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 for efficient solid state lighting, which has been the subject of many recent studies. In the past, the light emission from ZnO is mainly based on optical pumping method. However, electrically pumped light emission had also been observed in ZnO many recent studies. In this work, we report the use of 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.

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 Ω/□. The thickness of the ZnO composite film 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.
film is estimated to be about 1.5–2 μm. The sample was subsequently annealed at 60 °C for 2 h to remove the solvent. Afterwards, 2000 Å of Al was deposited onto the ZnO composite layer using thermal evaporation. The emitting area is 0.7 × 0.3 cm².

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 this experiment, TPD is used as the hole-transporting material. Although it is blue-emission material, 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. 5. 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 emission from the EL device with 90 nm ZnO nanoparticles.

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). 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.

This work is supported by the National Science Council, Taiwan, Republic of China, with Grant Nos. NSC94-2120-M-002-010 and NSC94-2112-M-002-009.