

# LUMINESCENCE OF POROUS SEMICONDUCTOR MEDIA COVERED WITH METALLIC FILMS

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## **Abstract**

Porous GaP and InP layers with a pore diameter and a skeleton wall thickness of about 50 nm are prepared on bulk substrates by anodization; microgranular ZnO structures are produced by thermal treatment of ZnTe single crystals in this work. The effect of coating in the prepared samples with thin Au, Cu, Ag and ITO films on their luminescence is investigated; the results are discussed in terms of increased energy transfer between the excited electron-hole pairs and surface plasmons where the surface plasmon resonance matches the energy of photoluminescence bands.

## **1. Introduction**

Metal inclusions in dielectric and semiconductor surfaces, particularly thin metal films, have significant effects upon many material properties. These effects are attributed to excitation of surface plasmon polaritons at the metal/dielectric or metal/semiconductor interfaces, which are waves that propagate along the surface of a conductor. There was an enormous explosion of investigations related to the role of surface plasmon polaritons in the enhanced transmission of light through periodic arrays of subwavelength holes in a metal film [1]. Plasmonic effects in metallic nanostructures are widely used in surface-enhanced Raman scattering (SERS) spectroscopy which is a plasmonics-based spectroscopic technique that combines modern laser spectroscopy with unique optical properties of metallic nanostructures, resulting in strongly increased Raman signals from molecules adsorbed on these nanostructures [2]. SERS is especially important for biological applications, such as single-molecule detection, cellular studies, gene nanoprobe, immunoassay readout, near-field scanning optical microscopy, etc.

The properties of surface plasmons can be tailored by altering the structure of a metal surface which opens large prospects for developing new types of miniaturized photonic device for applications in subwavelength optics, data storage, light generation, microscopy and biophotonics [3]. The subwavelength applications of metal structures, which circumvent the problem of the diffraction limit of light, are based on the hybrid nature of surface plasmon polaritons, which are light waves coupled to free electron oscillations in a metal. Due to this specific nature, surface plasmon polaritons can be laterally confined below the diffraction limit which makes it possible to develop subwavelength waveguide components including interferometers, ring resonators, and other integrated optical circuits [4, 5]. Negative refraction and metamaterial

issues of plasmonics [6], plasmonic aperture antennas [7], and the large prospects of plasmonics for nanoimaging and nanospectroscopy have also been demonstrated [8].

Enhancement of light emission from nanostructured semiconductors coated with thin metallic films and from light emitting diode (LED) is an important application of plasmonic effects. It was shown that the excited surface plasmons play a key role in the enhanced blue light emission from GaN-LEDs coated with silver films, and the enhancement depends on the geometries of GaN-LED and silver film [9]. Surface plasmon enhancement of emission was observed in GaN-LED based on quantum wells (QWs) [10–13] and in CdSe quantum dots (QDs) [14]. Among other materials, enhancement of the light emission of ZnO films was observed by coupling through localized surface plasmons of Ag island films [15, 16] and Al coatings [17]. The effect of thin metal coatings on the luminescence of porous CuInSe<sub>2</sub>, CuGaSe<sub>2</sub>, CuInS<sub>2</sub>, and CuGaS<sub>2</sub> surfaces [18, 19], as well as on TiO<sub>2</sub> nanotubes [20], has been investigated.

The goal of this paper is to study the plasmonic effects in nanostructured layers of GaP, InP, and ZnO covered with thin metallic films.

## 2. Sample preparation and experimental details

Crystalline (100)-oriented substrates of sulfur doped *n*-InP with a thickness of 500 μm and a free electron concentration of  $1.3 \times 10^{18} \text{ cm}^{-3}$  were supplied by CrysTec GmbH, Germany. Before anodization, conventional photolithography was used to open windows in the photoresist covering for the top surface of the samples. Anodic etching was applied to these samples through opened rectangular windows with a breadth of 35 μm. An electrical contact was made on the backside of the anodized samples with a silver paint. The anodization of the InP substrates was carried out in 500 ml of a 5% HCl aqueous solution at 25°C in a common two-electrode cell with an applied voltage of 5 V, where the sample served as a working electrode. A platinum wire (0.5-mm diameter) mesh with a surface of 6 cm<sup>2</sup> was used as a counter electrode. A Keithley's Series 2400 Source Measure Unit was used as a potentiostat.

(111)-oriented *n*-GaP substrates used in this study were cut from Te-doped liquid encapsulation Czochralsky-grown ingots with a free electron concentration of  $1 \times 10^{18} \text{ cm}^{-3}$  at 300 K. Porosity was introduced by anodic etching of samples in a 0.5M aqueous solution of sulphuric acid at a current density of 5 mAcm<sup>-2</sup> for 30 min using the above-mentioned conventional electrochemical cell with a Pt working electrode.

Microgranular ZnO samples were prepared on the basis of bulk Na-doped ZnTe single crystals with a free hole concentration of  $3 \times 10^{18} \text{ cm}^{-3}$ . ZnTe bulk crystals were annealed at 700°C in air for 1 h.

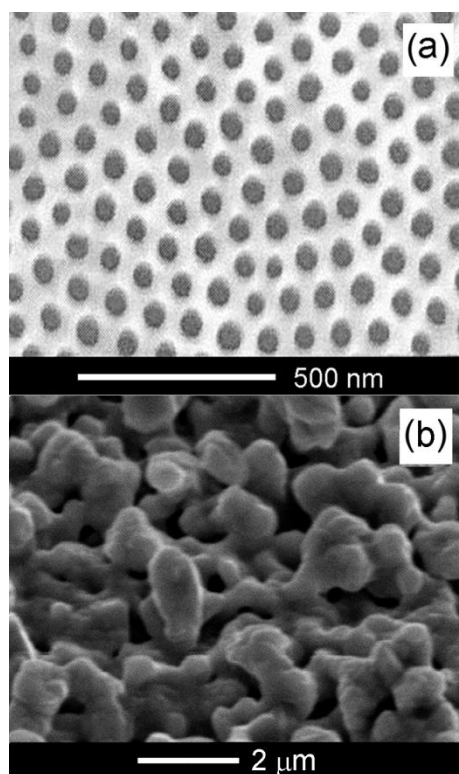
Thin Ag, Au, and Cu coatings were deposited onto nanostructured sample surfaces by means of a Cressington magnetron sputtering coater in order to study the plasmonic effects on luminescence. ITO films were deposited on the surface of porous InP by a spray pyrolysis method described elsewhere [21].

The morphology of the prepared samples was studied by microanalysis using Zeiss Sigma and TESCAN Vega TS 5130MM scanning electron microscopes (SEM). The continuous wave photoluminescence (PL) of ZnO and GaP samples was excited by the 351 nm and 488 nm lines of an Ar<sup>+</sup> SpectraPhysics laser, respectively, and analyzed with a double spectrometer with a FEU 106 photomultiplier ensuring a spectral resolution better than 0.5 meV. The samples were mounted on the cold station of a LTS-22-C-330 optical cryogenic system. The PL spectra were

measured at a temperature of 10 K. The PL of InP samples was excited by a LD Pumped all-solid state MLL-III-532 laser and analyzed through the same double spectrometer with a FEU 62 photomultiplier in a spectral range of 1.1–1.5 eV and with a PDA10DT InGaAs photodetector in a spectral range of 0.6–1.1 eV. The PL spectra were measured at a temperature of 10 K.

### 3. Results and discussion

A porous structure with pore diameters of about 50 nm and the thickness of skeleton walls comparable with the pore diameter is prepared under the above-mentioned technological conditions in InP substrates (Fig. 1a). It should be noted that a similar morphology is obtained in GaP substrates. The morphology of the prepared ZnO sample (Fig. 1b) exhibits a granular structure with mean granule dimensions of about 1  $\mu\text{m}$ . X-ray diffraction (XRD) and PL analyses showed that annealing at 700°C leads to a total transformation of the initial ZnTe crystals into wurzite ZnO [22].

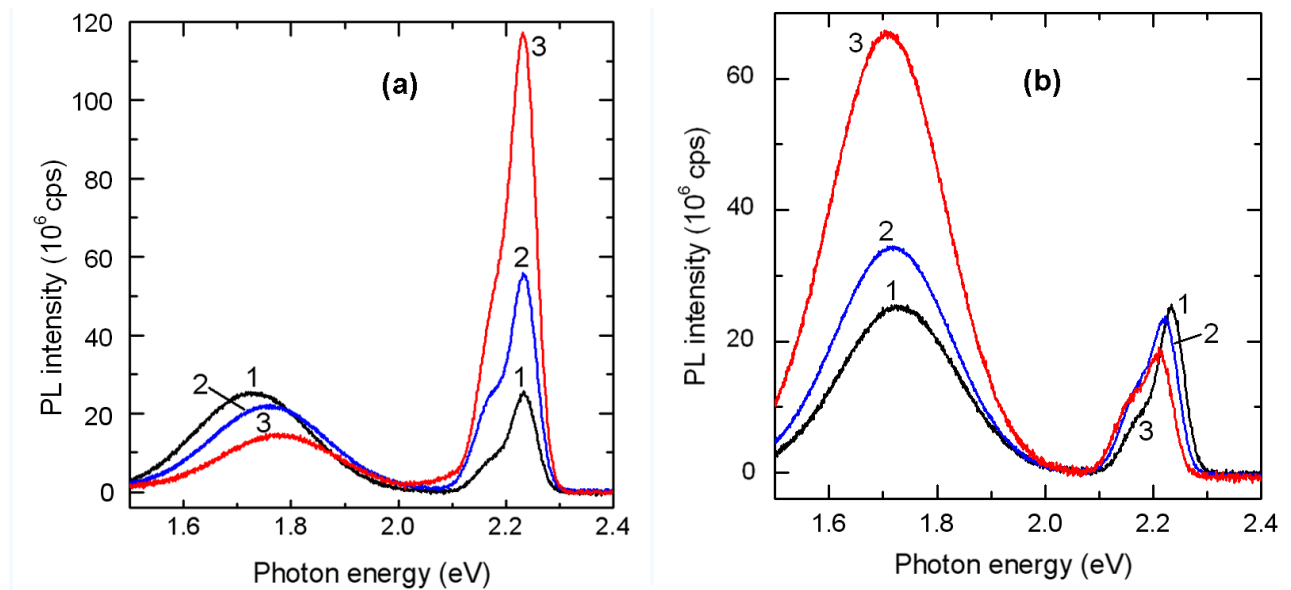


**Fig. 1.** (a) SEM image of a porous InP sample prepared by anodic etching and (b) morphology of the ZnO micro-granular material prepared by thermal treatment of bulk ZnTe crystals.

The PL spectrum for the porous GaP sample is dominated by a broad emission band at  $\sim 1.75$  eV and a narrower emission at  $\sim 2.2$  eV (Fig. 2, curve 1). The PL band at 1.75 eV is attributed to the molecular complexes  $\text{Zn}_{\text{Ga}}\text{-O}_{\text{P}}$  and/or  $\text{Cd}_{\text{Ga}}\text{-O}_{\text{P}}$  forming an isoelectronic trap in GaP [23]. An emission band at 2.2 eV observed previously in GaP doped with sulfur was assigned to electron–hole recombination at sulfur–carbon pairs [23–25]. Since our samples are doped with Te instead of S, one can suggest that the observed emission at about 2.2 eV is related to Te–C pairs.

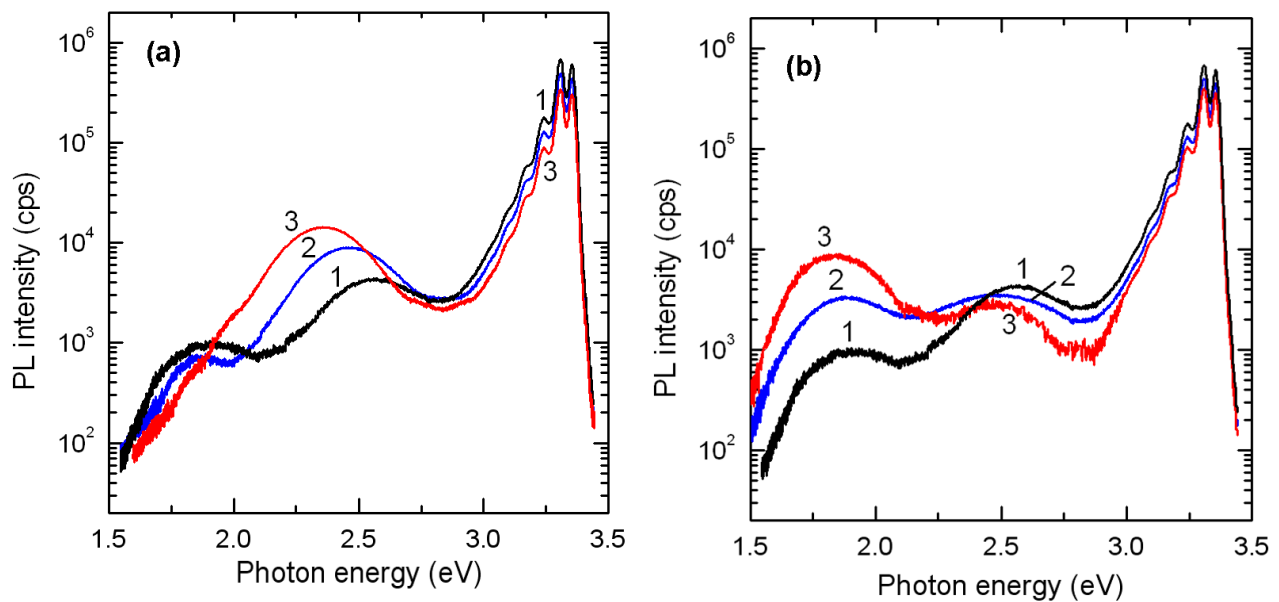
The deposition of thin Au films enhances the PL band at 2.2 eV and slightly decreases the intensity of the 1.75-eV PL band (Fig. 2a). It was previously shown that the surface plasmon resonance frequency at Au/semiconductor interfaces is about 2.3 eV [12] and the density states of the SP mode become dramatically larger while approaching the SP frequency. This large density of states enhances the excited electron–hole energy transfer to plasmon excitation and increases the spontaneous emission rates. It is evident that the metal film deposited on the porous structure is not continuous because its thickness is lower than the pore diameter and the porous skeleton wall thickness. This means that the resonance plasmon frequency can vary in a certain range. It is known that the energy of localized surface plasmon modes depends on the form and size of metal structures [15]. One can suggest that the enhancement of luminescence at 2.2 eV is due to surface plasmons because the energy position of this PL band is close to the resonance energy of the surface plasmons at the Au/porous GaP interface. On the other hand, the decrease in the intensity of the PL band at 1.75 eV can be attributed to the absorption of light in the metal film. Note that the deposition of metal films thicker than 20 nm leads to the overall decrease in the PL intensity.

The deposition of Cu films on the surface of the porous GaP sample, conversely, enhances the PL band at 1.75 eV and attenuates the PL band at 2.2 eV (Fig. 2b). This means that the resonance energy of the surface plasmons at the Cu/porous GaP interface is closer to the position of the 1.75-eV PL band. Similar effects were observed in the luminescence of porous  $\text{CuGaSe}_2$  and  $\text{CuGaS}_2$  surfaces covered with thin Cu films [18, 19]. Localized surface plasmon resonance of Cu nanoparticles has been reported in this spectral range [26].



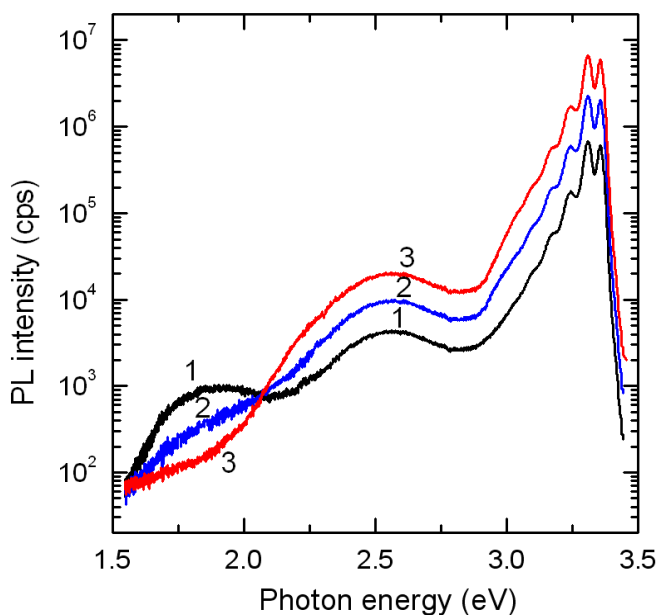
**Fig. 2.** Low-temperature (10 K) PL spectra of a porous GaP sample after anodization (curve 1) and after covering with Au (a) and Cu (b) films with a thickness of 10 (curve 2) and 20 nm (curve 3).

Figure 3 illustrates a similar effect of Au and Cu film coating on the luminescence of microgranular ZnO. The high optical quality of the resulting ZnO material is demonstrated by the PL spectrum, which is dominated by an emission band related to the recombination of donor bound  $D^0X$  at 3.356 eV and a band associated with donor–acceptor (DA) pair recombination at 3.31 eV [27]. The visible emission is a combination of red (about 1.8 eV) and green (about 2.4 eV) PL bands. Usually, the visible emission from ZnO is attributed to different defects, such as oxygen ( $V_O$ ) and zinc vacancies ( $V_{Zn}$ ) or a complex defect involving interstitial zinc ( $Zn_i$ ) and interstitial oxygen ( $O_i$ ) [28–30]. One can see from Fig. 3 that, similarly to the porous GaP samples, the coating of microgranular ZnO surfaces with Au films leads to an increase in the intensity of the green PL band, while the intensity of the red PL band is increased by coating with Cu. This behavior is explained in terms of plasmonic effects as described above.



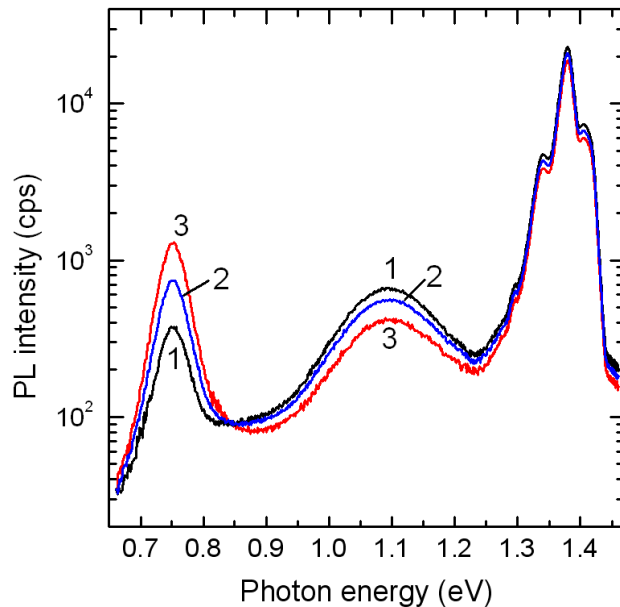
**Fig. 3.** Low-temperature (10 K) PL spectra of a microgranular ZnO sample without metal coating (curve 1) and coated with Au (a) and Cu (b) films with a thickness of 20 (curve 2) and 30 nm (curve 3).

Coating of ZnO samples with Ag films leads to a decrease in the red luminescence intensity and an increase in both the green luminescence and the near bandgap emission related to exciton and DA pair recombination (Fig. 4). A surface plasmon resonance energy at Ag/semiconductor interfaces in a range of 2.8–3.0 eV was previously reported [9, 10, 12]. Therefore, the results of this study show a broad-band effect of Ag coating on the microgranular ZnO surface. Note that an enhancement of the near band edge ultraviolet emission from ZnO films by localized surface plasmons of Ag island films were previously reported [15, 16].



**Fig. 4.** Low-temperature (10 K) PL spectra of a microgranular ZnO sample without metal coating (curve 1) and coated with Ag films with a thickness of 20 (curve 2) and 30 nm (curve 3).

Finally, we will discuss the possibilities of controlling the PL intensity in porous InP layers by coating with conducting films. Due to the narrow bandgap of InP, the energy of luminescence bands in a range of 0.7–1.4 eV is far from plasmonic resonances in all the above used metals (Ag, Au, and Cu). On the other hand, previous investigations suggested that surface plasmon resonance features in the near infrared spectral range may be inherent in ITO thin films [31]. Taking this into account, we studied the effect of ITO coatings on the luminescence of porous InP layers. Figure 5 presents the PL spectrum of a porous InP layer with the morphology shown in Fig. 1a, which is dominated by an emission band related to DA pair recombination at 1.38 eV with phonon replicas and a shoulder at 1.41 eV associated with exciton recombination [32, 33]. The other two broader PL bands observed in the spectrum at 1.1 eV and 0.75 eV were previously attributed to a complex center consisting of a phosphorus vacancy and an acceptor impurity [34] and a deep center of unidentified nature [35, 36], respectively. One can see from Fig. 5 that the infrared luminescence of the porous InP sample is enhanced by the deposition of a thin ITO film and the luminescence intensity increases with an increase in the film thickness from 10 to 20 nm. Note that the enhancement of the PL intensity is observed with ITO films thicker than 5 nm. However, it is difficult to control the film thickness lower than 5 nm. The longer the PL band wavelength, the more significant the luminescence enhancement. This effect suggests that the PL enhancement is also due to surface plasmons which exhibit a wide resonance at the ITO/porous InP interface.



**Fig. 5.** Low-temperature (10 K) PL spectra of a porous InP sample after anodization (curve 1) and after covering with ITO films with a thickness of 10 (curve 2) and 20 nm (curve 3).

#### 4. Conclusions

The results of this study have shown that it is possible to control the PL of porous GaP and InP layers and microgranular ZnO by coating with conducting films. The PL bands at 2.2–2.4 eV in porous GaP and microgranular ZnO are enhanced by coating with Au films, while the PL band at 1.75–1.80 eV is enhanced by Cu film coating. Deposition of Ag films leads to an increase in the PL intensity in a spectral range of 2.4–3.4 eV in ZnO samples, while deposition of ITO films enhances the PL of porous InP layers in a spectral range of 0.7–1.2 eV. These effects are attributed to an increase in the electron–hole energy transfer to plasmon excitations due to the matched resonance of surface plasmons with the energy of respective PL bands, which in turn leads to enhanced spontaneous emission rates.

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