

CHAPTER III

LITERATURE REVIEWS

Zinc oxide (ZnO) is a semiconductor compound, which has a band gap of 3.44 eV and an exciton binding energy of 60 meV. In 2004, Tsukazaki et al prepared ZnO at room temperature by laser molecular beam epitaxy using nitrogen source with repeated temperature modulation technique. Violet electroluminescence and blue light-emitting LED were successfully prepared [11]. Because violet emission exhibits very high energy, ZnO is an interesting material to use for light emitting materials.

There are several techniques to synthesize ZnO such as thermal evaporation [15], wet-chemical [16], electrochemical [16] and solid-state pyrolytic reaction [12,17]. By thermal evaporation of Zn, a mixture of tetrapod nanorods and nanowires was obtained for preparation in argon or nitrogen flow, while only tetrapod nanorods was obtained for preparation in air [15]. The wet-chemical [16] and electrochemical routes [16] used to synthesize wurtzite zinc oxide nanoparticles showing peculiar luminescent properties. The ZnO nanoparticles show only one excitonic photoluminescence (ZnO-I) was synthesized by several methods, i.e., (i) electrochemical and TOAB-capped (ii) wet- chemical-uncapped and aged for 6 months and (iii) wet-chemical and PVP capped methods. The defect luminescence along with the weak excitonic luminescence (ZnO-II) was synthesized only by wet-chemical freshly prepared and uncapped ZnO nanoparticles. Although ZnO-I was shown only UV luminescence, ZnO-II was shown both UV and green luminescence [16]. An amorphous ZnO powder were prepared by solid-state pyrolytic reaction [12,17].

Light emission of ZnO depends on several parameters such as atmosphere [15], particle sizes of ZnO [15,16], morphology [12,17] and curing temperature [18]. Preparation of ZnO nanostructures under different atmospheres affected the light emission properties [15]. The photoluminescence (PL) of ZnO nanostructures prepared by thermal evaporation of Zn under different conditions was shown in figure 3.1. The sharp UV emission and broad visible emission were observed for every ZnO

nanoparticle samples. ZnO nanostructures fabricated in humid argon flow emitted higher UV emission than green light emission. Because their average sizes were smaller than those obtained in air while ZnO nanostructures fabricated in air showed stronger green light emission than UV emission. However, no clear conclusion on the size versus ratio of UV to green light emission can be drawn from this result.

In addition, several researchers found that the emission properties depend on the particle sizes. Roy et al. [15] found more green light emission than UV emission when particle sizes of ZnO increased. The result of Bendre and Mahamuni's work [16] was shown in figures 3.2. UV luminescence peak position as a function of ZnO particle size was shown for ZnO-I (only UV emission) and ZnO-II (both UV and green light emission) quantum particles. In the case of both ZnO-I and ZnO-II nanoparticles, the spectral position of UV luminescence shows red shift with increasing particle size. The weak size dependence of band gap luminescence in the case of ZnO-II is most probably due to the presence of shallow levels in these quantum particles.

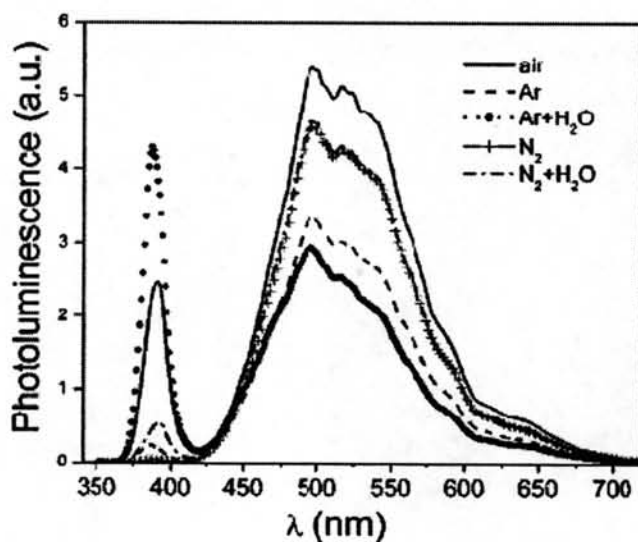


Figure 3.1 Photoluminescence of ZnO nanostructures prepared under different conditions. [15]

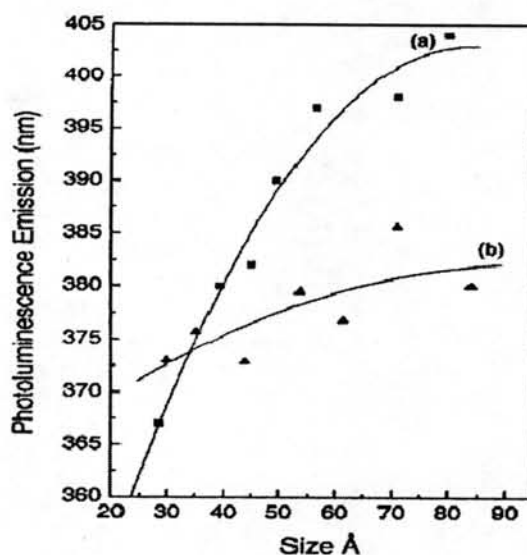


Figure 3.2 Band gap photoluminescence emission peak position as a function of size for ZnO quantum particles that show (a) only UV luminescence feature (ZnO-I) and (b) the defect green luminescence along with the UV luminescence (ZnO-II) [16]

Besides, emission spectrum depends on the morphology of ZnO. Wang et al [12,17] prepared amorphous ZnO powder by solid-state pyrolytic reaction. The amorphous ZnO films were then deposited onto indium tin oxide (ITO) coated glass substrates by electrophoretic deposition (EPD). The PL spectrum of amorphous ZnO film was shown in figure 3.3. In figure 3.3(A), two features can be observed from these spectra. First, the emission peak of amorphous ZnO is at 380 nm, which is a blue shift from crystal ZnO. Second, amorphous ZnO exhibits higher UV emission than crystal ZnO; however, the visible emission of both ZnO was nearly quenched. Figure 3.3(B) shows the UV spectrum of amorphous ZnO which consists of two peaks of emission at 382 nm and 358 nm, while that of crystal ZnO contains only a band-edge emission at 390 nm. The dual excitonic emissions of amorphous ZnO may be derived from different emission band of amorphous ZnO.

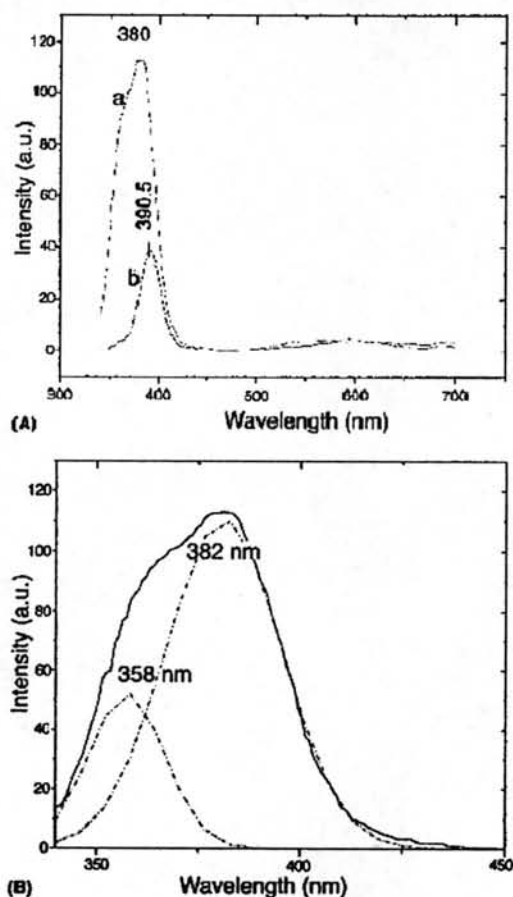


Figure 3.3 (A) Room temperature steady-state PL for ZnO. (a) Amorphous ZnO (b) ZnO nanocrystallites for comparison (B) Spectrum separation procedure of the UV emission of amorphous ZnO. [17]

In addition, size of ZnO nanoparticle depends on curing temperature which was demonstrated by Jeon et al. [18] ZnO nanoparticle embedded in polyimide (PI) were produced during imidization of poly(amic acid) (PAA). PAA/Zn films were cured at 200, 300 and 400 °C. Low density of 5 nm size of ZnO was obtained when Zn/PI was cured at 200 °C. After curing at 300 °C, a mixture of diameter size of ZnO ~7 nm and ~3 nm were observed. The average diameter of 10 nm was obtained when curing at 400 °C. The shape of nanoparticles embedded in the PI matrix was sphere. Increasing curing temperature can grow the particle size of ZnO.

After reviewing the effect of particle size, morphology, curing temperature of ZnO nanoparticle on light emission, the ZnO/polymer blends were explored. Hung and Whang (2005) studied the luminescence of ZnO nanoparticles mixed with poly(hydroxyethyl methacrylate) (PHEMA) nanocomposites [9].

3-(Trimethoxysilyl)propyl methacrylate (TPM) was used as a stabilizing agent to modify ZnO nanoparticle's surfaces. The absorption of unmodified ZnO nanoparticles underwent series of red-shifts when the aging time of ZnO solutions were prolonged due to aggregations of ZnO nanoparticles. However, the absorption of TPM-modified ZnO nanoparticles was obviously lower degree of red shift than that of unmodified ZnO nanoparticles. Besides, the absence of TPM stabilizer caused an increase in particle size of ZnO and an agglomeration of ZnO in PHEMA matrix. In addition, the emitting colors of the ZnO/PHEMA nanocomposites under daylight and under UV light were investigated. Photographs of both TPM-modified and unmodified ZnO/PHEMA nanocomposites under daylight showed excellent optical transparency. Additionally, color emission under UV light can be controlled by using the precise size of ZnO nanoparticles. The color of TPM-modified ZnO/PHEMA nanocomposites under UV light changed from blue to green when ZnO particle was changed from 2.2 to 3.2 nm. However, unmodified ZnO/PHEMA nanocomposites showed yellow and orange when unmodified ZnO's size was changed from 3.2 to 6.1 nm.

In 1998, five kinds of metal embedded fluorinated polyimide films were prepared by thermal curing of poly(amic acid)s containing metallic salts or organometallic complexes [19]. Copper and palladium complexes oxidized perfect or imperfect metal oxide particles, while silver complex and gold salt were converted to metal particles after thermal imidization. They are attractive materials that have high transparency in the NIR region and interesting optical properties producing from the precipitated nanometer-sized of metallic particles.