. 73 1817
[3] Singh S K, Singhal R. and Siva Kumar V V 2017 Superlattice. Microst. 103 195-204
[4] Kang H S, Ahn B D, Kim J H, Kim G H, Lim S H, Chang H W and Lee S Y 2006 Appl. Phys. Lett. 88 202108
[5] Singhal R, Pivin J C and Avasthi D K 2013 J. Nanopart. Res. 15 1641
[6] Singhal R, Kabiraj D, Kulriya P K, Pivin J C, Chandra R and Avasthi D K 2013 Plasmonics 8 295-305
[7] Barrera R G, Noguez C and Anda E V 1992 J. Chem. Phys. 96 1574
[8] Kundu T K and Chakravorty D 1994 J. Mater. Res. 9 2480
[9] Kreibig U and Vollmer M 1995 Optical Properties of Metal Clusters (Springer, Berlin)
[10] Koleva M E, Nedyalkov N N, Karashanova D, Atanasova G B and Stepanov A L 2019 Appl. Surf. Sci. 475 974-81
[11] Koleva M E, Nedyalkov N N, Atanasov P A, Gerlach J W, Hirsch D, Prager A, Rauschenbach B, Fukata N and Jevasuwan W 2016 J. Alloys Compd. 665 282-7
[12] Ortiz M E, Marco A, Saiz N and Lizana M 2004 Arch. Environ. Contam. Toxicol. 47 234-9