Photoluminescence and cathodoluminescence studies of stoichiometric and oxygen-deficient ZnO films

X. L. Wu
National Laboratory of Solid State Microstructures and Department of Physics, Nanjing University, Nanjing 210093, People’s Republic of China

G. G. Siu and C. L. Fu
Department of Physics and Materials Science, City University of Hong Kong, Kowloon, Hong Kong, People’s Republic of China

H. C. Ong
Department of Electronic Engineering, City University of Hong Kong, Kowloon, Hong Kong, People’s Republic of China

(Received 31 October 2000; accepted for publication 8 February 2001)

Photoluminescence and cathodoluminescence (CL) spectra of stoichiometric and oxygen-deficient ZnO films grown on sapphire were examined. It was found that the intensities of the green and yellow emissions depend on the width of the free-carrier depletion region at the particle surface; the thinner the width, the larger the intensity. Experimental results and spectral analyses suggest that the mechanism responsible for the green (yellow) emission is the recombination of a delocalized electron close to the conduction band with a deeply trapped hole in the single ionized oxygen vacancy $V_{o}^{+}$ (the single negatively charged interstitial oxygen ion $O_i^{-}$) center in the particle.

The understanding of the luminescence mechanism, together with further improvement of the luminescence efficiency, has become a subject of current investigations on laser properties of ZnO. Generally, ZnO can emit three luminescence bands in the ultraviolet (UV), green, and yellow. The $\sim 370$ nm UV emission has been well understood to be due to the direct recombination of photogenerated charge carriers (exciton emission). However, for the visible emissions, various mechanisms have been presented, but exact mechanism is still in controversy. Due to the complexity of the microscopic details, it seems difficult to contrive exact mechanisms responsible for the origins of these visible emissions.

In this letter, we report an investigation on the photoluminescence (PL) and cathodoluminescence (CL) spectra of stoichiometric and oxygen-deficient ZnO films. The experimental results show that the intensities of the obtained green and yellow PL bands are strongly affected by the width of the free-carrier depletion region at the particle surface. Spectral analyses suggest that the green and yellow emissions arise from optical transitions in the single ionized oxygen vacancy ($V_{o}^{+}$) and the single negatively charged interstitial oxygen ion ($O_i^{-}$) inside the grain, respectively.

ZnO thin films were deposited on (0001) sapphire by pulsed laser deposition at a growth temperature ($T_g$) of 500–700 °C monitored by an optical pyrometer. The oxygen background pressure $p_{O_2}$ was adjusted from 0.01 to 10 mTorr to vary the ratio of O to Zn in the films. By means of a stylus profilometer, the thicknesses of the films were evaluated to be 400–500 nm. The O and Zn contents were obtained using energy-dispersive x-ray (EDX) analysis. The CL spectra were measured in a scanning electron microscope (SEM) using an Oxford Instrument MonoCL system with an accelerating voltage of 6 kV and a beam current of 2.33 nA. An electron penetration depth was evaluated to be $\sim 300$ nm according to the Kanaya–Okayama model. The SEM images clearly show the existence of ZnO particles with the radius $R$ of 100–200 nm. The PL signals were collected through a focusing lens on a SPEX 1403 RAMALOG system using the 488 nm excitation line of an Ar$^+$ laser. A low laser power was used to avoid film degradation caused by laser irradiation.

Figures 1(a)–1(c) show the CL spectra of three typical ZnO film samples. In spectrum (a), two emission bands can be observed at $\sim 375$ and $\sim 540$ nm. The intensity of the 375 nm band increases with the ratio of O to Zn ($R_{O:Zn}$) in the film, reaching a maximum in the stoichiometric sample. In spectrum (c), a small peak appears at 405 nm. For the visible emission, its intensity decreases with increasing $R_{O:Zn}$ and vanishes in the stoichiometric film. The UV emission has been attributed to the free-excitonic transition. Since the electron beam can only penetrate a limited depth, the CL spectra cannot completely represent the light-emitting properties of the whole particle.

Figures 2(a)–2(c) show the PL spectra of the three samples, measured with an excitation of the 488 nm line of the Ar$^+$ laser. These spectra all show an asymmetric broadband in the green, but their intensities obviously decrease with increasing oxygen content. This broadband can be Gaussian divided into two bands in the green and the yellow whose positions have a slight change with the sample. A sharp feature of the two bands is that although the absolute intensity decreases from sample A to C, the relative (green/yellow) integrated intensities have different values. They are

0.76, 0.72, and 1.02 for samples A, B, and C, respectively. This result implies that the defect centers for producing the two PL bands are different and compete with each other.

The two visible emission bands cannot come from the introduced impurities, because no impurity was detected in our samples using EDX analysis. Recently, Vanheusden et al. found that the intensity of the green emission in ZnO powder correlates very well with both the free-carrier electron density \( n_e \) and the paramagnetic oxygen–vacancy density \( [V_{o}^+] \), although a noticeable difference in absolute scale exists between \( n_e \) and \( [V_{o}^+] \). Since the intensity of the current green emission also has a correlation with the oxygen deficiency in the film, the \( V_{o}^+ \) defects may be a source for the green emission. To verify this point, we note the lack of the green emission in the CL spectrum of sample C. Band bending at particle surfaces will create an electron depletion region at the particle surface of width \( W \). In the electron depletion region, all oxygen vacancies are in the diamagnetic \( V_{o}^{++} \) state under flatband conditions. \( W \) can be written as

\[
W = \left( \frac{2 \epsilon_{ZnO} V_{bi} / eN_D}{\epsilon_{ZnO}} \right)^{1/2},
\]

where \( V_{bi} \) is the potential at the boundary, \( e \) the electron charge, \( N_D \) the donor density, and \( \epsilon_{ZnO} \) the static dielectric constant of ZnO. Assuming that the maximum \( [V_{o}^+] \) appears in the sample with a maximum visible PL intensity, it can be inferred that samples A and C have a minimum and maximum \( W \) (see Fig. 3), respectively. Since the \( V_{o}^+ \) centers only exist in the bulk, the magnitude of \( W \) directly affects the intensity of the green emission in the CL spectra. For a certain penetration depth of the electron beam, the larger \( W \), the weaker the green emission intensity. This is the case in our experiments. For the yellow emission, it has been suggested to be due to the interstitial oxygen \( O_{i} \). A reason for this assignment is that the enhancement of the yellow emission is accompanied by a reduction of the green emission. This is similar to our results. The \( O_i \) density \( [O_i] \) will decrease with increasing \( T_g \), whereas \( [O_i] \propto p_{O_2}^{1/2} \) because \( (1/2)O_2=O_i \). Therefore, the influence of \( T_g \) and \( p_{O_2} \) on the yellow emission is competitive with each other.

Below, we analyze the dependence of the relative intensity of the two visible emissions on \( T_g \) and \( p_{O_2} \). In the stoichiometric film, the densities of the nonionized oxygen and zinc vacancies can be written as

\[
[V_o^+] = [V_{Zn}^+] = \exp \left( -\frac{E}{2kT} \right),
\]

where \( E \) is the formation energy for a pair of \( V_{o}^+ \) and \( V_{Zn}^+ \), \( k \) the Boltzmann constant, and \( T \) the thermodynamic temperature. The oxygen vacancy ionizes singly: \( V_{o}^+ = V_{o}^+ + e^- \). Under the same \( p_{O_2} \), \( [V_{o}^+] \) and \( [O_i^-] \) increase and decrease with \( T_g \), respectively. Under the same \( T_g \), \( [V_{o}^+] \) and \( [O_i^-] \) decrease and increase with \( p_{O_2} \), respectively. Hence, the relative intensity (green/yellow) is also a competing effect, dependent upon the influence of \( T_g \) and \( p_{O_2} \) on \( [V_{o}^+] \) and \( [O_i^-] \). From Figs. 2(b) and 2(c), it can be seen that high \( T_g \) has a larger influence on the relative intensity than high \( p_{O_2} \). Sample C has \( p_{O_2} = 1 \times 10^{-2} \) Torr, being far larger than \( p_{O_2} = 1 \times 10^{-4} \) Torr of sample B. Thus, sample C should have smaller relative intensity. However, sample C actually has larger relative intensity than sample B. This is obvious because sample C has higher \( T_g \) than sample B. In sample B, \( p_{O_2} = 1 \times 10^{-4} \) Torr is larger than \( p_{O_2} = 1 \times 10^{-5} \) Torr of sample A, but the relative intensity in sample A is larger than that in sample B. This also indicates that the influence of \( T_g \) on the relative intensity is more pronounced than that of \( p_{O_2} \). For the shifts of the wavelengths of the two visible PL peaks, a possible explanation is due to changes in the local environments of the defect centers in different samples. The 405 nm (3.06 eV) CL peak in sample C can be assigned to the \( V_{Zn}^- \) center, because the...
peak only appears in the sample with a maximum $p_{O_2}$ ($[V_{Zn}] \propto p_{O_2}^{1/2}$). Since the $V_{Zn}^-$ centers only exist in the depletion layer (see Fig. 3), the 405 nm emission can only be observed in the sample with a large $W$. A theoretical calculation also shows a similar result.\(^8\)

Two possible mechanisms have been presented for these emission bands: (1) recombination of a shallowly trapped (delocalized) electron with a deeply trapped hole, or (2) recombination of a shallowly trapped hole with a deeply trapped electron. The key to distinguishing the two mechanisms is to obtain the particle-size dependence of the positions of the UV and green emission bands.\(^9\) Under the effective-mass approximation, the size dependence of the band gap ($E^*$) can be represented as follows:\(^{12}\) $E^* = E'_g + \hbar^2/8\mu R^2 - 1.8e_1^2/4\pi\varepsilon_0\varepsilon_s R$, where $E'_g$ is the band gap of the material, $\mu$ the effective mass of the exciton, and $\varepsilon_s$ the high-frequency dielectric constant. For the edges of the conduction ($e$) and valence ($h$) bands versus particle size, we can give the following expressions for the absolute values of the shifts of the band edges as a function of particle radius $R$: $\Delta e = E'_g + \hbar^2/8m^*_e R^2 - 0.9e_1^2/4\pi\varepsilon_0\varepsilon_s R$ and $\Delta h = \hbar^2/8m^*_h R^2 - 0.9e_1^2/4\pi\varepsilon_0\varepsilon_s R$. When ZnO particles consist of about 50–5000 molecular ZnO units, the validity of the effective-mass approximation is applicable.\(^11\) Now we assume that the energetic position of the deeply trapped charge carrier is independent of particle size, the shift of the energetic position of the trapped emission as a function of particle size is determined by the shift of the conduction- or valence-band edge.

From the above formula, an approximate linear relation can be drawn between the energies of the exciton emission and the trapped emission.\(^11\) For mechanism (1), the slope of the linear relation is 0.64 and for mechanism (2) the slope is 0.36. From our experimental result, a slope of about 0.69 can be obtained, as shown in Fig. 4. So the mechanism responsible for these emissions should be due to the recombination of an electron with a deeply trapped hole in the $V_o^+(O^-)$ and $V_{Zn}^-$ center.

In conclusion, we have examined the PL and CL spectra of stoichiometric and oxygen-deficient ZnO films. Four emission peaks in the UV, violet, green, and yellow are observed. The 375 nm band is identified to be from the exciton emission. The violet, green, and yellow emissions are attributed to the radiative recombination of a delocalized electron close to the conduction band with a deeply trapped hole in the $V_{Zn}^-$, $V_o^+$, and $O^-$ centers, respectively, by analyzing the film properties and the dependence of these emission peak intensities on $T_g$ and $p_{O_2}$.

This work was supported by Grant Nos. 59832100 and 60076007 from the National Natural Science Foundation of China.


\(^12\) L. Brus, J. Phys. Chem. 90, 2555 (1986).