

## Photoluminescence Excitation Spectroscopy Studies of Anodically Etched and Oxidized Porous Zn

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### ABSTRACT

Photoluminescence excitation (PLE) spectroscopy studies were performed for anodically etched porous Zn, which exhibited a PL in the blue/violet spectral range peaking at 420 nm (2.95 eV), and oxidized porous Zn at 380°C for 10 min and 12 h. A broad absorption band was observed at 4.07 eV (305 nm), 3.49 (355 nm) for anodically etched porous Zn. In contrast, both the oxidized porous Zn and sintered ZnO exhibited an almost identical one broad absorption band at 3.85 eV (322 nm), when PLE spectra were measured at 378 nm (3.28 eV). The oxidized porous Zn and sintered ZnO, which displayed both UV and green luminescence band, showed an additional absorption band at 389 nm (3.19 eV) and 467 nm (2.66 eV). In contrast, no significant absorption band was detected for a 10-min oxidized porous Zn, which only displayed one UV luminescence void of deep-level luminescence. These absorption bands determined by PLE studies enabled a clear understanding of an emission mechanism for the UV and green luminescence from ZnO.

**Key words :** ZnO, Photoluminescence, Porous Zn, Oxidation

### 1. Introduction

Zinc oxide, ZnO, is a well-known inexpensive II-VI n-type direct bandgap ( $E_g \sim 3.2$  eV at room temperature) semiconductor. ZnO exhibits good piezoelectric, photoelectric, and optical properties. Insulating ZnO films are used in piezoelectric application. However, the highly conductive films with high transparency, produced by reducing their electrical resistance, can be used as transparent conducting films, solar cells, and flat panel displays. ZnO exhibits an ultraviolet (UV) near band-edge emission at 380 nm and a deep-level emission with a peak in the range of 450 ~ 730 nm. Visible emissions are related to intrinsic defects in ZnO crystal. ZnO displays not only the same crystal structure as GaN, which well known material for the fabrication of Light Emitting Diodes (LEDs) and Laser Diodes (LDs), but also large exciton binding energy. Thus, the semiconductor zinc oxide based electroluminescence devices<sup>1)</sup> and UV lasers<sup>2,3)</sup> are reported.

Several processing methods are used to produce ZnO as single crystals, as powders, and as thin films, including sol-gel chemistry,<sup>4,5)</sup> spray pyrolysis,<sup>6,7)</sup> metal organic Chemical Vapor Deposition (CVD),<sup>8,9)</sup> molecular beam epitaxy,<sup>10)</sup> D.C. and/or RF sputtering,<sup>11,12)</sup> thermal evaporation,<sup>13)</sup> spark processing,<sup>14)</sup> and anodic etching of Zn.<sup>15,16)</sup> Furthermore, low dimensional nanocrystalline ZnO, in the form of powders as

well as thin films, is also investigated. ZnO prepared through any of the methods mentioned above reveals a UV luminescence band at 3.2 eV and a broad green PL band with a maximum in the range 1.95 ~ 2.75 eV, which is well below the UV band gap.

ZnO possesses large bond strength, as indicated by its high melting point of 2248 K in the II-VI compound semiconductor, extremely stable excitons. It is not expected that a degradation of the material due to generation of dislocation during device operation will be an important issue. Due to a thermal stability of ZnO, it can also withstand high temperature annealing associated with doping and formation of Ohmic contacts. In addition, ZnO is also an inexpensive material. Thus, ZnO should have the greatest potential for realizing the next generation of UV lasers operating at room temperature. A control of green luminescence, substantial increase of luminescence efficiency, and p-type ZnO films are needed to fabricate devices such as LEDs and LDs.

The electrochemical etching is a relatively simple, and especially extensively used technique that transform crystalline Si into a porous material with high efficiency photoluminescing properties. Similarly, anodic etching of Zn yields a porous structure with luminescing properties.<sup>15-18)</sup>

In the following study, the PLE studies of porous Zn (p-Zn), and oxidized p-Zn, and sintered ZnO will be described. Furthermore, this paper will also present the correlation between the emission energy gap determined by photoluminescence (PL) and absorption band determined by PLE.

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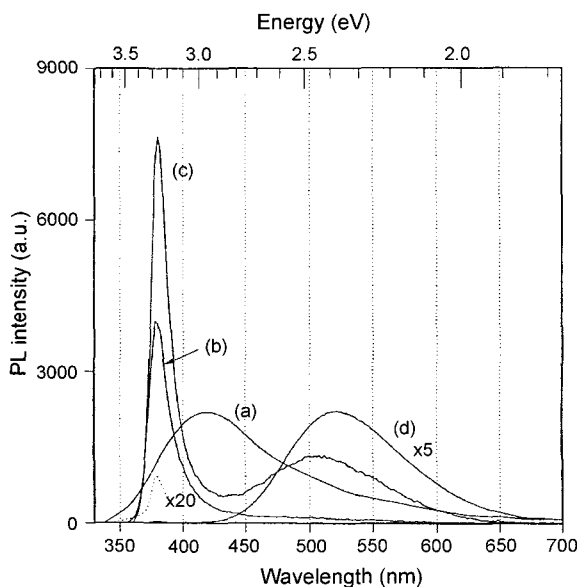
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## 2. Experimental

Square pieces of Zn ( $5 \times 5 \text{ mm}^2$ , purity 99.999% with traces of Fe, Ca, and Mg less than 5 ppm) were cut from a Zn sheet. The surfaces were ground down to 2400 grit SiC paper, and polished down to a  $1 \mu\text{m}$  diamond finish, and ultrasonicated in ethanol to remove any debris before anodic etching. Anodization was conducted in a 40% HF/ethanol solution at a current density of  $10 \text{ mA/cm}^2$  for 10 min. The specimen was immediately rinsed with deionized water and then dried at room temperature. Oxidation of anodically etched porous Zn was performed in air at  $380^\circ\text{C}$  for 10 min and 12 h. For comparison, bulk ZnO samples were prepared by pressing ZnO powder (99.99% purity) into pellets 10 mm in diameter and 1 mm thick, followed by sintering in air for 2 h at  $1250^\circ\text{C}$ .

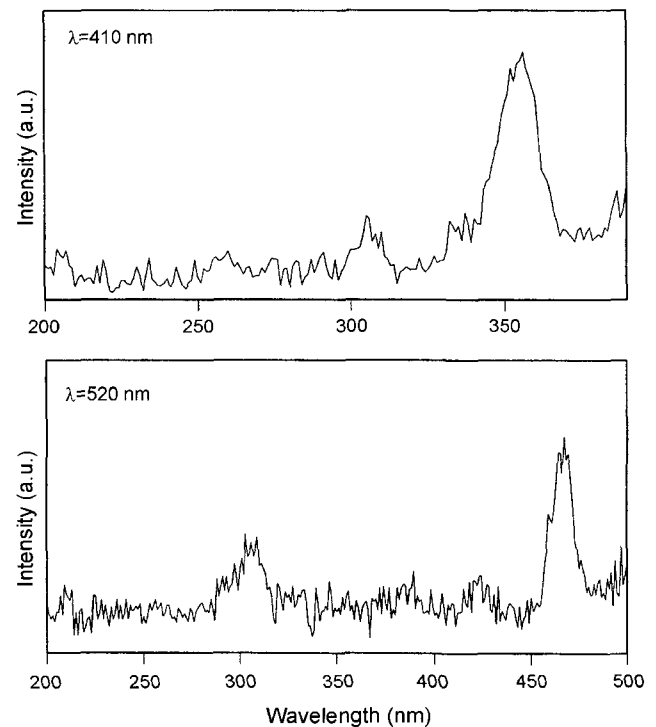
For photoluminescence measurements a continuous-wave He-Cd laser (325 nm), having a power density of  $1 \text{ W/cm}^2$ , excited the sample. In order to remove parasitic plasma lines from the laser, a narrow interference filter was used. A long band pass filter was inserted after the sample to block any scattered laser light. It had a 50% transmittance at 365 nm. For PLE measurements, a 1000 W Xe lamp was used to generate white light. The white light was passed through a 0.15 m single grating scanning monochromator into a sample chamber. The  $2 \times 3 \text{ mm}$  beam size of scanning light was detected by Si detector before illuminating the sample and then the excitation spectrum was dispersed by 0.5-m single grating monochromator. The spectrum was collected by an air-cooled GaAs photomultiplier.



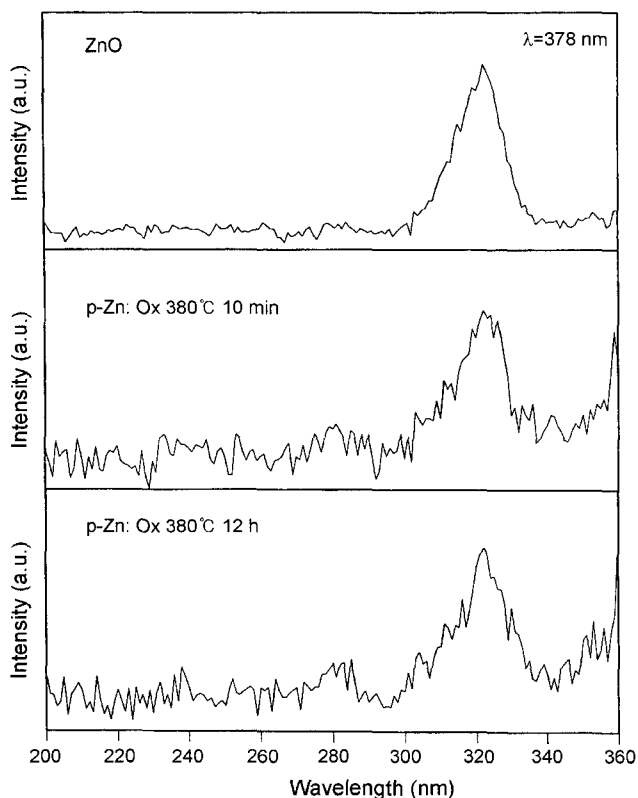
**Fig. 1.** Room temperature photoluminescence spectra of (a) as prepared porous Zn (p-Zn), (b) 10 min-annealed p-Zn, (c) 12 h annealed p-Zn at  $380^\circ\text{C}$ . The PL spectrum of sintered ZnO is shown in (d). A 325 nm line of He-Cd laser was used as an excitation source.

## 3. Results and Discussion

The details of preparing conditions, luminescence properties, morphology, and characteristics of anodically etched porous Zn as well as annealing behavior of porous Zn have been published earlier papers<sup>15-18)</sup> and will not be repeated here for brevity. Fig. 1 depicts the room temperature PL spectra of p-Zn and oxidized p-Zn. Further, the room temperature PL spectrum of ZnO is also presented. Anodic etching of Zn displays a broad blue/violet luminescence band peaking at 420 nm, as shown in Fig. 1(a). Oxidation temperature was set at  $380^\circ\text{C}$ , due to a good UV PL property as previously reported.<sup>17,18)</sup> A sharp UV emission peak dominates at 379 nm for all the oxidized p-Zn, which corresponds to the band-edge emission, especially for the 10-min annealed samples (Fig. 1(b)). However, the sintered ZnO displays a broad green luminescence band with a very weak UV luminescence band. Note that the PL intensity of sintered ZnO is increased 5 times for clarity of comparison. The UV luminescence band of sintered ZnO is increased 20 times, which is marked as dotted line in figure. Anodic etching of Zn exhibited an increase of surface area; thus annealing of p-Zn promotes rapid oxidation. It is well known that the passivation of dangling bond via rapid thermal oxidation in porous silicon reduces non-radiative recombination sites and improves luminescence stability and quantum efficiency. Thus, a short time of annealing yields band-edge emission from ZnO with a very weak deep-level defect-related luminescence. The deep level emission in ZnO is usually related to structural defects and



**Fig. 2.** Photoluminescence excitation (PLE) spectra of as prepared p-Zn measured at 410 (3.02 eV) and 520 nm (2.38 eV).

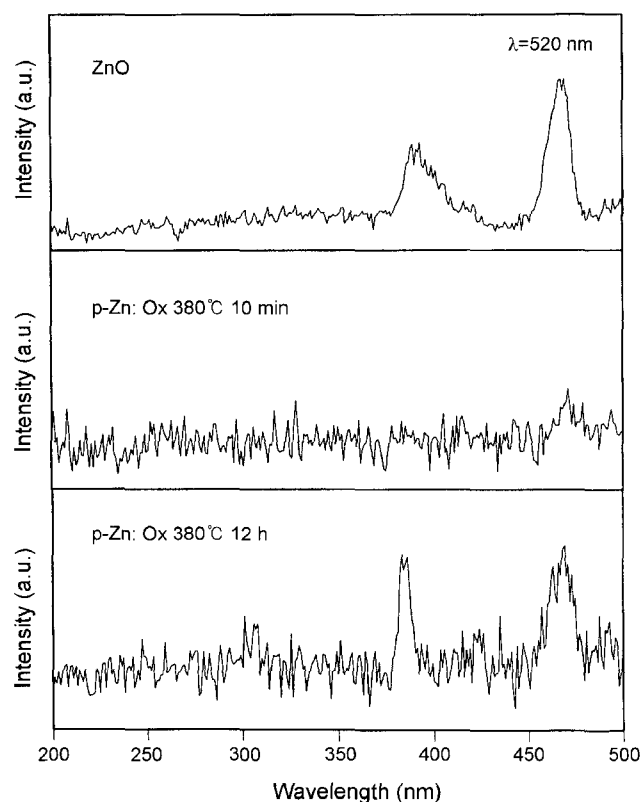


**Fig. 3.** Photoluminescence excitation (PLE) spectra of sintered ZnO, 10-min annealed p-Zn, and 12 h annealed p-Zn at 380°C. The PLE spectra were measured at 378 nm (3.28 eV).

impurities, especially in relation to oxygen vacancy.<sup>19,20</sup> The increase of green luminescence for the long duration of annealing time might be resulted from the increase of oxygen vacancies and an increase of deep level defects.

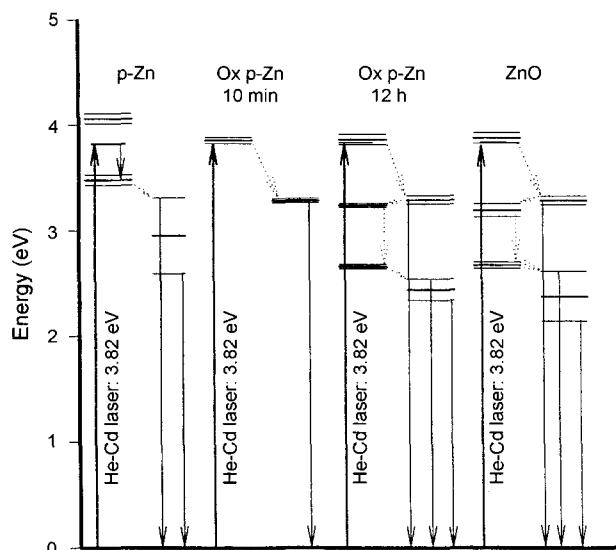
Fig. 2 displayed a series of PLE spectra, which was observed for anodically etched p-Zn at 410 nm (3.02 eV) and 520 nm (2.38 eV). In the UV region, a strong absorption band near 3.49 eV (355 nm) was detected along with a weak absorption band at 4.07 eV (305 nm), when the detection wavelength was set at 410 nm for anodically etched p-Zn. As the detection wavelength was set at the tail side of luminescence, i.e., at 520 nm (2.38 eV), a strong absorption band at 2.66 eV was observed with an unaltered weak 4.07 eV absorption band.

When the PLE spectrum was obtained at 378 nm (3.28 eV) for the sintered ZnO as well as oxidized porous Zn, as depicted in Fig. 3, one could detect almost identical broad absorption band at 3.85 eV (322 nm). Thus, band edge emission from ZnO is related to this higher energy absorption band. Thus, electrons are efficiently pumped into this excited state by a 3.82 eV (325 nm) line of a He-Cd laser from ground state and return to ground state via radiative transitions, i.e. band edge emission. Fig. 4 displays a series of PLE spectra of the sintered ZnO as well as oxidized p-Zn, which was obtained at 520 nm. The sintered ZnO showed a broad absorption band at 390 nm (3.18 eV) and 467 nm



**Fig. 4.** Photoluminescence excitation (PLE) spectra of sintered ZnO, 10-min annealed p-Zn, and 12 h annealed p-Zn at 380°C. The PLE spectra were measured at 520 nm (2.28 eV).

(2.66 eV). The 12 h annealed p-Zn exhibits a similar absorption peak at 2.66 eV compared to ZnO. However, there exist some differences between two samples. Specifically, a slight blue shift to 3.23 eV (about 50 meV) of UV absorption band is observed for the 12 h annealed p-Zn. Further, the Full Width at Half Maximum (FWHM) of the UV absorption band is decreased to 0.035 eV for 12 h annealed p-Zn from 0.113 eV of the sintered ZnO. Thus, one could conclude that the oxidized p-Zn possesses better optical quality compared to the sintered ZnO, as shown in PLE and PL results. No appreciable absorption energy state within the forbidden energy gap of ZnO is detected for 10 min annealed p-Zn, as demonstrated in Fig. 4. This is indeed the case for the 10 min annealed p-Zn, as shown in the PL spectrum in Fig. 1. Further, a recent study of scanning tunneling microscopy and scanning tunneling spectroscopy confirms that there is no electronic state within the band gap for the 10 min annealed p-Zn.<sup>21</sup> The energies of the absorption peaks, as taken from Figs. 2 ~ 4, were displayed in energy level diagram in Fig. 5, along with 325 nm line of He-Cd laser. It also included energy levels obtained from PL spectra. Here we could clearly understand the emission spectra from anodically etched p-Zn, annealed p-Zn, and the sintered ZnO. For anodically etched p-Zn, any electrons pumped into excited states by the 3.82 eV (325 nm) He-Cd laser from ground state resulted in de-excitation into a 3.49 eV (355



**Fig. 5.** Schematic energy level diagram of as prepared p-Zn, 10-min annealed p-Zn, 12 h annealed p-Zn, and the sintered ZnO as derived from Figs. 1 ~ 4. Energy levels had been broadened to account for the broader absorption peaks and emission peaks using FWHM value.

nm) absorption band, then they would thermalize to 2.95 eV (420 nm) via non-radiative transitions, and finally revert to ground state via radiative transitions. For the case of 10 min annealed p-Zn, an excitation energy of 3.82 eV (325 nm) resulted in de-excitation into a 3.28 eV via non-radiative transition and a return to ground state via radiative transitions, which corresponds to the band-edge emission from ZnO. The 12 h oxidized p-Zn and the sintered ZnO display similar energy level schematics as can be seen in Fig. 5. Any electrons excited by the 3.82 eV He-Cd laser would have enough energy to pump into a similar absorption band at 3.85 eV. Then, they would revert to an emission band at 3.28 eV and result in radiative emission. Some of the excited carriers are transferred to a slightly lower absorption band and reverted to the lower absorption band (2.66 eV) and then yielded to an emission band via non-radiative transition and finally an emissive transition to ground state. It is observed that the absorption bands are quite broad, i.e., very broad defect states in the mid-gap for the sintered ZnO compared to oxidized anodically etched p-Zn. Thus, sintered ZnO displays a prevailing green luminescence with a very weak band edge emission of ZnO.

#### 4. Conclusions

This paper shows the relationship between the PL and PLE spectra obtained for anodically etched p-Zn, annealed p-Zn, and the sintered ZnO. The schematic energy levels (or quasi-energy bands) are proposed based on the obtained experimental results. The oxidized porous Zn and sintered ZnO, which exhibit both near band-edge emission and deep-level defect related luminescence, show an absorption band at 3.19 and 2.66 eV. However, no absorption band is

detected for the oxidized porous Zn, which only display one near band-edge UV emission.

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