

Electroluminescence from ZnO nanoparticles/organic nanocomposites

Chun-Yu Lee

Graduate Institute of Electro-optical Engineering, National Taiwan University, Taipei, Taiwan 10617, Republic of China

Yau-Te Haung

Graduate Institute of Electronics Engineering, National Taiwan University, Taipei, Taiwan 10617, Republic of China

Wei-Fang Su

Graduate Institute of Materials Science Engineering, National Taiwan University, Taipei, Taiwan 10617, Republic of China and Department of Materials Science Engineering, National Taiwan University, Taipei, Taiwan 10617, Republic of China

Ching-Fuh Lin^{a)}

Graduate Institute of Electro-optical Engineering, National Taiwan University, Taipei, Taiwan 10617, Republic of China; Graduate Institute of Electronics Engineering, National Taiwan University, Taipei, Taiwan 10617, Republic of China; and Department of Electrical Engineering, National Taiwan University, Taipei, Taiwan 10617, Republic of China

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The authors report ultraviolet electroluminescence from ZnO nanoparticle-based devices prepared by the phase-segregation technique. The conditions for phase segregation are investigated using confocal microscopy. With proper parameters for phase segregation, the ZnO nanoparticles and *N,N'*-diphenyl-*N,N'*-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine: poly(methyl methacrylate) can be separated into two layers upon spin-coating process. The method allows electrons and holes to recombine in the ZnO nanoparticles. The *I-V* curve shows stable and excellent rectification. For the device with 90 nm ZnO nanoparticles, it exhibits a very narrow spectrum with a peak at 392 nm and no defect-related emission. The emission peak well corresponds to the ZnO band-gap energy.

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Zinc oxide is attracting extraordinary attention due to its promising properties such as wide direct band gap of 3.3 eV and very high exciton binding energy of 60 meV. These properties make ZnO light emitting diodes potentially useful in efficient solid state lighting, which has been the subject of many recent studies.¹⁻³ In the past, the light emission from ZnO is mainly based on optical pumping method.⁴⁻⁷ Optically pumped lasing had also been observed in ZnO nanocrystals.^{8,9} However, electrically pumped light emission from ZnO has remained a challenge. Only a few electroluminescent (EL) devices were fabricated successfully.^{10,12,13} In most of the ongoing works, ZnO EL devices are prepared in epitaxy films and single crystalline nanorods. In 2006, Ye *et al.* reported on the electroluminescence at the wavelength of 600 nm from *n-ZnO/p-Si* heterojunction by metal-organic chemical-vapor deposition technique.¹¹ In 2004, Park and Yi reported on the fabrication of *n-ZnO/p-GaN* nanorod electroluminescent devices by catalyst-free metal-organic vapor-phase epitaxy.¹² The EL spectra show a weak blue emission peak at 450 nm and a relatively strong yellow emission centered at 560 nm. The above works involve the epitaxial growth of ZnO, which is usually inconvenient and expensive. In this work, we report the use of ZnO nanoparticles to fabricate the ZnO EL devices with ultraviolet (UV) emission by spin-coating method. The method has the prominent advantage of making the cost of devices less expensive.

We utilized organic-inorganic composite film, combining spin-coating method, to prepare ZnO EL devices. The composite film consists of the ZnO nanoparticles and *N,N'*-diphenyl-*N,N'*-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine (TPD): poly(methyl methacrylate) (PMMA). The strong UV emission peak was observed at 392 nm when we applied forward-bias voltage at 7 V. Because the ZnO nanoparticle solubility in chloroform is different from TPD:PMMA, it is possible to use such an organic hole-transporting material that phase segregates from the ZnO nanoparticles during the spin-coating step. A layer of ZnO nanoparticles is formed on top of the TPD:PMMA film. The ZnO nanoparticle concentration and proportion in TPD:PMMA were experimented to successfully achieve phase segregation for EL devices with UV emission.

The procedure of device fabrication is as follows. First, we cleaned the indium tin oxide (ITO) glass using de-ionized water, acetone, and isopropyl alcohol sequentially. Then the EL film was fabricated by spin-coating process. The solution was formed by dissolving the ZnO nanoparticles, TPD, and PMMA in chloroform or mixture of chloroform and toluene with proper proportion. The ZnO nanoparticles were purchased from Aldrich. The ZnO nanoparticles were made by vapor phase synthesis. Two kinds of the ZnO nanoparticles were used. The diameters of the ZnO nanoparticles are 90 ± 10 and 20 ± 5 nm, respectively. The concentrations of ZnO nanoparticles, TPD, and PMMA in the solution were varied in the range of 0.7–1.2 wt %. The solution was then spin coated onto an ITO coated glass substrate with a sheet resistance of $7 \Omega/\square$. The thickness of the ZnO composite

^{a)} Author to whom correspondence should be addressed; electronic mail: cflin@cc.ee.ntu.edu.tw

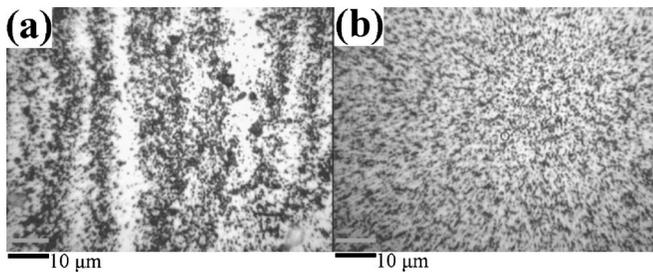


FIG. 1. 100 \times optical images of the ZnO/organic thin film for (a) chloroform solvent and (b) the solvent of chloroform and toluene.

film is estimated to be about 1.5–2 μm . The sample was subsequently annealed at 60 $^{\circ}\text{C}$ for 2 h to remove the solvent. Afterwards, 2000 \AA of Al was deposited onto the ZnO composite layer using thermal evaporation. The emitting area is 0.7 \times 0.3 cm^2 .

With phase segregation, the ZnO nanoparticles and TPD:PMMA will be divided into two layers upon spin coating. This method can improve the probability that electrons and holes recombine in the ZnO nanoparticles. The TPD works as the hole-transporting material. Holes are injected from the ITO contact into the highest occupied molecular orbital of the TPD matrix and are transported towards the valence band of the ZnO nanoparticles. In the same way, electrons are injected from the Al cathode into the conduction band of the ZnO nanoparticles. Finally, holes and electrons form the excitons in the ZnO nanoparticles and recombine immediately. Hence, for the EL device of ITO/TPD:PMMA/ZnO nanoparticles/Al, the spectral peak of the device corresponds to the ZnO band-gap energy.

In the past, the phase-segregation technique has been applied to fabricate EL devices of CdSe nanoparticles.¹⁴ However, the condition of the phase segregation for ZnO nanoparticle devices is very different from that for CdSe nanoparticle devices. It is necessary to investigate the proper proportion among ZnO nanoparticles, TPD, PMMA, chloroform, and toluene. At the beginning, we dissolved the ZnO nanoparticles and TPD together in chloroform. Then we deposited the solution on ITO glass by spin coating. Nevertheless, the film was broken and very rough. This means that the film is discontinuous. Afterwards, we modified the parameters of phase segregation for the ZnO nanoparticles. We used PMMA as a host matrix in the ZnO nanoparticles/TPD mixture. PMMA can improve the film-forming property.¹⁵ Therefore, we could get the unbroken film.

The solvent selection is also an important issue for phase segregation. When we only used chloroform as the solvent, the distribution of ZnO nanoparticles was not uniform on the TPD/PMMA film although the film was not broken. The 100 \times optical image in Fig. 1(a) shows that the distribution of ZnO nanoparticles forms many streaks of structures. To further improve the phase segregation, we added toluene into the solvent of chloroform. The purpose is to reduce the solubility of the ZnO nanoparticles in the solvent. On the other hand, toluene is still a good solvent for PMMA and TPD. The optical image in Fig. 1(b) shows that the distribution of the ZnO nanoparticles is improved significantly, compared to Fig. 1(a).

Various parameters for the phase segregation had been tried. The confocal microscopy (WiTec, Alpha SNOM) was utilized to further examine all of the composite thin films.

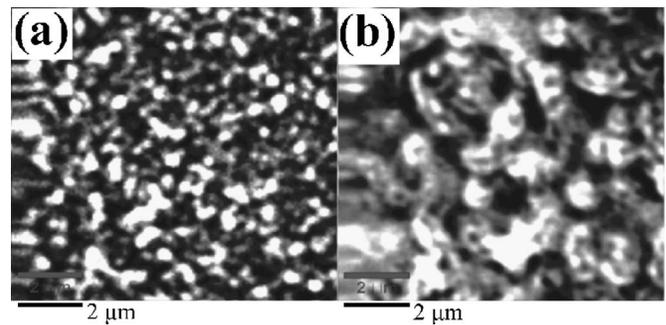


FIG. 2. Confocal images of the TPD:PMMA/ZnO nanoparticles thin film for the solvent of chloroform and toluene in the x - y plane: (a) the surface and (b) 1000 nm below the surface.

When the concentration of the mixture solution and the ratio of the ZnO nanoparticles to TPD:PMMA are properly selected, the ZnO nanoparticles will aggregate on top of the film. Figures 2(a) and 2(b) show the confocal images in the x - y plane that are 0 and 1000 nm below the top surface, respectively. More ZnO nanoparticles are shown in Fig. 2(a) than in Fig. 2(b). In other words, the ZnO nanoparticles tend to distribute on top of the film. This causes the nanoparticles/organic film to exhibit the layer structure shown by the schematic diagram in Fig. 3(a). To confirm that the ZnO nanoparticles aggregate on top of the film, the depth-profile confocal image was also taken, as shown in Fig. 3(b). On the contrary, when the ratio of the ZnO nanoparticles to TPD:PMMA is not appropriate, the ZnO nanoparticles will not separate from the TPD:PMMA layer. Figure 3(c) shows the corresponding depth profile of the thin film taken from the confocal microscopy. The ZnO nanoparticles aggregate in block.

In this experiment, TPD is used as the hole-transporting material. Although it is blue-emission material,¹⁶ it has no contribution to light emission in our devices by spinning process. We used the same parameters to fabricate devices without using the ZnO nanoparticles. The device shows no light emission and no electrical rectification.

The I - V characteristics of the ZnO nanoparticle devices were measured. Figure 4 shows the I - V curve for the ZnO nanoparticle devices, using Al as the cathode material. For good film-forming property, such as that of the ZnO nanoparticles:TPD:PMMA film shown in Fig. 3(b), the I - V curve (curve a) shows stable and excellent rectification. The turn-on voltage is about 4 V. However, for bad film-forming property, the corresponding I - V curve (curve b) exhibits no rectification behavior. Because the film is broken, it leads to no current injecting into the ZnO nanoparticles. Hence the

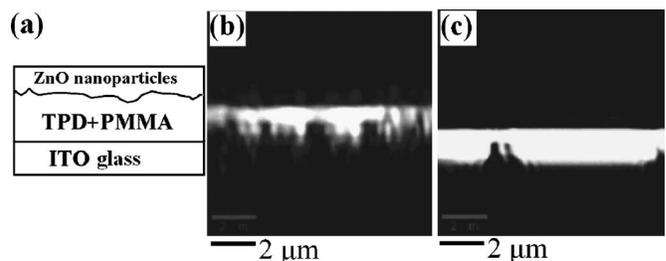


FIG. 3. (a) Schematic diagram of the ZnO nanoparticles/organic thin film and (b) confocal image (depth profile) of the ZnO devices with phase segregation; (c) confocal image (depth profile) of the ZnO devices without phase segregation.

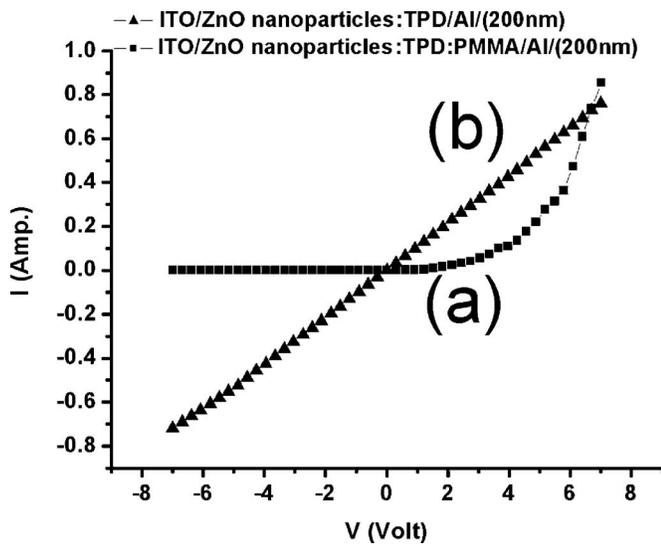


FIG. 4. Current-voltage characteristics of the ZnO devices: (a) with phase segregation and (b) without phase segregation.

phase segregation plays a very important role for device performance.

The normalized electroluminescence spectra of the ZnO nanoparticle-based devices at forward bias of 7 V are shown in Fig. 5. For the device with 90 nm ZnO nanoparticles, its emission spectrum is very narrow. The emission peak is at 392 nm, which corresponds to the band-gap energy of ZnO pretty well. The full width at half maximum (FWHM) of the spectrum is 35 nm. The inset is a photograph of light emis-

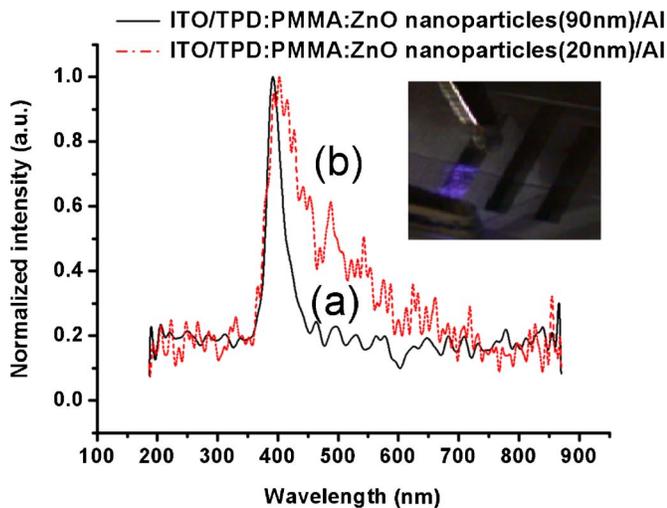


FIG. 5. (Color online) Normalized electroluminescence spectra for ZnO EL devices: (a) ITO/ZnO nanoparticles (90 nm)/TPD:PMMA/Al and (b) ITO/ZnO nanoparticles (20 nm)/TPD:PMMA/Al. The applied voltage is about 7 V. (Inset: photograph of light emission from the EL device with 90 nm ZnO nanoparticles.)

sion from the EL device with 90 nm ZnO nanoparticles at a forward bias of 7 V. It is worth noting that this device has very different spectral behaviors from those reported previously in ZnO nanorod and ZnO thin film EL devices.¹⁰⁻¹³ This device shows a UV electroluminescence peak at 392 nm and has no broad defect-related band at longer wavelengths. For the 20 nm ZnO device at the same forward bias of 7 V, it also has a peak around 392 nm. However, the electroluminescence spectrum showed the broad defect-related band at longer wavelengths, presumably due to the high concentration of defects (oxygen vacancies).¹⁰⁻¹³ Therefore, the qualities of the ZnO nanoparticles influence the electroluminescence spectrum.

In conclusion, we report the use of phase-segregation technique to fabricate the ZnO nanoparticle EL devices. The UV-emission peak has a FWHM of 35 nm at a drive voltage of 7 V. To optimize the phase segregation, we take the confocal microscopy for the ZnO nanoparticle film. When the phase segregation is achieved, the ZnO nanoparticles and TPD:PMMA separate into two layers. The *I-V* curve exhibits excellent rectification. The optimized film shows a narrow UV EL peak at 392 nm, which corresponds to the band-gap energy of ZnO. The processing procedure revealed in this work shows a convenient way to fabricate ZnO EL devices with a very low cost.

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