Investigating the Photonic Behaviors of ZnO Nanocrystals

Y.Y. Tay[a, b], S. Li[b] and M.H. Liang[a]

[a] *School of Materials Science and Engineering, Nanyang Technological University, Singapore.*

[b] *School of Materials Science and Engineering, NSW 2033, Australia.*

The photonic behavior of size dependent ZnO is recently rigorously investigated. In this work, we examine ZnO nanocrystals of size less than 5 nm by correlating this photonic behavior to the material's crystal structure as well as the effect of relevant defects present in the material. There is a red shifting of their luminescence property that is different from quantum size effect which expects a blue shifting instead.

1. Introduction

Zinc Oxide (ZnO) is a wide band gap semiconductor and has an efficient near UV (~ 3.29eV, 370nm) emission, and commonly yield to have green (~510nm, 2.43eV) emission and sometimes yellow (~597nm, 2.08eV) or orange (~640nm 1.94eV) emission. However, the origins of these visible emissions remain controversial, particularly the green emission [1].

On the other hand, nanotechnology is an emerging interesting field. Particularly when particles size of pure ZnO reaches nanoscale e.g. smaller than 5nm in diameter, quantum size effect will occur causing blue shifting of the emission as a result of bandgap widening [2]. In this work, the crystal size of ZnO was physically reduced from 202 nm to 3.0 nm to investigate size effect on photoluminescence behavior of ZnO.

2. Experiment

ZnO (99.5% pure Analyticals Carlo Erba) powder was first annealed at 1200^{o}C in ambient condition with ramping rate of 5^{o}C/min and a dwelling time of 1hr. To reduce the crystal size physically in a control fashion, high energy ball milling was carried out with different duration.

The prepared ZnO materials were characterized using X-ray Diffractometer (XRD). Data were recorded using a Theta/Theta Bruker Diffractometer with a Cu Kα radiation with a divergence slit of 2^{o} and a 0.2mm width receiving slit. The crystal sizes of the as prepared ZnO powders were verified using JEOL 3010 HRTEM. Photoluminescence (PL) measurement was performed using Accent Rapid Photoluminescence Mapping System (RPM 2000) with a He-Cd laser source with an excitation wavelength of 325nm.

[a] corresponding author; email: s3197272@unsw.edu.au

3. Result and Discussions

The XRD line profile of the size reduced ZnO is shown in Figure 1. This characteristic peak which corresponds to the plane (012) of ZnO reveals substantial broadening with reduced crystal size. Complemented by the TEM images in Figure 1 (b), it is possible to reduce the crystal size of ZnO from 202 nm to 3.0 nm in the nanoscale region.

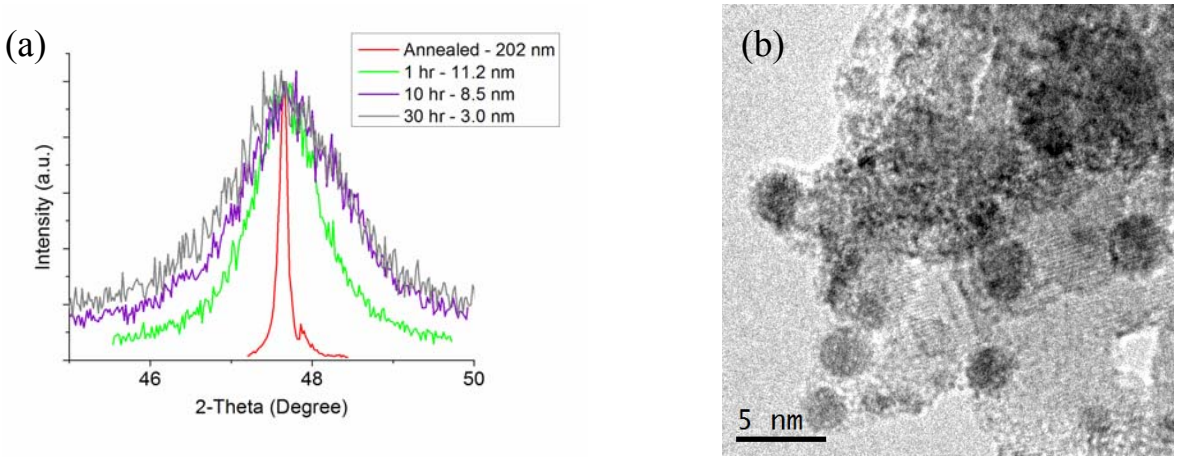

Fig. 1. (a) XRD line profile of ZnO plane (012) (b) TEM image of ZnO with average crystal size of 3.0 nm

In Figure 2, the peak emission of as-received ZnO shifts from 617nm to 677nm for annealed ZnO. The annealed ZnO at 1200°C has a peak emission at 677 nm. Annealing at extremely high temperature has possibility of causing an outward diffusion of Zinc [4]. Therefore, it is likely that this emission has a strong relationship with the presence of zinc vacancies. Less oxygen vacancies will be formed as the atmosphere has a substantial amount of oxygen that suppresses the latter's formation.

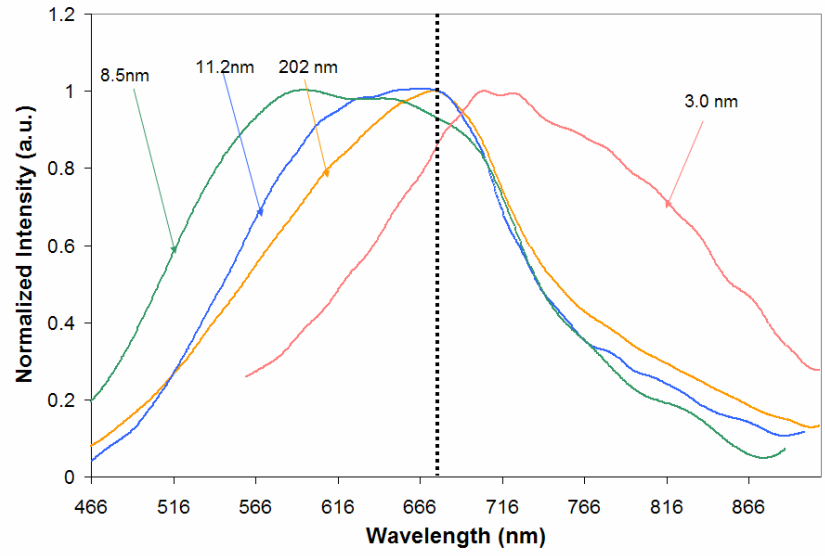

Fig. 2. Photoluminescence of ZnO of various crystal sizes. Annealed ZnO has a crystal size of 202 nm.

When the crystalline size reduces to 11.2nm its peak emission remains at 677nm, however, the emission spectrum for each individual begins to broaden in the direction of shorter wavelength (higher energy) towards the green region. Since the size shrinks, the materials surface area begins to increase. This might induce tension between the binding atoms which has a higher probability of inducing oxygen vacancies which cause the broadening of the PL towards the green region. With much surprise while we are expecting the green emission band of the 3 nm ZnO nanocrystal to enhance, the emission peak red-shifts to ~701 nm instead, forming a red emission band. It is not clear why there is a dramatic red shift although a shifting of the emission band towards shorter wavelength would be expected as a result of quantum size effect. It is likely that when the crystalline size is reduced tremendously, the surface area would be expected to increase and this causes distortion on the surface structure which induces vacancies on the surface. On the other hand the occurrence of the quantum size effect is coupled with the aforementioned situation and drastic change may occur. For example the band structure/electronic structure is drastically altered since it is dependent on the lattice structure via arrangement of the atoms and important contributions from the vacancies as well as the interaction between atoms [5]. In this manner, the red emission might form due to changes in the bandgap. Its emission mechanism is currently investigated and will be available in the future.

5. Conclusions

In conclusion, ZnO can be physically reduced to nanoscale of less than 5 nm. While the size is reduced, oxygen vacancies are formed causing broadening of the PL emission towards the green region. The PL emission however red shifted when the size reaches less than 5 nm. Such shift could probably be attributed to the coupling of the lattice distortion and oxygen vacancies that induces changes to the electronic band structure.

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