Chapter 4

Defects Affected Field Emission Properties of ZnO Nanowires

4-1 Field Emission Mechansims Review

The field emission (FE) properties of ZnO nanorods have been explained using traditional Fowler–Nordheim (F-N) theory, and thus the emission characteristic has been simply attributed to the high aspect ratio of the nanorods. Essentially, the I-V characteristics seem to follow the F-N law. However, when performing FE studies over a large current range, there have been some systematic deviations from the F-N model at high emitted currents. As a result, the FE mechanisms were reviewed.

The proposed emission mechanisms also vary widely. Some authors have demonstrated results supporting the to the F–N tunneling theory, suggesting that emission results from a traditional tunneling process through a very sharp, high aspect ratio nanostructure, with a constant work function [143] , [144]. On the other hand, Collins and Zettl [145], [146] and Bonard *et al.*[147] observed changes in the slope of the I-V behavior which they claim suggests a more complicated model than the F–N tunneling theory. Furthermore, both Gulyaev *et al.*[148] and Rinzler *et al.*[149] have reported unusual temperature-driven changes in field emission current. Gulyaev *et al.* conclude that the strong thermal dependence indicates that low work function emitters are needed. Rinzler *et al.*, on the other hand, maintains that emission results from a sharp, high work function material. They explain abrupt changes in emission behavior at high temperature are the result of a thermally induced restructuring of

the nanotube cap leading to an increase in field enhancement. Thus, the reported results and interpretations suggest that the field emission process is more complicated than is predicted by an emission model assuming tunneling from a metallic electrode through a simple potential barrier. This suggests that multiple emission mechanisms may coexist.

It is also worthwhile to understand the details of field emission from tip surfaces and emitter absorptions. In fact, it was demonstrated that surface contaminants dominate room temperature emission phenomena if the surface is not rigorously cleaned. Genuine metallic field emission behavior is obtained only after the removal of surface adsorbates from tips. Only clean tip surfaces truly follow the free electron tunneling model for which F–N is the low temperature expression [150]. For the CNT emitters, different experimental results and theoretical models concerning adsorptions including the space charge [51] and cathode adsorption models [52]. Base on the above results in uncovering the relevant emission mechanisms, there is a need to perform similar experiments with ZnO nanorods.

According to the F-N theory, the emission from single nanorod could be written as

$$J=A(\beta^2V^2/\Phi d^2)\exp(-B\Phi^{3/2}d/\beta V) \quad (4\text{-}1)$$

where J is the current density; A=1.56×10-10 (AV^{-2} eV); B=6.83×109 ($VeV^{-3/2}$ Vm^{-1}); β is a field enhancement factor; Φ is the work function; E=(V/d) is the applied field; d is the distance between the anode and the cathode, and V is the applied voltage.

If the expression is plotted in log scale, also known as the F-N plot, a linear relationship between the log (I/E^2) and 1/E appears. The slope of the F-N plot, S, can be written as;

$$S=B\Phi^{3/2}/\beta \quad (4\text{-}2)$$

It is clear that the slope of the F-N curve is a function of the work

function (Φ) and the field enhancement factor (β). Any changes in the two quantities can affect the slope to form a nonlinear relationship in the FN-plot. For example, if there are many β from the emitter, the total current expression in FN-plot is nonlinear as shown in Fig. 24.

It is well known that β is strongly dependent on the geometric configuration of the samples. [151] For one sample, the variation of β due to the change in its geometric configuration means that such variation would be irreversible and a serious damage to the morphology of the sample should be observed. While the emitters are higher and sharper than the surrounding, ones can be dulled back and β can thus be changed. Besides, the screen effect we discussed in chapter 3 also influences the β value. Moreover, if the absoprate is formed, the shape (β) and the work function (Φ) will change dramatically to affect the FE properties. This will be further examined in the next section.

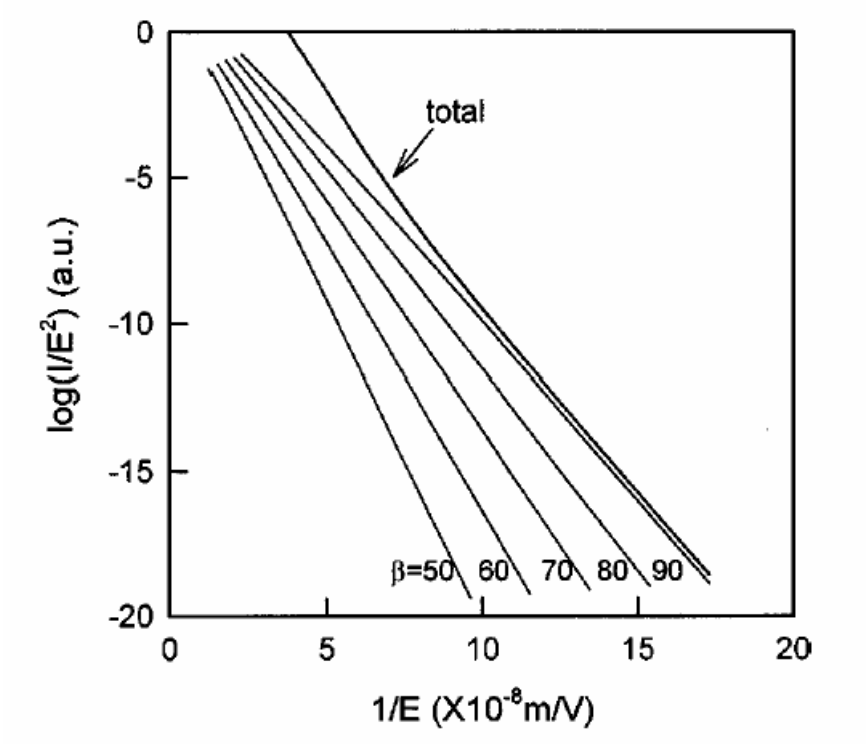


Fig. 25 Simulation result of the FN plot by assuming the total current is emitted from nanorods with five different field enhancement factors (β).[152]

4-2 F-N tunneling affected by defects

FE concerning electrons tunneling to the vacuum through a field-modified surface barrier has been extensively studied. The Fowler-Nordheim (FN) theory of FE has been proved to be quite successful in describing electron emission from metallic surfaces [151]. Besides, Dong *et al.* proposed that the single ZnO nanorod emitter gave high FE current originated from adsorbates and the emission behavior followed the F-N relationship [50]. The pressure and the ambient gas affected the FE properties due to adsorption and desorption process of the adsorbates [153]. The adsorbate state was reported to modify the effective work function of the sample [151]. The change of work function was attributed to the surface coverage of adsorbates. However, the effects between material quality and adsorbates on the FE properties are still ambiguous. In this section, the relation between FE phenomena and defect amount of ZnO nanorods were studied. We found that the non-linearity of the F-N plot can be traced to defects. As defects contained increased, the slope difference of F-N plot was more obvious. The reason might be the adsorbate formation from the surface defects adsorption of ZnO nanorods under FE.

The sample fabricated process was mentioned in chapter 3. The micro structure and composition properties were investigated by FESEM and EDX. The integrated emission was dominated by a comparatively small number of very strong emitting sites spread out over the entire sample surface. Indeed, the number of detectable emission sites depends on the area of the measured surface. One cm^2 area will include more amounts of these stronger emitting sites than a local measurement in one mm^2 window [142]. As a result, the local FE measurements were conducted to find the emission mechanism. The cathode made by

patterned nanorods of ZnO remained 100 μm away from the anode which is a tungsten tip with radius of 600 μm. We have made four samples with different amount of Zn-vapor. The emission current was measured by a Keithley 237 I-V meter. The base pressure of the FE chamber was better than 10^{-5} torr.

Electron microscopy images have revealed the microstructure of vertically nanorod arrays in Fig. 25. The diameter and length of the nanorods were in the range of 100~200 nm and 1 um, respectively. A wetting layer under these nanorods was found, and the direction of the nanorods was random according to the morphologies of that wetting layer. The EDX spectrum showed that there is only Zn and O elements on the Si substrate.

Figure 26 illustrats the local field emission property of the four samples of ZnO nanorod array grown on the p-Si substrate. The emission current-voltage characteristics were analyzed using the F-N equation [137]. Different turn-on field and emitted current from the four samples in Fig. 26 might be due to different field enhancement factor caused by their small diameter and less electrostatic screening effect provoked by the proximity of neighboring nanorods. Of course, some errors in our experiment might occurr to explain the difference, for example, the probe distance error, the direction of current collection from different emitters and the adsorbate effect.

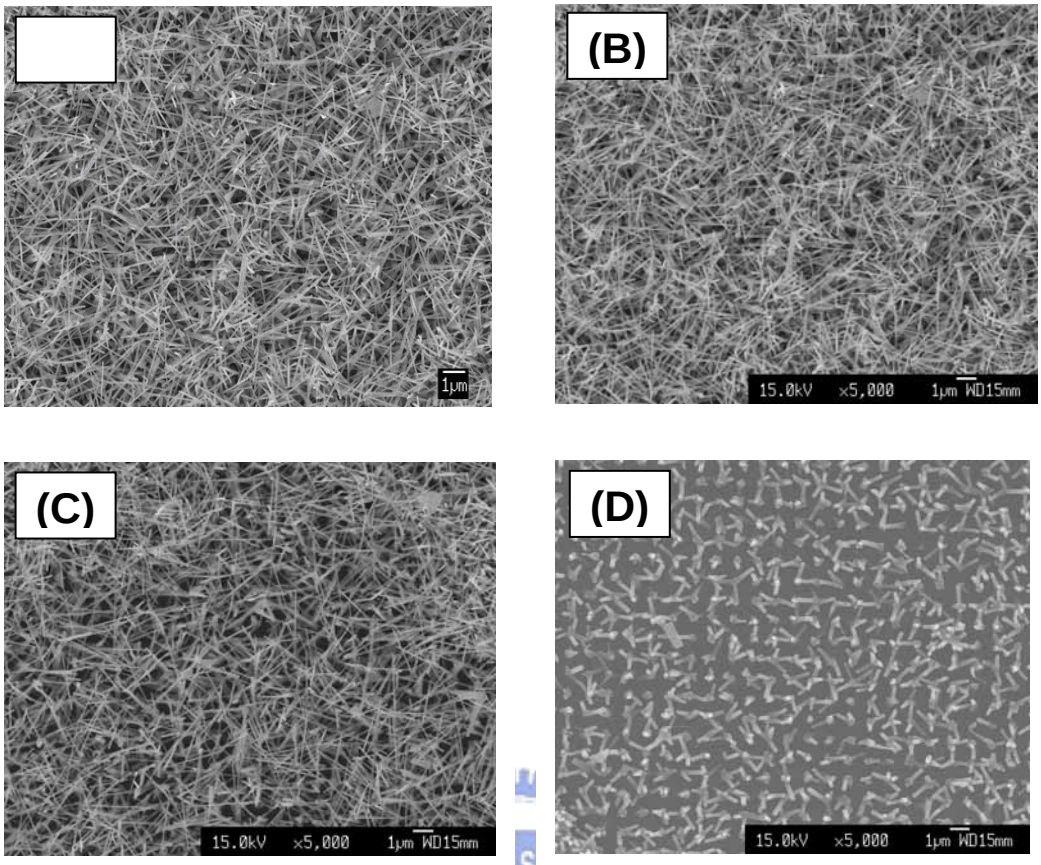


Fig. 25 The same SEM image of ZnO nanorods with four Zn vapor concentration. And the field enhancement factors (β) might be similar.

Figure 27 presents the F-N logarithmic plot. Linear behavior was exhibited over the measurement range only in sample A, so the emission was indeed caused by the F-N tunneling mechanism. But a decreasing slope at high field was shown in the F-N plot from the other samples. The various nonlinearity change in the F-N plot were found to be similar to that from the CNTs which was attributed to the space charge effect [154]- [155] and adsorbate effects [156].

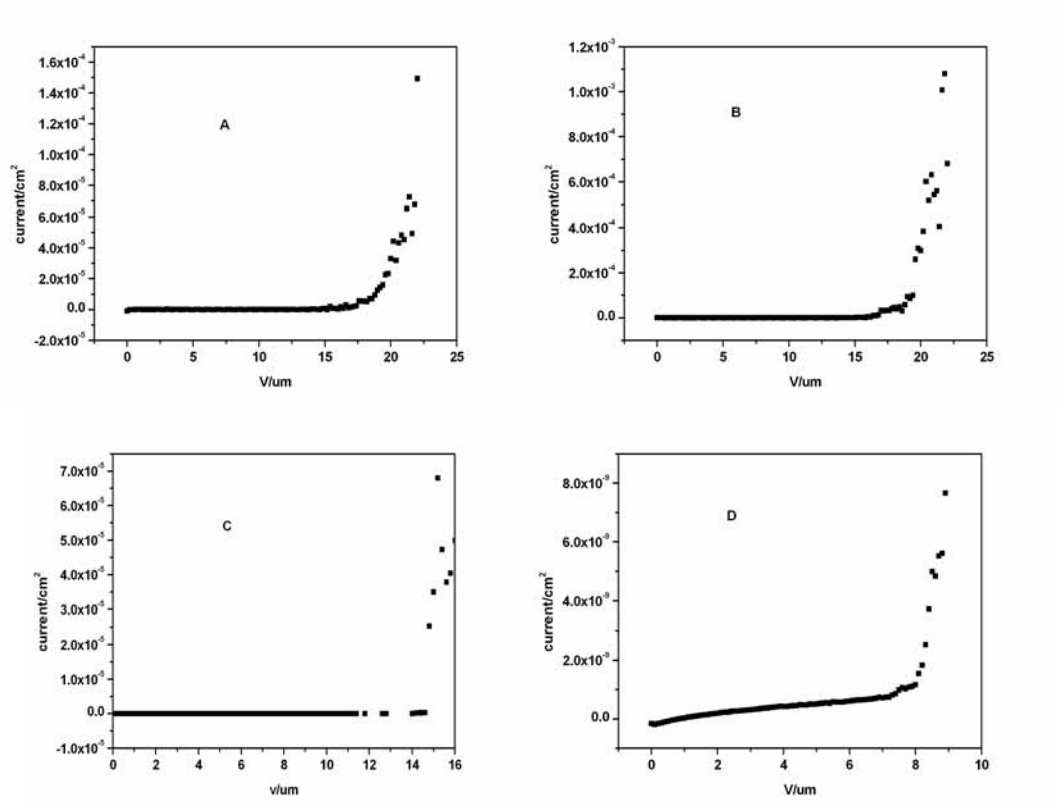


Fig. 26 The field emission characteristics of A, B, C, and D.

Althought the samples with similar high aspect ratios were in the same ultrahigh vacuum chamber, the change of β can not be neglected due to different space charge effect or adsorbates. Therefore, the variation of the slopes of the F-N curves must be attributed to the modification of the Φ and β together from eq. (4-2). Therefore, at low applied field, the electrons are mostly emitted from the nanorods with high β and low Φ value, while at high field the nanorods with a low β and high Φ value will emit electrons and contribute to the emission. Thus the nonlinearity in the F-N plot is formed. We also calculated the two slopes, S_I and S_{II}, and their difference for each samples as shown in TABLE 4. It is interesting that the S_{II} of the four samples are similar which measns they have similar material characteristics (Φ) and emission properties (β) at high field region.

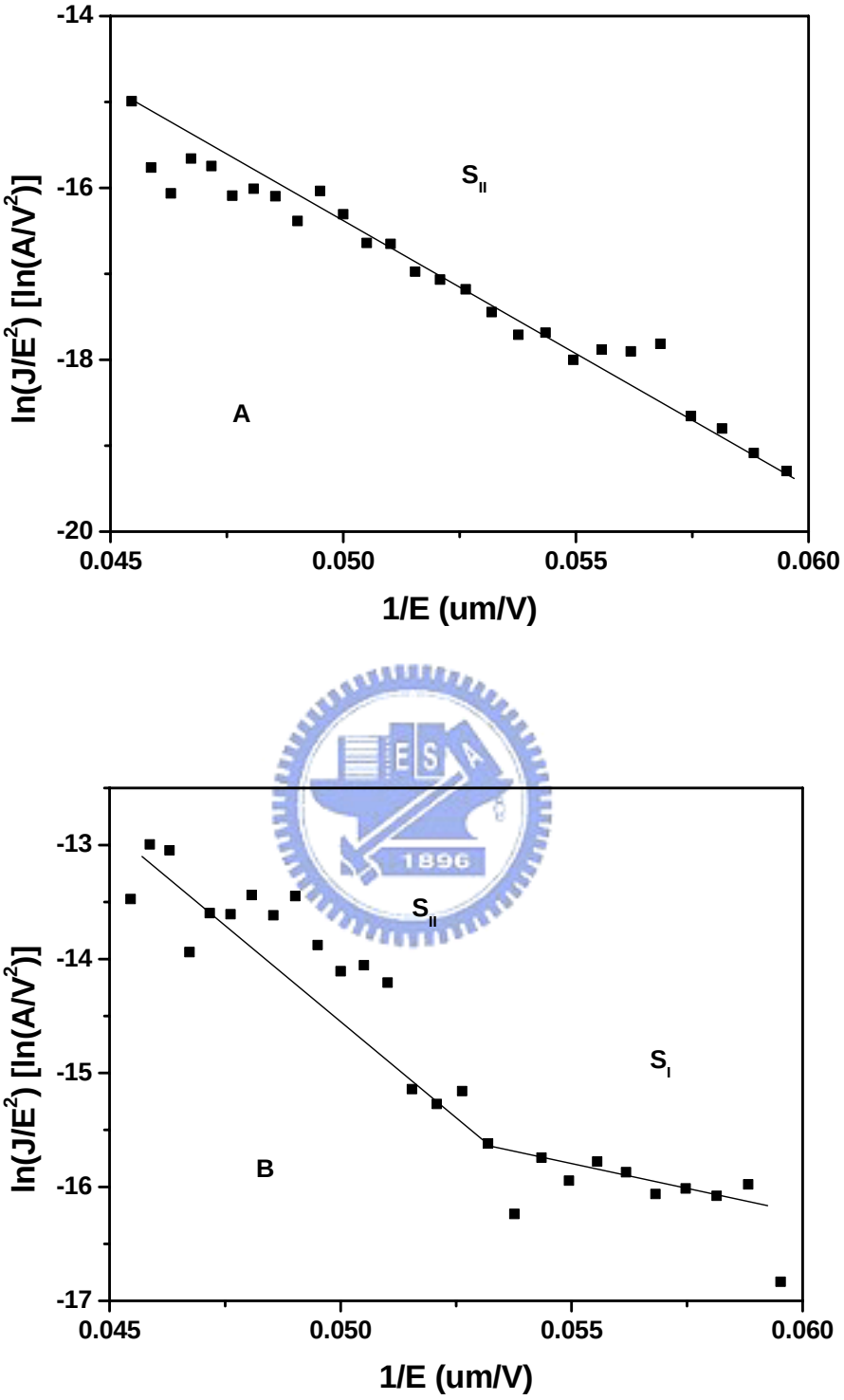


Fig. 27 the F-N logarithmic plot with four samples: A, B, C and D. The nonlinearity and different change in the FN plot were due to the space charge and adsorbate effects

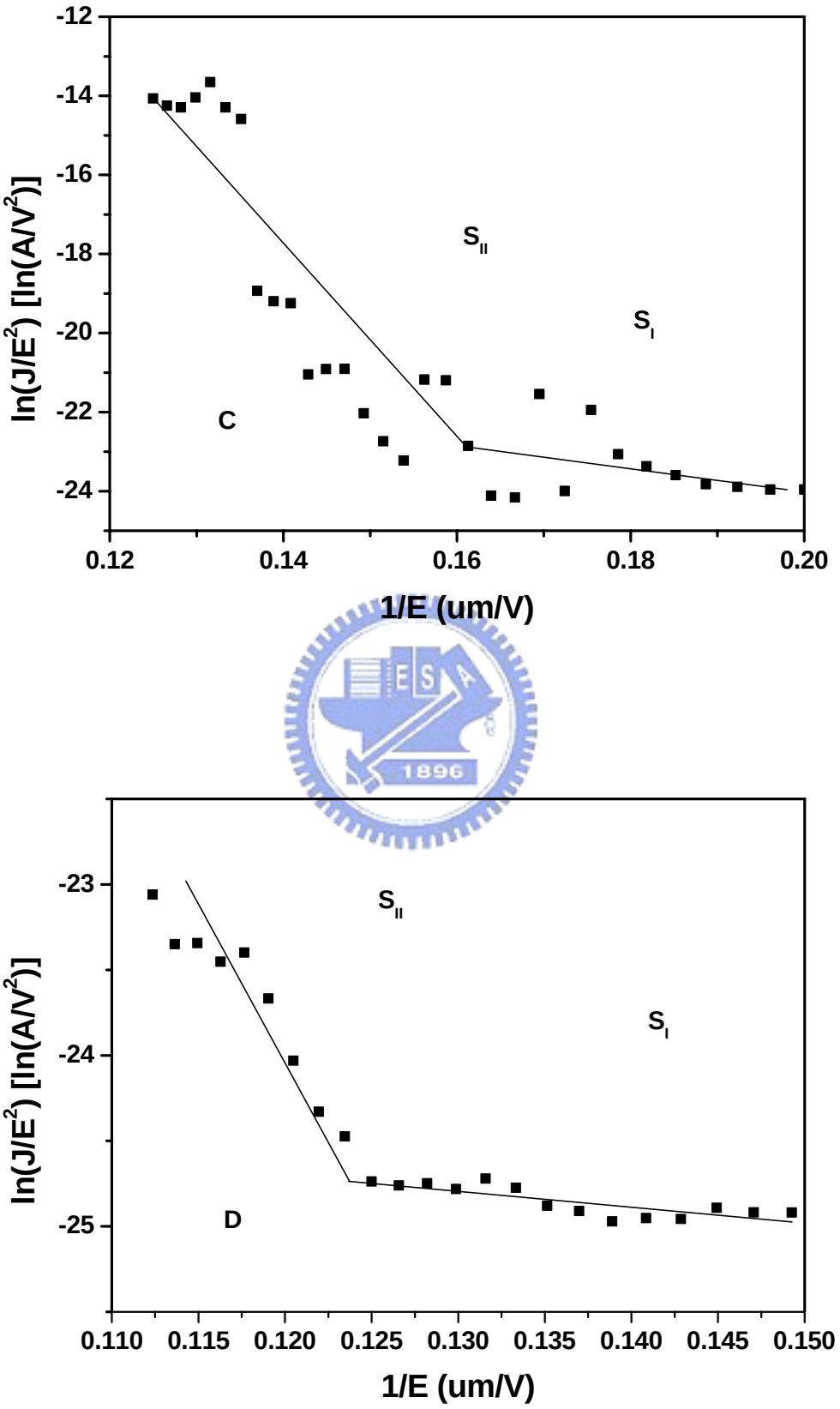


Fig. 27 the F-N logarithmic plot with A, B, C and D. (continued)

Sample	Slope of S_I	Slope of S_{II}	Slope Difference
A	-306	-306	0
B	-111	-291	180
C	-39	-225	186
D	-10	-206	196

Table 4 Slope difference from FN-plot of A, B, C and D samples

As a result, we might naturally categorize the whole emission curve into adsorbate-controlled and desorption-controlled regimes [151]. The adsorbate states strongly enhance the emission efficiency at low field, which can be attributed to the modification of the effective work function of the samples by the adsorbates. As the field increases, the quantity can be derived by considering the desorption process for the emission current providing the energy to remove the cathode adsorbates. When desorption is significant, it follows the FN mechanism to deviate a linear slope. But absorption and desorption were only occurred at the surface of ZnO nanorod, the defect contained inside still affect the FE behacior at high field. That is the reason for the different S_{II} value for the four samples.

We also measured the Φ of our ZnO nanorod by ultraviolet photoelectron spectra (UPS) and found it to be 5.2eV which is the same as the reported value in the literature [157]. Adsorption with the residual gas in the vacuum could lower the Φ and the adsorbate states could strongly enhance the emission efficiency. But the ability to form adsoprtion might come from the material itself, for example, defect and vacancy. To investigate the problem, PL measurements of four samples were carried out and the spectra were shown in Fig. 28. The emitting band, green emission at about 500 nm, can be ascribed to singly ionized oxygen vacancies in ZnO. [158]

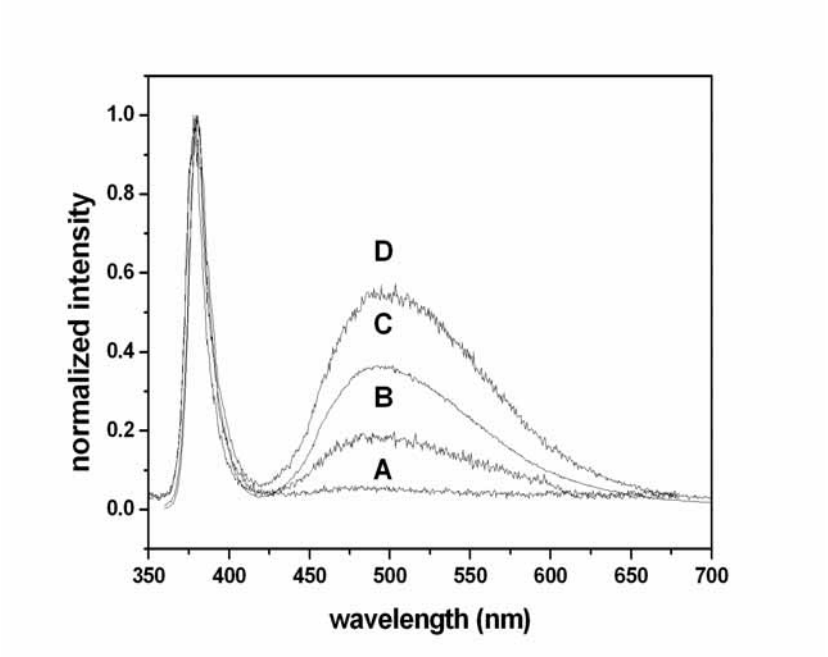


Fig. 28 PL spectra of four samples with the different content of ionized oxygen vacancies and other defects.

The physical meaning of slope difference from Fig. 27 is about the current density difference. One can realize from the definition:

$$\frac{\ln(\frac{J_1}{E_1^2})}{\frac{1}{E_1}} - \frac{\ln(\frac{J_2}{E_2^2})}{\frac{1}{E_2}} \cong \ln(\frac{J_1}{J_2}) \qquad (4\text{-}3)$$

where we assume E_1 and E_2 are similar and thus negligable. J_1 and J_2 are the current density from S_I and S_{II}, respectively. We think the S_I region is attributed to the defect which could form an adsorbate with the residual gas or absorb electron from the applied voltage resulting in a decreased emission current. As raising the field, desorption might happen along with a drastic increase in electron tunneling to vacuum. This large emission current formed the S_{II} region. Hence, the dependence from Fig. 28 and Table 4 was observed. From these data, it can be seen that the defect contained in ZnO nanorods were proportional to the loss of emission current under FE which resulted in the slope change of the F-N plot.

The formation of the surface states can dramatically lower the effective work function [159]. Recently, the FE of graphitic ribbons was investigated by Tada and Watanabe using the time-dependent density functional theory (TD-DFT) [109]. They found that the dangling bond states and not the edge states contribute primarily to the FE. Their results cannot be derived from the conventional Fowler-Nordheim theory for the FE with the free-electron approximation.

The FE and electronic-states origins of graphitic nanostructures were investigated [160]. They found that the character of the local electronic states responsible for FE changes and thus the FE current varies, depends on the conditions of hydrogen termination and the direction of the electric field. The Dangling-Bond states are the predominant source for the FE because the electronic orbitals tend to appear at the edge and protrude along the direction of the electric field. Thus, the study can provide a theoretical interpretation for the features observed in their experiment. We naturally expect that a similar property could be observed from ZnO nanorods. Substantially emission current from the atomic vacancy sites might contribute to the initial emission in FE.

As a result, we could explain our two slopes in the FN plot. The first slope might be attributed to the defect consuming electron and the decreasing emission current. Electron in surface defects could have reaction with the residual gas to form adsorbates due to raising temperature when voltage is applied. As the voltage keeps increasing, desorption process might happed and electrons are forced to tunnel throught the vacuum to form the second slope. In other words, the first part could be explained as a space charge effect and the second part could be a conventional F-N theory for the FE with the free-electron approximation. Our study emphasizes that a good structure of emitters can help understand the FE mechanisms and form a stabler FED device.

4-3 Field Emission Induced Blue Emission

ZnO belongs to the direct band semiconductors and has a band gap of 3.37 eV at room temperature (RT). This ensures that UV and blue emission can be obtained at RT. ZnO film is also a promising material for short-wavelength laser and LED etc. As a result, it is an excellent candidate for possible optoelectronic devices such as field-emission displays and diode lasers [161], ultraviolet and blue light-emitter, detector, and also high power, high frequency electronic devices. [162] In 1997, the optically pumped excitonic UV laser emission from ZnO thin film was first reported by scientists in both Hong Kong and Japan [163],[61]. Since the wavelength of UV emission from ZnO is shorter than that of the blue emission from GaN [164]-[165], it is quite certain to collect far more information and to improve the writing-reading rate of information processing as the material ZnO is being used as a light emitter [166]. Because the shorter wavelength lasers can give smaller diffraction-limited spot and thus store information in much higher density. Therefore, for further increasing storage capacity, the search of shorter wavelength, long-lasting laser diode has become the important goal for applications [165]. On this aspect, ZnO nanowires device is surely an expected emitter to give shorter wavelength.

Blue and UV emission has been explored from Zn-rich ZnO thin film [166]. Although there is experimental evidence that electron emission is related to defects in the ZnO films, the emission from ZnO nanowires is still poorly understood up to now. Bonard *et al.* reported field-emission related luminescence from single-wall and multiwall carbon nanotubes and suggests that the light emission was caused by electron transitions between different electronic levels participating in

the field emission process [165]. To our knowledge, no reports have been published on monochromatic blue light emission from ZnO nanorods. This section aims to demonstrate the blue-light emission from field excitation property of ZnO nanorods grown on silicon substrate and discuss the mechanism of the emission.

We prepared the sample through the process mentioned in chapter 3. The morphologies and the optoelectronic properties of the samples were investigated by FESEM and EL. FE experiment setup was the same as that in the front section. FESEM images have revealed the microstructure of vertically nanowire arrays in Fig. 29(a). Every single nanowire is prismatic appearance. The average diameter and length are found to be 70~100 nm and 2~3 um, respectively. A wetting layer under these nanowires is found, and the direction of the nanowires is randomly oriented according to the morphologies of that wetting layer. The EDX spectrum of those ZnO nanorods shows in Fig. 29(b) that there are only Zn and O elements coexisting on the Si substrate.

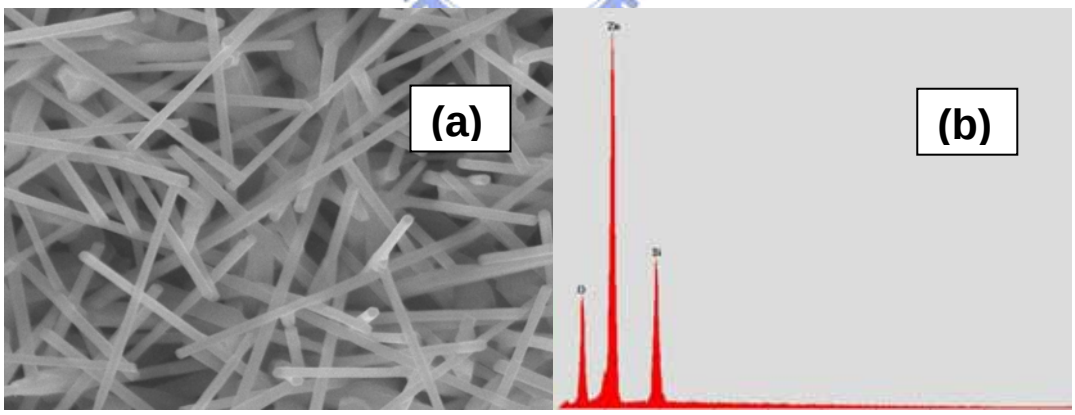


Fig. 29(a) FESEM images revealed the microstructure of vertically ZnO nanorod. (b) The EDX spectrum of ZnO nanorods .

Figure 30 (a) shows the pictures of green light and blue light under the FE measurements at 8~10 V/μm in a vacuum chamber. Green light was observed by the emitting electrons from those nanorods and impinging on the phosphor powders-coated on the conducting glass

plate. Few blue spots were also found at the same time. On the other hand, blue light was clearly observed from the other glass plate without phosphor-coated as shown in Fig. 30 (b). The blue emission was steady and lasts for hours. Figure 30 (c) demonstrates the blue-light picture taken with a longer exposing time.

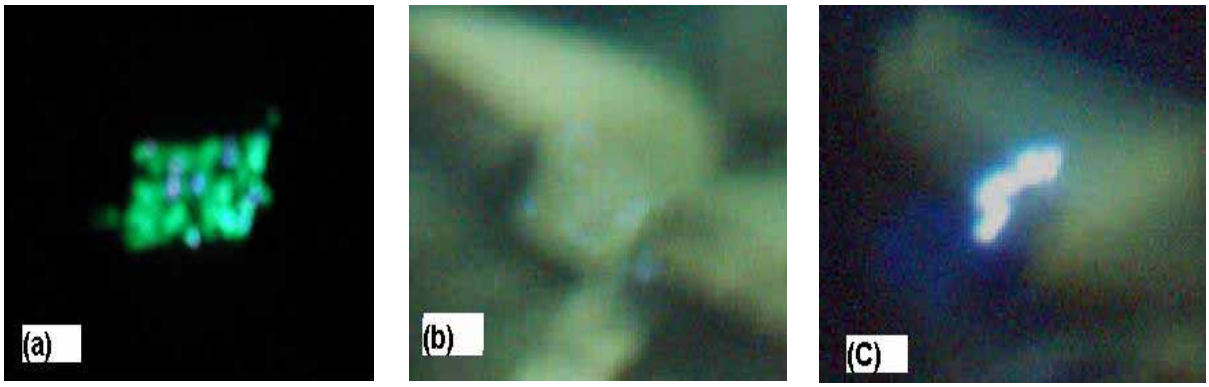


Fig. 30 (a) the green light due to phosphor. Blue spots and with longer exposing time without phosphor are in (b) and (c)

Fig. 31 demonstrates the PL spectrum of the ZnO nanorods. The main emitting bands, a strong ultra-violet (UV) emission at around 380 nm and a weak green emission at around 500 nm are observed. The appearance of a strong UV peak is due to the near band edge emission of the wide band gap of ZnO nanowires. The green emission can be ascribed to singly ionized oxygen vacancies in ZnO. [158] But the wavelengths of blue emission are not clearly observed from PL spectrum because all kinds of luminescence signal are collected for the high energy of KrF laser. The few blue spots are only existed in the sample. As a result, we can not see the blue spot during PL measurement.

After the FE experiment, we examined the spot location about composition of the sample by EDX and there were not any signal for other element. Hence, the blue spots does not come from other kinds of element, resulting that the mechanism of luminescence could refer to the defect level recombination on its own material. The emission is neither from

the plasma nor the electrical arcing because the emitting time and brightness could be well controlled by the external applied power. Hence, the blue light emission might be attributed to the recombination radiation of electrons with holes at some energy level through the field emission. There might be some energy level existing in the ZnO nanorod due to the non-stoichiometry characteristics.

Fig. 32(a) and (b) illustrats the integrated field emission property of ZnO nanorods. The emission current-voltage characteristics are analyzed using the F-N equation. As one can see, there are also two linear regions in the FN-plot which might be attributed to the defects or adsorbates as discussed in section 4-2. But, there is something different. The slope at high field is greater than that at low field. The slope reflects the current density. At the field region of 8~10V/um, carriers were recombining to occur blue emission resulting in the decrease of current density.

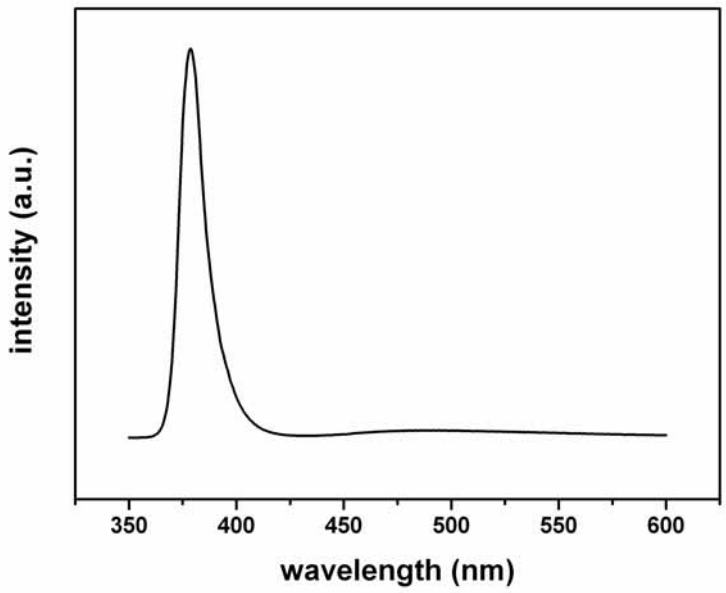
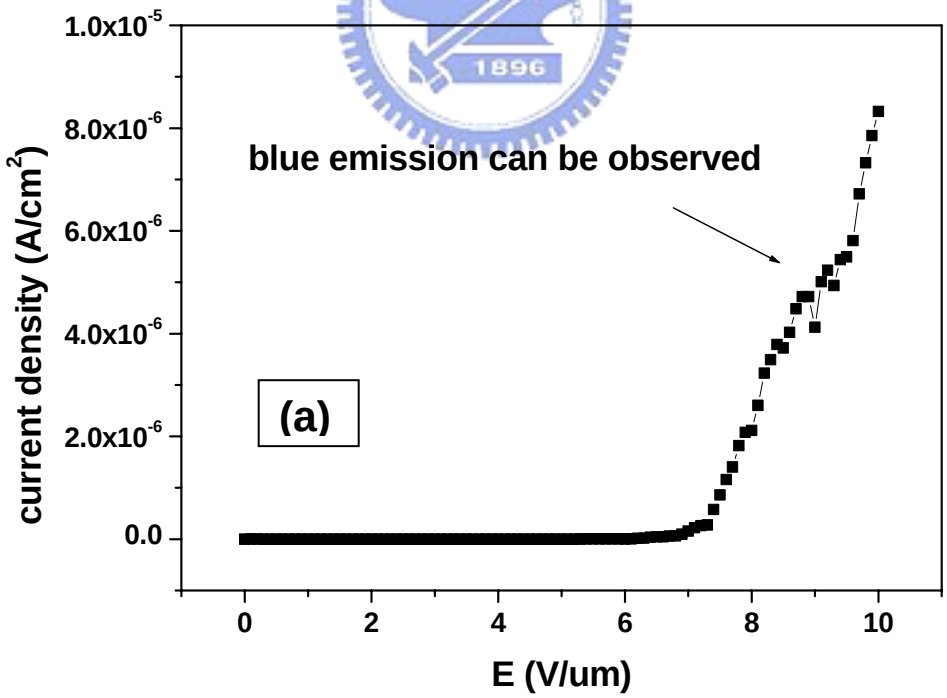


Fig. 31 PL spectrum of the ZnO nanorods.

Fig. 33 displays images of the blue-light spots from ZnO nanorods and the single blue spot in the dark chamber is in the inset. The blue light is induced by field emission and lasts for hours. The intensity of blue light

is also increased as the applied voltage increases. The emission current is 5~10 uA at the field of 8~10 V/um. As field inreased above 11 V/um, the current enlarged to 15~17 uA, but the blue spots disappeared. However, when the field is decreased, blue spots appeare again.

We calculated the slope of the three regions in Fig. 32(b), S_I, S_E and S_{II}, and they 93, 15.3 and 96, respectivitly. The slope from S_I and S_{II} are similar but larger than that of S_E resulting from the electron-hole recombination to blue light. According to the section 4-2, defect amount could be proportional to the PL spectrum and slope difference. Hence the defect amount of this blue-emission sample with a smaller S_I value is larger than that of sample A. But the FE property is similar to sample A for electron would be less consumed by defect to form the adsorbate, which made the slope of F-N plot a liner line.



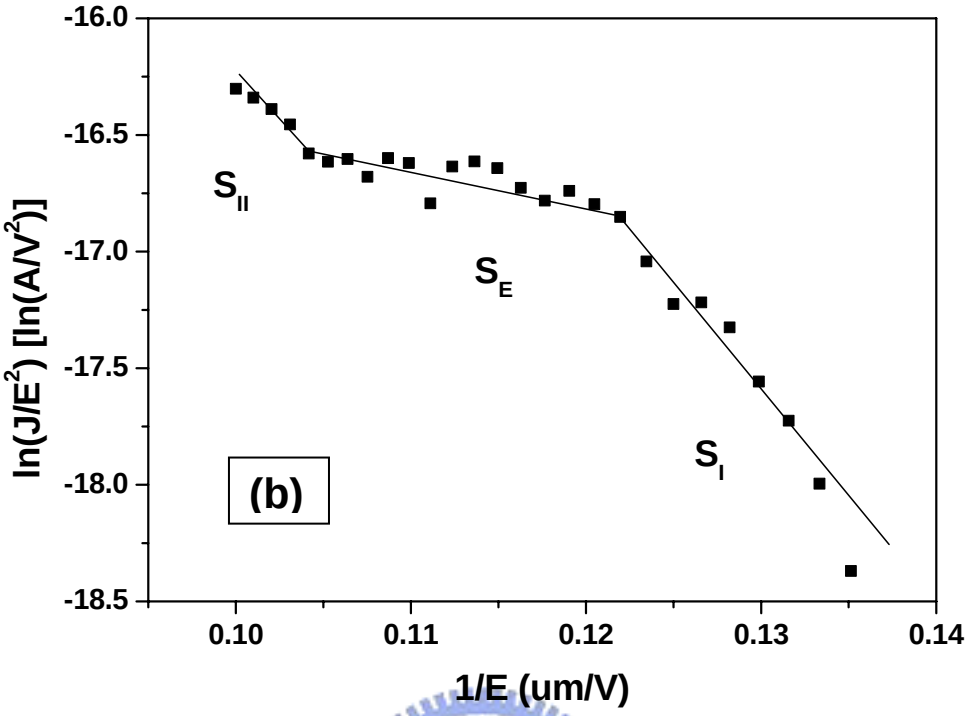


Fig. 32 (a) illustrated the integrated field emission property and (b) is the F-N plot of the blue-emission ZnO nanorods.

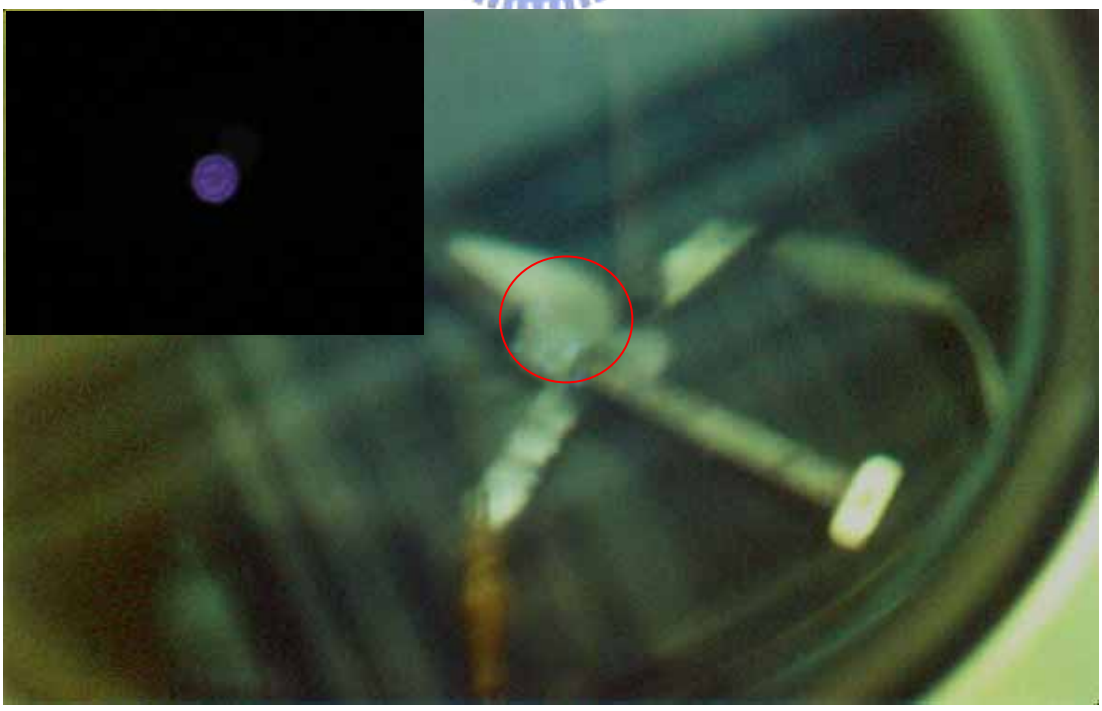


Fig. 33 The blue spot of ZnO nanorods under field emission.

Fig. 34 shows the band diagram of ZnO nanorods. One possible defect level, wavelength about 404~407 nm, is related to the transition of electrons from the conduction band to one of the deep level. A self-activated center formed by a doubly ionized zinc vacancy defect and an ionized interstitial zinc donor have also been reported. [166]. Based on the calculation by Y. M. Sun *et al.*, [167] those levels formed by some defects in ZnO films are approximately 3.06eV from the conduction band to the V_{Zn} level within the band gap. The emission from the oxygen vacancy might be due to the other possible energy level with the wavelength about 435nm. The oxygen vacancies can produce two defect donor levels [168]. Fu *et al* suggest that the oxygen vacancy is an intrinsic donor and the zinc vacancy works as a shallow acceptor level [169]. They predicted that the blue light emission can occur in the ZnO film through the transition process of electrons from the shallow donor of oxygen vacancy to the valence band. On the other hand, Zn interstitials can also be produced in Zn-rich samples, which are expected to act as donor centers [167]. The energy level of Zn interstitials is located at around 2.9 eV above the valence band [170]. This might be another energy level to emit blue light.

Althought we can find those defect levels to emit blue emission under FE, not all our samples can observe the blue spots. Here is another thought that device under such high field is in the early breakdown regime and occupied gap states are likely to be impact ionized by injected carriers under high electric field [171]. The generated carriers would impact other occupied states and then make it ionized. Finally, the multiplications of impact ionized process cause the current to increase extensively. This process was called impact ionization mechanism. Some energy states in the ZnO nanorods are called luminescence centers [172] and our optical emission is the results of electrons and holes radiative recombined in these

centers. In addition, the applied filed could affect the emission. If the field is not large enough, only small amounts of the generated carriers would impact other occupied states to form luminescence centers and then make it to be recombined. On the contrary, a field too large would remove all carriers to emission current causing blue light to be hardly visible.

In conclusion, the non-stoichiometry characteristic might induce the emission from luminescence centers in ZnO nanorods under FE. The electron can be excited to conducting band due to the applied electronic field. Some electron tunneled to the vacuum while others transited to luminescence centers which resulted in the emission of blue-light.

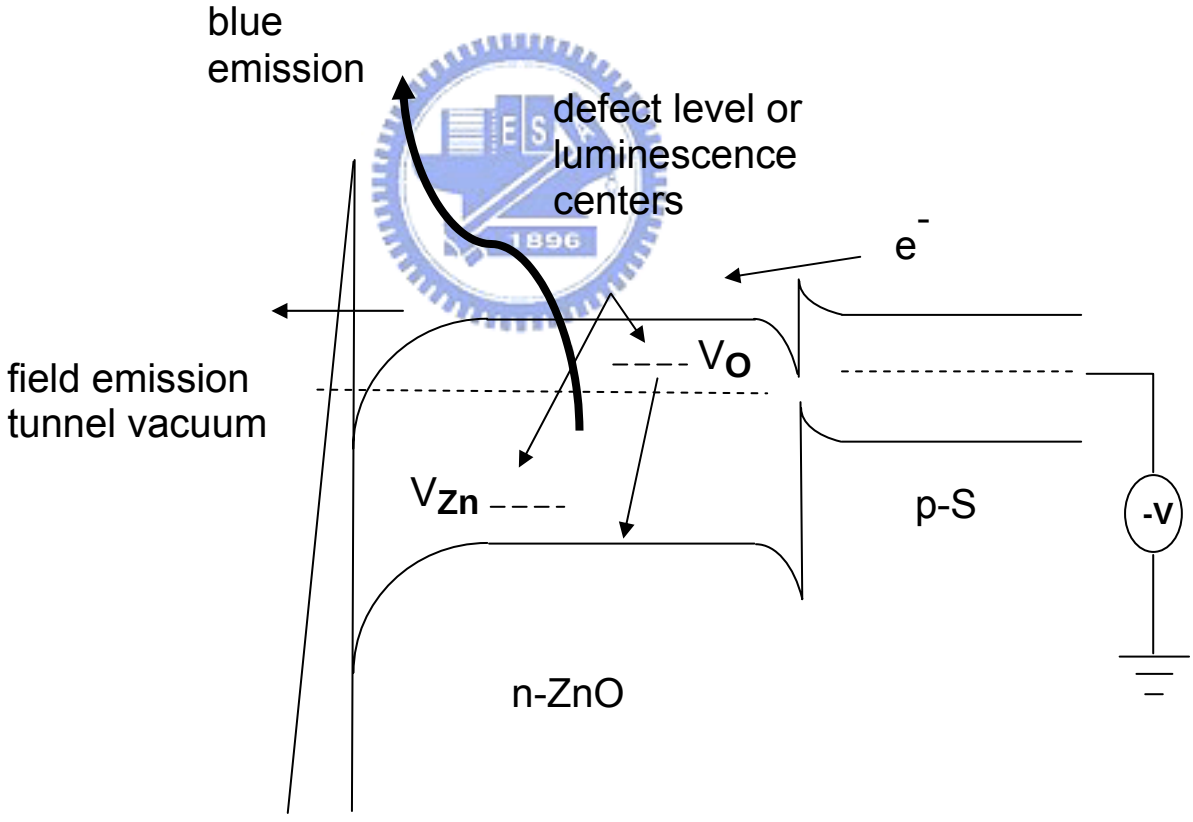


Fig. 34 The energy level and relative wavelength. band diagram of ZnO nanorods for blue light emission was also shown.

4-4 Conclusion

The FE experiments were conducted for four different ZnO nanorods to indicate the F-N tunneling model. The nonlinearity of FN plots was observed which was similar to the adsorption phenomenon of CNT. The slope change had proportional relationship with the work function difference. The oxygen defects in ZnO nanorods might easily cause adsorption to lower fork function which decreased the slope of FN plots and could affect the FE properties.

Blue light is observed by naked-eyes while field emission experiments were conducted. The emission may be due to the defect levels recombination in ZnO band structure. ZnO nanorod is a promising candidate for UV and blue light emitter.

In the design of broad-area field-electron sources there are some key requirements. These apply to all sources, including Spindt arrays, and includes (this is not an exhaustive list):

- The need to be able to generate sharp features that field emit.
- The need to generate controllably, with sufficient density and uniformity.
- Emission currents shall be stable and not unduly noisy.
- Emitters shall be robust against poor vacuum conditions.
- Emitting sites shall be stable against burn out and other degradation.
- Large-scale manufacture shall be straightforward and cost-effective.