Effect of compaction pressure of green body and heating current on photoluminescence property of ZnO crystal grown by electric current heating method

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Abstract. In this study, we reported the effect of applied compaction pressure on green body and electric current heating on ceramic bar on the ZnO crystal growth and its photoluminescence characteristic. Crystals grown on ZnO bar sintered by 1100 °C were mostly on (1 0 1) orientation. Sample with 3.0 ton and 3.0 A for applied pressure and current, respectively revealed the shortest photoluminescence (PL) wavelength of 409.5 nm with highest emission energy of 3.03 eV.

1. Introduction

ZnO has gained substantial interest in the research community because of its large exciton binding energy (60 meV) and wide direct band gap (Eg ~ 3.37 eV) at room temperature (R.T.). This large exciton binding energy paves the way for an intense near-band-edge excitonic emission such as lasing action at R.T. and higher temperatures, because this value is 2.4 times larger than that of the room temperature thermal energy (kBT = 25 meV). In addition, the interest in ZnO is fueled and fanned by its prospects in electronics and photonics applications, viz. transparent electrodes in solar cells, flat display devices and novel solid-state ultraviolet (UV) lasers owing to its direct wide band gap [1–7].

Many works have been done on the fabrication of ZnO micro/nanostructures with high aspect ratios using metalorganic chemical vapor deposition [8], thermal evaporation and thermal decomposition [9]. But these techniques appear to be involved process with many complex steps, require sophisticated equipment and rigorous experimental conditions. However, some of them have drawbacks like long reaction time, toxic tempelts and exotic metal catalysts, and low purity or poor crystallite quality of products, which may influence the quality and applications of ZnO. So there is still the need for developing a method that can produce the ZnO micro/nanostructures in laboratory environment with high quality, high repeatability and low cost process for a wide range of applications. Hence, a novel technique called ECH for the preparation of ZnO micro/nanocrystals [10-12].

When a certain direct current flowed through a sample of ZnO ceramic bar, the sample was Joule-heated, and the crystal growth occurred. ZnO is a key technological material. The lack of a centre of symmetry in wurtzite, combined with large electromechanical coupling, results in strong piezoelectric
and pyroelectric properties and the consequent use of ZnO in mechanical actuators and piezoelectric sensors. In addition, ZnO is a wide band-gap (3.37 eV) compound semiconductor that is suitable for short wavelength optoelectronic applications. The high exciton binding energy (60 meV) in ZnO crystal can ensure efficient excitonic emission at room temperature and room temperature ultraviolet (UV) luminescence has been reported in disordered nanoparticles and thin films. The objective of this research was to investigate the effect of compaction pressure and current on the crystal growth and its PL characteristics.

2. Experimental procedures

The amount of 10 grams of ZnO powder with 99.00% purity was measured using digital weighing machine. The weighted ZnO powder was grinded manually with mortar and pestle for 6 hours at room temperature to achieve find particles. Ceramic bar of ZnO with average dimension of 13.00 mm x 2.50 mm x 1.00 mm each were formed by adopting powder metallurgy methods. It contained three basic steps which were powder grinding, die compaction and sintering. Firstly, half of the amount of 30ml ethanol was added into ZnO powder gently. The mixture was grinded on hotplate manually and heated with temperature around 70.0°C. Another half of the amount ethanol was added slowly into the mixture during grinding process. Grinding process was end once the mixture was dry. The amount of 1.5 gram ZnO powder was prepared to make green body using compaction die with dimension of 14.95 mm x 30 mm x 40 mm. Different green body was made by different in applying compaction pressure of 2 and 3 tons, respectively. The green body of different applied compaction pressure was then sintered under 1100 °C with rate of 16.5 °C/min for 3 hrs. The sintered ceramic was then cut into 13.00 mm x 2.50 mm x 1.00 mm each prior to ECH. The current applied into the ECH was vary from 2.5 to 3.5 A. Figure 1 shows the ECH process until the crystal grew on the surface of ceramic bar.

![Figure 1. Electric current heating applied into ceramic bar for ZnO crystal growth. It is shown on the 3rd figure the crystal grew on the surface of ceramic bar.](image)

Characterization and observation were carried out for XRD RIGAKU Miniflex II, UV-vis, scanning electron microscope Carl Zeiss EVO 50, and PL spectroscopy NIR 300/2.

3. Results and Discussion

Sample of SZ2, SZ3, SZ4, SZ12, SZ13, SZ14 and SZ15 were chosen to conduct ECH process. The treatment of each sample is listed in table 1.

### Table 1. The percentage of relative density of ZnO bars after sintered used in this research.

| Pressure Applied (Ton) | Current (A) | Sample | Volume (cm³) | Density (g/cm³) | Relative density (%) |
|------------------------|-------------|--------|--------------|-----------------|---------------------|
| 2.0                    | 2.50        | SZ3    | 0.0249       | 5.1807          | 92.41               |
|                        | 3.00        | SZ4    | 0.0248       | 5.2823          | 94.23               |
|                        | 3.50        | SZ5    | 0.0263       | 5.3612          | 95.63               |
| 3.0                    | 2.50        | SZ15   | 0.0308       | 4.8377          | 86.29               |
|                        | 3.00        | SZ12   | 0.0289       | 5.0519          | 90.12               |
|                        | 3.50        | SZ13   | 0.0318       | 5.1887          | 92.56               |
|                        | 3.50        | SZ14   | 0.0357       | 4.6779          | 83.44               |
Figure 2 shows the comparison of XRD of all samples where red colour of planes correspond to Cu powder and black colour of planes were contributed by ZnO crystal. The XRD results showed most of the crystals grew on the plane (1 0 1). The crystal was in rock like shape. This was proved by the plane (1 0 1) had the highest intensity in all the samples except SZ13 and SZ14. The highest intensity of crystal grew in SZ13 was plane (1 0 0). The highest intensity of crystal grew in SZ14 was contributed by Cu since large amount of Cu powder was placed on top of ZnO bar. This had affect the growth of ZnO crystal.

![Figure 2](image1.png)

**Figure 2.** XRD of all samples where red colour of planes correspond to Cu powder and black colour of planes were contributed by ZnO crystal.

Figure 3 shows the comparison of the crystals grown and PL spectra between samples. Crystal like structures were grown on the surface of ceramic bars such as flower like (SZ12), grass like (SZ13),

![Figure 3](image2.png)

**Figure 3.** Comparison of SEM images and PL spectra between samples.
needle shape like (SZ4), KLCC tower like (SZ15), fish sting like (SZ2), and hexagonal shape like (SZ14). Under the PL spectrometer, the wavelength of samples SZ3, SZ4, SZ2, SZ15, SZ12, SZ13, and SZ14 were respectively 415, 411, 412, 413, 409, 412, and 415 nm. The shortest wavelength belonged to SZ12 has the highest intensity of about 1 million a.u. and 10 to 15 times higher than the other samples. The sample SZ12 which was under 3 tons and 3 A has the highest emission energy of 3.03 eV. This result was consistent with the result of UV-Vis spectrometer (see figure 4). The wavelength (in nm) and the excitonic energy (in eV) of SZ3, SZ4, SZ2, SZ15, SZ12, SZ13, and SZ14 are respectively 372 (3.34), 387 (3.21), 371 (3.34), 376 (3.30), 387 (3.20), 376 (3.30), and 376 (3.30). Sample 12 had emitted the longest wavelength and thus own the lowest excitonic energy. This showed that electron in SZ12 can be excited most easy among all samples.

4. Conclusion

In summary, it can be concluded that the sintered ZnO ceramic bar (SZ12) fabricated under 3 tons compaction pressure of green body with dimension of 13.0 mm x 2.5 mm x 1.0 mm and under ECH with input current of 3 A has the optimum value among the investigated samples. SZ12 sample revealed that it had the lowest exciton energy of 3.20 eV, the highest emission energy of 3.02 eV, the most significant crystal growth of flower like crystal.

![Figure 4. The result of UV-Vis spectrometer between samples.](image)

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