

Green Photoluminescence in ZnO Nanostructures

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Abstract. In photoluminescence (PL) spectrum of ZnO, typically one or more peaks in the visible spectral range due to defect emission can be observed in addition to one UV peak due to band edge emission. The origin of the defect emission is controversial and several mechanisms have been proposed. In this work, we fabricated ZnO nanostructures with different methods (evaporation and chemical synthesis). We found that the preparation method influences the peak position of the defect emission. Different hypotheses for the origin of the green emission in our nanostructured samples are discussed.

INTRODUCTION

In the photoluminescence (PL) spectra of ZnO nanostructures, one UV peak and one or more peaks in the visible spectral range are observed. The UV emission from ZnO is generally believed to be due to exciton emission while emission in the visible range is due to extrinsic or intrinsic defects. Green emission [1,2] is commonly observed although other colors like yellow [3] are also reported. A number of mechanisms for the green emission has been proposed. It was suggested that the green emission originated from the transition between singly oxidized oxygen vacancies (V_o^+) and photoexcited holes [4,5]. This assignment was based on the correlation between the green PL emission and the electron paramagnetic resonance (EPR) signal at $g \approx 1.96$ on two phosphor powders [4]. However, such an assignment is quite controversial because it has been reported that V_o^+ also gives an EPR signal at $g \approx 1.99$ [6]. The signal at $g \approx 1.96$ can also correspond to shallow donors like interstitial Zn (Zn_i) [7]. Meanwhile, it was also reported that impurities like copper ions (Cu^{2+} and Cu^+) can also cause green emission in ZnO [8]. In this work, we investigated the origin of visible photoluminescence in ZnO nanostructure samples prepared by different methods. We found that the fabrication method significantly affects both the visible luminescence (peak position and relative intensity compared to the

UV emission), as well as the EPR signal, but EPR and defect PL intensities were not necessarily related.

EXPERIMENTAL DETAILS

Room temperature PL and EPR studies were performed on four different ZnO nanostructure samples: tetrapods from thermal oxidation of pure Zn pellets in air and heating a ZnO:graphite mixture (1:1 molar ratio), multipods from heating a mixture of ZnO, germanium oxide (GeO_2), and graphite (1:0.1:1 molar ratio), and nanorods synthesized by a chemical method (solution of zinc nitrate hydrate and hexamethylenetetramine). The obtained nanostructures were examined by PL using a HeCd laser excitation source (325 nm), and EPR using Bruker EMX EPR Spectrometer.

RESULTS AND DISCUSSIONS

Figure 1 shows the PL spectra of all the four ZnO nanostructure samples. It is observed that tetrapod nanorod samples prepared by evaporation of pure Zn and ZnO:graphite mixture show strong UV and broad green emission. Although they exhibit similar green emissions (2.45 eV vs 2.38 eV), only one of them (samples from evaporation of ZnO:graphite mixture) shows a significantly strong EPR signal at $g \approx 1.96$, as shown in Figure 2. We may conclude that the oxygen

vacancy hypothesis cannot be used to explain the green emission from all nanostructured samples [2]. It is possible that two different mechanisms are responsible for the green emission from the two tetrapod samples. In the former case (samples from evaporation of Zn in air), the green emission results from the transition between a delocalized electron and a deep trap. Such a hypothesis agrees with the mechanism proposed by Van Dijken et al. [9,10] In the latter case, the emission originates from the transition involving a shallow donor and a deep trap. The donor-acceptor hypothesis is in agreement with other works in the literature [11].

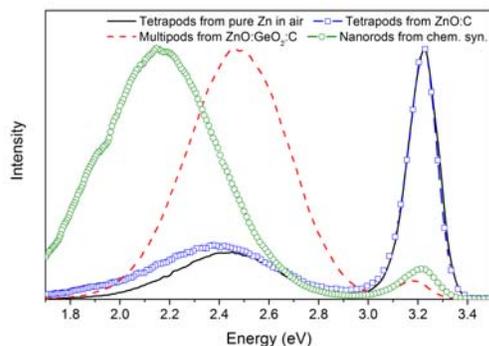


FIGURE 1. Room temperature PL spectra of the four ZnO nanostructures.

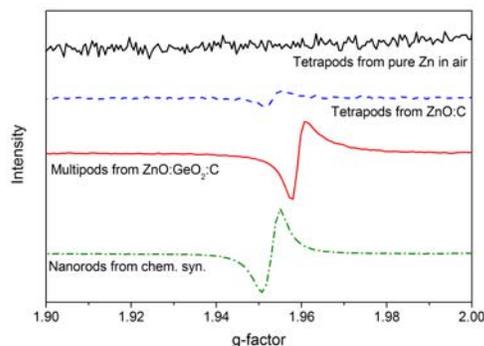


FIGURE 2. EPR spectra of the four ZnO nanostructures.

Strong green PL and $g \approx 1.96$ EPR signal are observed from the multipod samples fabricated from heating a ZnO:GeO₂:C mixture. The slight shift on both the EPR signal ($\Delta g \approx 0.006$) and green emission ($\Delta E \approx 0.08 \text{ eV}$) compared to samples fabricated from ZnO:C mixture is likely to be attributed to the introduction of different type of intrinsic defects, since no Ge was detected. However, the reason behind this shift requires further studies.

The nanorods samples fabricated from chemical synthesis exhibit strong yellow PL emission and EPR signal at $g \approx 1.96$. This finding also contradicts the

results reported by Vanheusden et al. [4]. Very likely, EPR signal corresponds to shallow donors. The visible emission (green or yellow) can originate from either conduction band-deep level or shallow donor-deep level transitions. Different types of deep level are likely to be involved in green and yellow emissions. Further studies are needed to conclusively establish the identity of these deep levels.

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CONCLUSIONS

In this work, PL and EPR were performed on four different ZnO nanostructures. We found that there is no general relationship between the green emission and the $g \approx 1.96$ EPR signal, and that the existence of this signal and the type of intrinsic defects in ZnO nanostructures are strongly dependent on the synthesis conditions.

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