



Full Length Article

Non-plasmonic enhancement of the near band edge luminescence from ZnO using Ag nanoparticles

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ABSTRACT

The effect of Ag nanoparticles (NPs) on the optical properties of ZnO has been investigated. Samples of pure and Ag doped ZnO were synthesized by the combustion method. X-ray diffraction, transmission electron microscope and UV–vis spectrophotometer measurements confirmed the growth of Ag NPs in the ZnO matrix. The near band edge (NBE) emission from ZnO excited by a 325 nm He–Cd laser was significantly enhanced in the presence of ~5 nm diameter Ag NPs. The experimental results suggest that the origin of enhanced NBE emission is due to direct interaction between the laser photons and Ag NPs, which in turn leads to photoemission transfer of electrons from the Ag NPs to the conduction band of ZnO. This is different from previously reported mechanisms where the photoemission transfer of electrons was mediated by plasmon decay.

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1. Introduction

ZnO has attracted considerable attention as a low cost, environmentally friendly photonic material because of its direct band gap (3.37 eV at room temperature) and large exciton binding energy (60 meV) [1–4]. It generally has two photoluminescence (PL) emission regions, namely near band edge (NBE) emission in the ultraviolet (UV) due to the recombination of excitons and visible emission due to the recombination of carriers trapped at deep level defects. Doping ZnO with impurities has been investigated in order to improve its optical properties for white light applications [2,3], as well as for enhancing the NBE emission for UV applications [4] where it is reported that incorporation of Ag nanoparticles (NPs) in ZnO significantly improved the NBE emission efficiency as a result of the resonant coupling between the ZnO excitons and Ag NP localized surface plasmons [5]. Localized surface plasmon resonance (LSPR) describes the large collective oscillation of the conduction electrons in small metallic NPs [6] and can amplify the electric field of incident electromagnetic radiation near the metallic NPs by two orders of magnitude [7]. Enhancement of the NBE emission of ZnO nanorods has been reported when Au NPs have been sputtered onto their surface. Because the enhancement factor varied considerably with coating time, Lin et al. [8] suggested that simple surface passivation could not account

for the effect. To explain the enhancement of the NBE as well as suppression of the visible luminescence, it was proposed that the visible emission from ZnO was absorbed by the Au NPs due to surface plasmon resonance (of almost matching wavelength) and that energetic electrons resulting from non-radiative decay of the plasmons were able to transfer from the Au NPs to the conduction band of the ZnO. Similar experimental results were obtained by Cheng et al. [9] and although possible contributions from the surface passivation effect and the mechanism previously explained were considered, two additional mechanisms were proposed to account for the NBE emission enhancement and visible emission quenching. Firstly it was suggested that electrons normally trapped at the defect level of ZnO responsible for the visible luminescence are able to transfer directly to the Au NPs (having lower Fermi energy) and consequently hot electrons are created in high energy states which can transfer back to the conduction band of the ZnO nanorods. Secondly, it was suggested that the presence of Au NPs creates a new recombination path for ZnO excitons via coupling to surface plasmons, which results in efficient energy transfer (ET). This Purcell enhancement mechanism would rely on a subsequent radiative emission mechanism from the surface plasmons as explained by Lai et al. [10], who reported a negligible enhancement of NBE emission for ZnO films coated by Au but a large enhancement for coating by Ag and attributed this difference to the better match of the ZnO NBE luminescence energy with that of the Ag surface plasmons. The effect of sputtering Ag on ZnO thin films was studied by Cheng et al. [11]. The Ag islands on the ZnO

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surface were considered as oblate spheroids having LSPR modes associated with directions normal and parallel to the surface which were found to be close to the wavelengths of the NBE and visible emissions from ZnO, respectively. They noted that luminescence enhancement of the ZnO is possible due to the Ag NPs as a result of enhancement of the electric field and radiative decay rates, but that damping induced by non-radiative ET may also occur. For their samples the NBE emission was strongly enhanced while the visible luminescence could be slightly enhanced or suppressed depending on the experiment details. The effect of Ag NPs embedded in ZnO films grown by magnetron sputtering was reported by Liu et al. [12] who found that the absorption of the Ag NPs covered a wide spectrum, which was attributed to a broad distribution in their size and shape. The NBE emission of the ZnO was enhanced by a factor which correlated well with the density of Ag NPs and was attributed to the effect of LSPR, while a similar enhancement of the weak visible emission was also found because of the broad range of the plasmon resonance wavelengths.

In this paper, undoped and Ag doped ZnO were prepared by the combustion method with the aim to further understand the interaction mechanism between the NBE emission of ZnO and the Ag NPs. Despite the number of existing models dealing with the enhancement of the NBE emission of ZnO, we do not find a satisfactory explanation for the phenomenon, which we also observe, within the parameters of our experiment and therefore present an additional model. Despite the enhancement being as a result of the Ag NPs incorporated in the ZnO, it does not rely on their plasmonic nature.

2. Experimental

All chemicals were purchased from the market and used as received. Undoped and 1 mol% Ag doped ZnO were prepared by the combustion method. Silver nitrate (AgNO_3 , 99.9%) was used as the source of dopant. Zinc nitrate tetrahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, 98.5%) was used as a precursor and urea ($\text{CO}(\text{NH}_2)_2$, 99%) was used as a fuel. In a typical synthesis the Zn nitrate and urea mixed in the stoichiometric ratio of 2:7 were dissolved in a small amount of distilled water and a homogenous solution was obtained after stirring for 20 min. For doping, the necessary amount of AgNO_3 was added to the mixture before stirring began. The resulting solution was transferred to a muffle furnace which was maintained at a temperature of 500 °C. In a few minutes all the water evaporated, followed by decomposition and generation of a large amount of gases. These combustible gases ignite and burn with a flame, yielding a large amount of foamy solid. The resulting material was allowed to cool down to room temperature outside the furnace and then ground to fine powder. The colour of the samples changed from white to light grey when doped with Ag.

The structural properties were studied with a Bruker D8 X-ray diffractometer using $\text{CuK}\alpha$ radiation generated by an accelerating voltage of 40 kV and a current of 40 mA. The morphology and size of the Ag NPs were obtained from transmission electron microscope (TEM) images recorded with a Philips CM 100 instrument working at 60 kV and the samples were produced by the dipping amorphous carbon support grids into a dilute ethanol suspension of the powder samples. Diffuse reflectance spectra were measured using a Perkin Elmer Lambda 950 UV–vis spectrophotometer, while luminescence properties were measured using a 325 nm He–Cd laser PL system. The power of laser was measured to be 14 mW and the diameter of laser spot was measured to be 1.0 mm, giving an area of 0.79 mm² and an intensity of 18 mW/mm².

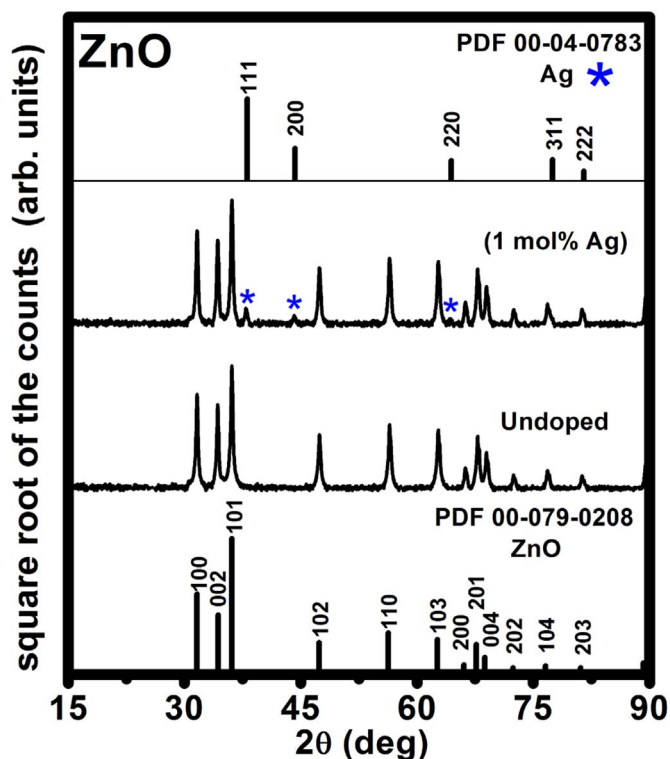


Fig. 1. XRD patterns of pure and Ag doped ZnO compared to standard patterns from the Powder Diffraction File. The square root of the counts is plotted on the vertical axis to emphasize the small peaks of the metallic Ag NPs (stars).

3. Results and discussion

Fig. 1 compares the X-ray diffraction (XRD) pattern of the undoped ZnO with that of the 1 mol% Ag doped ZnO. For the pure sample all the diffraction peaks can be matched to the Miller indices of planes for the hexagonal wurtzite structure of ZnO as given in the Powder Diffraction File (PDF 079–0208). For the doped sample additional peaks marked with asterisk (*) are observed. Their relative size is exaggerated by plotting the square root of the counts on the vertical axis. These additional peaks match the expected positions for face centred cubic Ag (PDF 04–0783). No additional diffraction peaks were observed, indicating only the formation of metallic Ag NPs in the ZnO matrix and no silver oxide (Ag_2O , AgO) phases.

No slight shift of the ZnO peaks to smaller angles in the doped samples was detected, which has previously been reported when larger Ag^+ ions substitute Zn^{2+} ions in the lattice [4]. The crystallite size of the undoped ZnO host particles was estimated using the well known Scherrer formula [13] and found to be about 30 nm. Since the XRD peaks related to the Ag NPs are small, their size was rather determined by TEM measurements instead of the Scherrer formula.

Fig. 2 shows TEM images of (a) undoped ZnO and (b) ZnO doped with 1 mol% Ag. As can be seen from Fig. 2(a) the ZnO nanocrystals are irregularly spherical with average diameter of 30 nm, which is similar to the calculated crystallite size from the XRD data. Fig. 2(b) shows additional small spherical Ag NPs of diameter about 6 nm present in the Ag doped sample. The grain structure of the ZnO host material is clearly affected by the addition of the Ag dopant, although there is not a significant difference in the width of the ZnO XRD peaks between the doped and pure sample in Fig. 1.

Fig. 3(a) shows diffuse reflectance spectra of pure and 1 mol% Ag doped ZnO. The sharp decline in reflectance as the wavelength

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