Chapter 3 Synthesized ZnO NWs by VLS Process Using Cu Catalyst

3.0 Preface

The ZnO NWs were synthesized using vapor-liquid-solid (VLS) growth process on copper coated p-type Si (100) substrate. Copper catalyzed the growth of ZnO NWs of diameters 80~150 nm and lengths of 2.5~4.0 μm. The ZnO NWs had hexagonal structure and exhibited <0002> orientation. The photoluminescence measurements showed that the ZnO NWs had a strong ultraviolet emission at around 381 nm and a very weak green emission around 520 nm.

3.1 Introduction

Large efforts are being invested to prepare structures with the nanostructured materials to achieve miniaturization in electronic and optical devices. The material, ZnO, is a wide-bandgap (3.437 eV) semiconductor with large excitation binding energy (~60 meV). It is a suitable material for applications, such as piezoelectric transducers, varistors, phosphours and surface acoustic wave (SAW) devices[185-188]. As recently demonstrated, the ZnO NWs have potential application in fabricating short-wave-length nano-lasers. A variety of methods have been reported to synthesize NWs of different materials. These methods include vapor-liquid-solid (VLS) mechanism process[186, 191-197], chemical vapor deposition[187], laser ablation[188-189], solution routes[190], and

template-based method[191]. In the VLS mechanism, gold particles which serve as catalytic sites is deposited on the substrate. Zinc vapor is generated using carbothermal or hydrogen reduction of ZnO powder[192], The reactant zinc vapor is absorbed by the liquid droplets at high temperature. As these droplets get supersaturated with reactant vapor, the NWs grow by precipitation on the silicon (Si) substrate from the droplets The NWs growth steps terminate, when the reactant vapor flow stops or the metal tip is completely evaporated during the reaction. The catalysts that have been used are Au[192-197], Pd[194], Ag[194], and Fe[198]. Here we report for the first time the ZnO-nanowire-growth on p-type Si (100) substrates using a VLS process catalyzed by copper instead of gold. This is a new method for preparing ZnO NWs through a rapid and cost effective thermal process. The two-step VLS growth method, used in this study reduced the liquid metal size and content efficiently to promote the growth of ZnO NWs. Furthermore, in this process we introduce the thermal annealing steps to make ZnO NWs approach vertically on the Si substrate. The angle from Si substrate to ZnO NWs was about 75~85 degree. We have, for the first time, successfully fabricated ZnO NWs which were oblique on Si substrate without buffer layer by VLS process using copper as catalyst.

3.2 Processes of the Synthesized ZnO NWs

In our experiment, p-type Si (100) substrate was cleaned following the procedure adopted by Yang et. al.[187] A thin layer of copper was deposited on the cleaned Si (100) substrate by rf-sputtering using a copper target. The copper thin film coated on Si substrate was about 70 Å and 150 Å thicknesses, respectively. The copper-coated Si substrate was heated in a rapid thermal

annealing (RTA) furnace at 900 ^{o}C for 1 hour. ZnO (99.99%, -325 mesh, Alfa Aesar) and carbon (99.99%, -325mesh, Alfa Aesar) powders were mixed, placed in a quartz boat, and loaded to the center of a tube furnace. The annealed copper/Si substrate was placed in the same boat with mixed powder. The ZnO NWs were grown with temperatures in the range 850 to 950^{o}C under flowing high purity Ar (99.998%) gas with the gas flow rates of 5.0-40.0 sccm. The synthesized samples had a gray-violet color. We introduced two heating schedules for the fabrication of ZnO NWs using VLS growth process: (i) directly increasing the growth temperature from room temperature to 850-950^{o}C, (ii) increasing the growth temperature to 800 ^{o}C, keeping the temperature constant for 6 minutes and then further increasing the growth temperature to 850-950^{o}C. We used XRD (MAC Science, MXP18, Japan), FE-SEM (Hitachi S-4700I, Japan), AFM (Digital instrument, U.S.A.), XPS (VG Scientific ESCALAB-250, UK), TA (Seiko SSC 5000, Japan), TEM (Philips tecani-20, U.S.A.), and PL (Hitachi F-4500, Japan) to carry out the characterizations of crystal structure, surface morphology, chemical composition and optical properties, respectively of the ZnO NWs.

3.3 The Characteristics of Cu Catalytic ZnO NWs

3.3.1 The Different Geometry of The ZnO NWs

The FE-SEM surface morphologies of ZnO NWs are shown in Fig. 3.1. The tilted 45^{o} image of Fig. 3.1(a) shows that the ZnO NWs have grown uniformly at high yield. The diameters of ZnO NWs are about 80-150 nm and 170-200 nm, catalyzed by 70 Å and 150 Å thick copper films, respectively and

their lengths are all about 2.5-4.0 μm. The thickness of copper thin film influenced the diameter of ZnO NWs. Thicker copper films coated on the Si substrate resulted in larger diameter ZnO NWs. Figures 3.1(c) and 3.1(d) show these different diameters of ZnO NWs formed with different thicknesses of copper thin films. The cross section of ZnO NWs in Fig. 3.1(c) shows that ZnO NWs have grown almost vertically on Si (100) substrate. Figure 3.1(b) shows that the top of ZnO NWs with copper tips appear smooth, and that the ZnO NWs have hexagonal structure as evidenced by XRD pattern.

Figure 3.2 shows a typical XRD pattern of the ZnO NWs. The peaks can be indexed based on the hexagonal structure of bulk ZnO (JCPDS no.80-0074). The ZnO NWs with different diameters have similar XRD patterns indicating that the NWs are highly oriented in (0002) direction and less-oriented in (100). The calculated lattice parameters of ZnO NWs are a = b = 3.261 Å and c = 5.434 Å. No other peaks of copper or impurity phases are found in any of our ZnO nanowire samples.

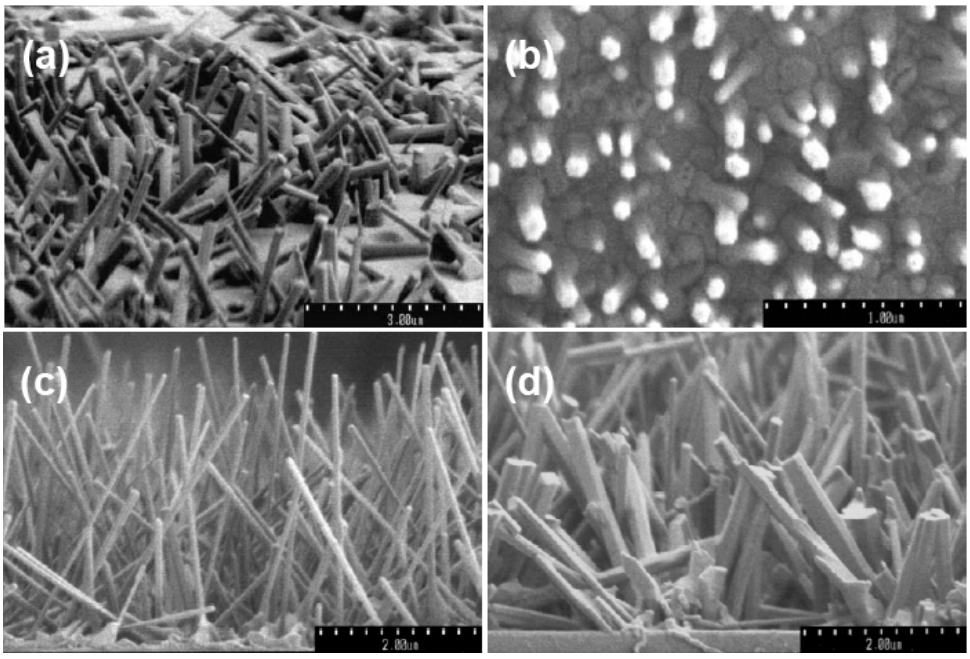

Figure 3.1 FE-SEM images of ZnO NWs: (a) tilt 45^{o} view. (b) top view. (c) Growth on 70Å thickness copper film growth. (d) Growth on 150 Å thickness copper film growth

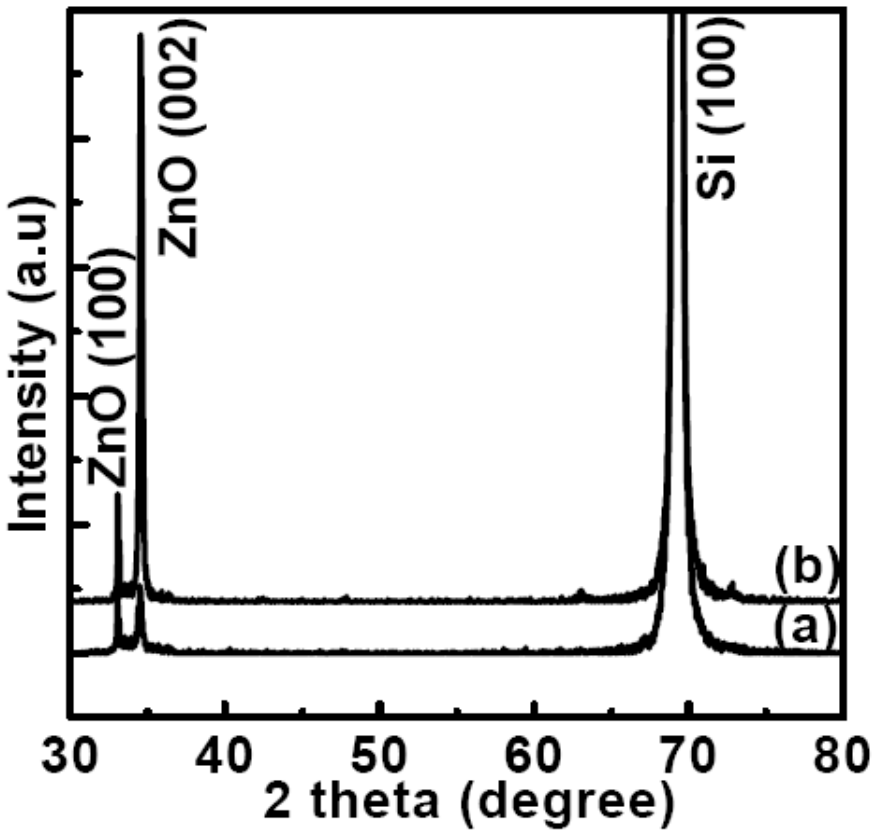

Figure 3.2 XRD patterns of ZnO NWs of diameters (a) 170-200 nm and (b) 80-150 nm.

AFM image of the copper film coated on Si substrate after the thermal annealing process is shown in Fig. 3.3(a). The thickness of copper film is about 70 Å. The nano-grain-copper metal film forms many small solid islands, which promote self-assembled-growths of ZnO NWs. The diameters of each of those copper islands are ~40-50 nm. Absorption reaction of zinc vapor occurs in copper metal islands, when copper islands are in liquid state at 900 ^{o}C. The growth of ZnO NWs ended until the supply of zinc vapor is stopped or copper tip is totally consumed. Figure 3.3(b) shows the surface morphology of about 150 Å thick copper film. The diameters of copper islands are larger than 70 Å

thick copper film as shown in figure 3.3(a) so the diameters of ZnO NWs on thicker catalyst copper film are larger than thinner one. These results are consistent with the evidence from FE-SEM photographs.

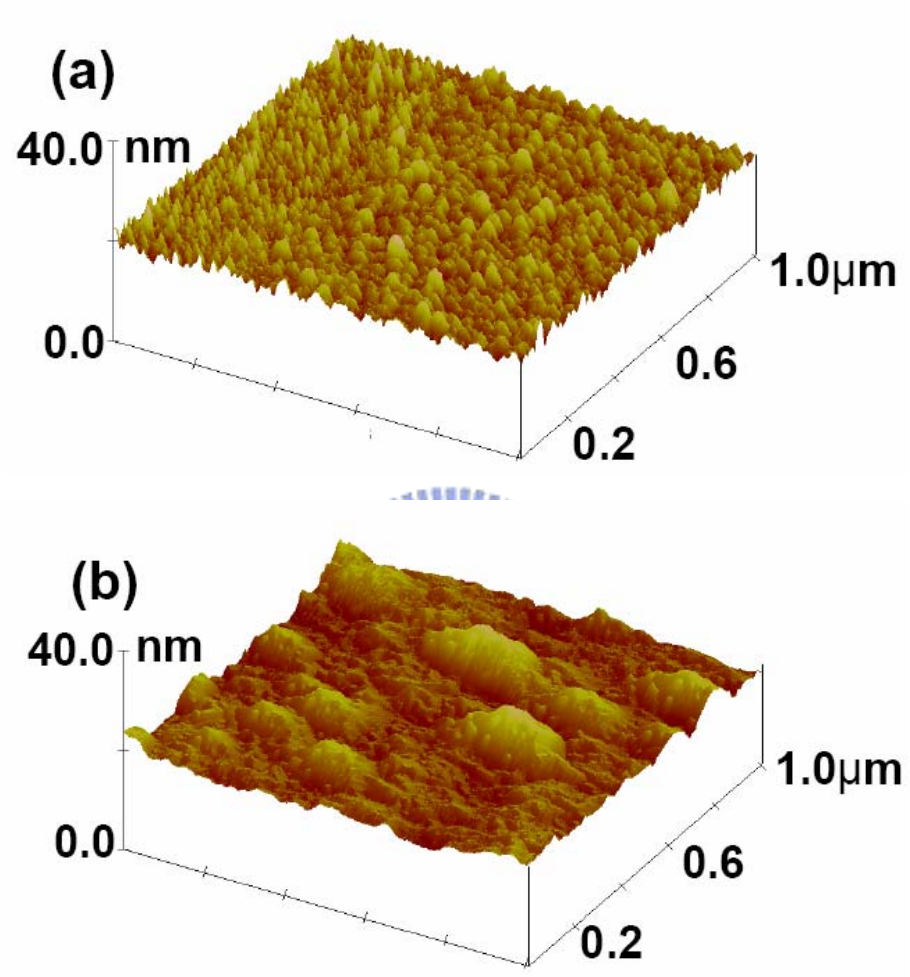

Figure 3.3 AFM images of copper films after thermal annealing process: (a) 70 Å thick copper film. (b) 150 Å copper film.

The XPS analysis of the ZnO NWs, scanned in the range of 0-1400 eV is shown in Fig. 3.4(a). No contaminant species are observed within the sensitivity range of the technique. The peaks at 1028.0 eV and 1050.3 eV are due to the binding energy of Zn_{2p3} and Zn_{2p1}, respectively. Peaks at 538.7 eV in

Fig. 3.4(c) are due to O_{1s}. Because the ZnO NWs are grown on the Si substrate, we also detect the peak corresponding to silicon. With further detailed examinations, the compositions of NWs are consistent with stoichiometric ZnO free of other impurities such as carbon.

Figure 3.5 indicates high-resolution TEM images of single-crystalline ZnO NWs. The very clear lattice fringes between two (0002) crystal planes with d-spacing of about 2.75 Å are observed, which is in good agreement with XRD patterns at Fig. 3.2. Furthermore, the $(10\bar{1}1)$ lattice plane corresponds to the image of the sidetop-wall of ZnO NWs, which agrees with Laudise's[18] observation. The corresponding selected area electron diffraction (SAED) pattern is shown in the inset of Fig. 3.5(a). The $(10\bar{1}0)$ planes of side-wall of ZnO NWs, indicate that the ZnO NWs are single crystalline and well faceted. Fig. 3.5(b) shows that for samples with thicker copper films of about 150 Å, the copper tip in front of the ZnO nanowire can be very clearly seen indication of a VLS process for the growth of ZnO NWs. Fig. 3.5(a) also verifies that ZnO NWs fabricated are single crystalline with no copper contamination, when the thickness of copper film is less than 70 Å.

3.3.2 The Properties of PL of The ZnO NWs

Figure 3.6 is the PL spectrum recorded on a fluorescence spectrophotometer using a Xe lamp with an excitation wavelength of 325 nm at room temperature of the ZnO NWs. The diameters of the NWs are in the range 80-150nm. The mean emitting bands, a strong ultraviolet (UV) emission at around 381 nm, and a very weak green emission at around 520 nm are

observed. The strong UV emission is due to the near band edge emission of the wide band-gap ZnO. It is reported that the high intensity of green emission can

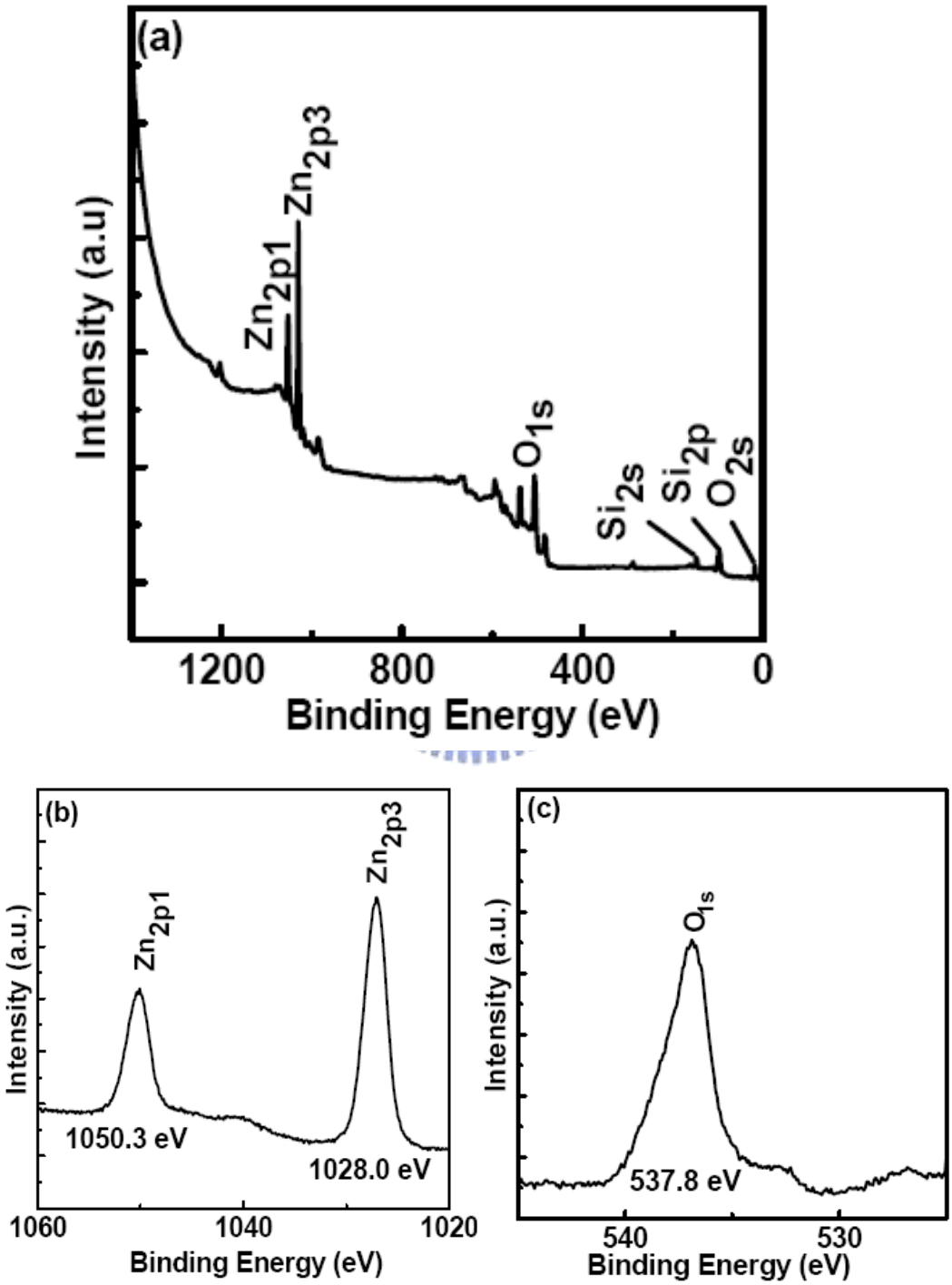

Figure 3.4 XPS spectra of ZnO NWs (a) scanned from 0 to 1400 eV. (b) binding energy of Zn_{2p1} and Zn_{2p3}. (c) binding energy of O_{1s}.

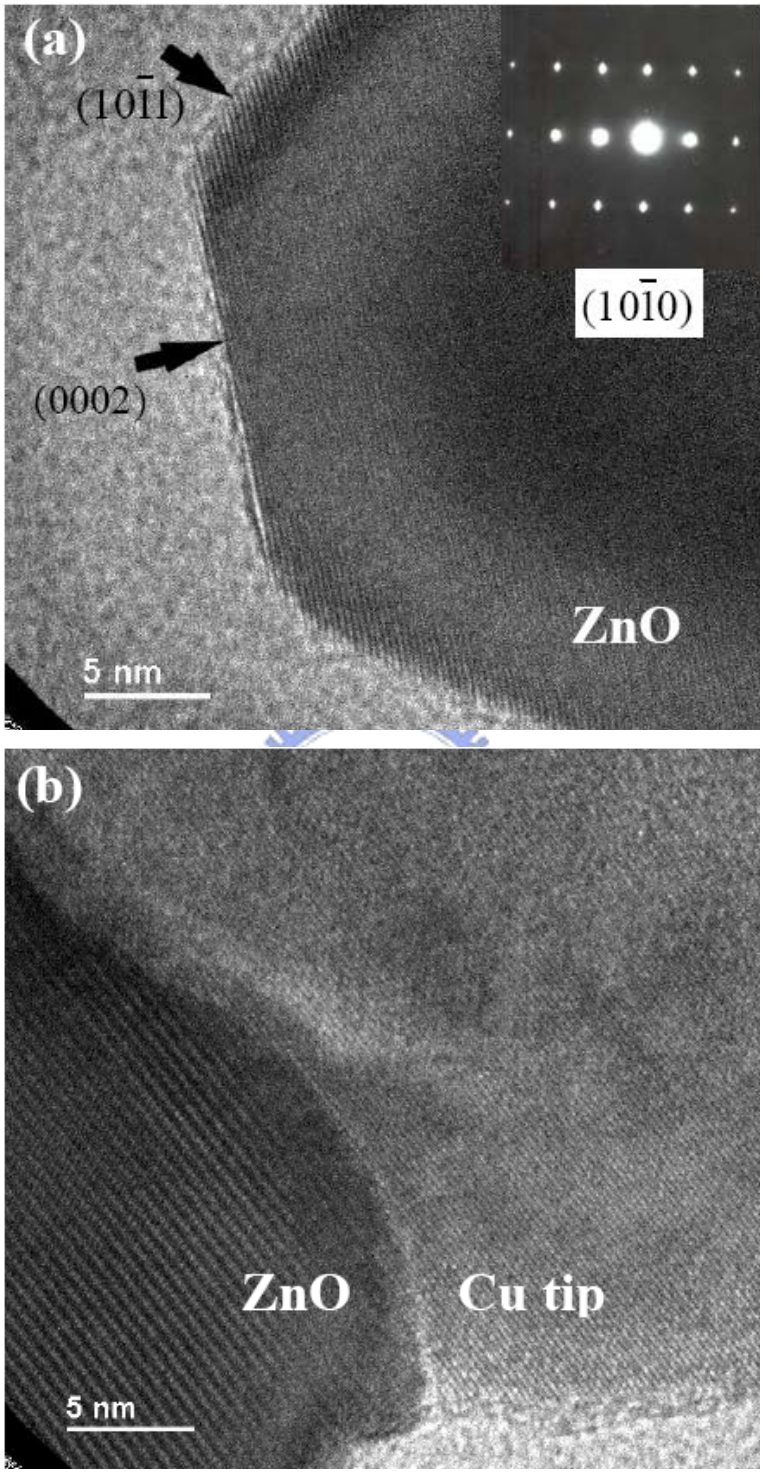

Figure 3.5 HR-TEM image of a single crystalline ZnO nanowire showing the lattice frings. The SAED patterns (inset) along $(10\bar{1}0)$ direction.

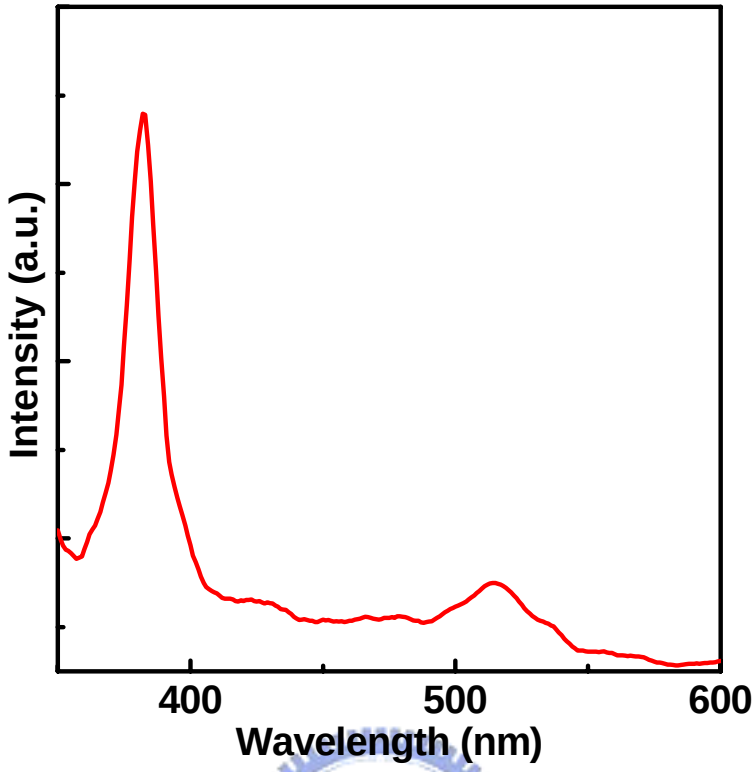

Figure 3.6 Emission spectrum of ZnO NWs using 325 nm incident Xe lamp at room temperature.

be ascribed to the high concentration of more singly ionized oxygen vacancies in ZnO[19]. It is therefore suggested that in our epitaxial ZnO NWs, there is low concentration of oxygen vacancies.

3.4 Summary

Single crystalline (0002)-oriented ZnO NWs are grown for the first time by copper-catalyzed VLS growth process on p-type Si(100) substrate. The diameters of ZnO NWs within 80-150 nm are controlled by the thickness of the copper thin film. Besides, the ZnO NWs are almost vertically grown on Si substrates by turning the thermal treatment contribution. The XRD and XPS studies determine that the composition of ZnO NWs is stoichiometric and their

structures are hexagonal. Room temperature PL spectrum of the NWs shows a strong near band-edge UV emission at 381 nm and a weak and broad deep-level green light emission at 520 nm. We believe that the ZnO NWs grown by the method discussed in this study could be used as semiconducting or optical light-emitting devices in nano-scale electronics and electro-optical applications at much lower production costs.