Chapter 5 ZnO Buffer Layer for the Synthesized of ZnO Nanowires

5.0 Preface

Vertical ZnO nanowires were successfully grown on epitaxial ZnO (002) buffer layer/Si (100) substrate. The nanowire growth process was controlled by surface morphology and orientation of the epitaxial ZnO buffer layer, which was deposited by radio-frequency (rf) sputtering. The copper catalyzed the vapor-liquid-solid growth of ZnO nanowires with diameter of ~ 30 nm and length of ~ 5.0 μm. The perfect wurtzite epitaxial structure (HCP structure) of the ZnO (0002) nanowires synthesized on ZnO (002) buffer layer/Si (100) substrate results in excellent optical characteristics such as strong UV emission at 380 nm with potential use in nano-optical and nano-electronic devices.

5.1 Introduction

Semiconductor nanowires such as Si,[211] Ge,[212] SiC,[213] BN[214] and InP[215] have been extensively investigated because of their interesting growth mechanisms, physical properties and potential applications in nano-electronic and nano-optical devices. Recently, the synthesis and characterization of zinc oxide (ZnO) nanowires have attracted great attention due to their electro-optical application.[216] ZnO is a wide-bandgap (3.437 eV) semiconductor material with large excitation binding energy (~60 meV).[217-221] Many conventional fabrication methods for the synthesis of high quality ZnO

nanowires, including vapor-liquid-solid (VLS) growth process,[222] laser-assisted catalytic growth (LCG)[223] and metal organic chemical vapor deposition (MOCVD),[224] have been reported.[225-230] To enhance the optical and electronic properties of the ZnO nanowires, we introduce a novel method for the growth of ZnO nanowires vertically along the c-axis on silicon substrate by adjusting the orientation between Si substrate and ZnO nanowires using an ultra thin ZnO buffer layer in the present study. Furthermore, this method also can decrease the VLS growth temperature. The wires have characteristic lengths of ~4.5-5.0 μm and diameters of 30 nm.

5.2 Experimental

The p-type Si (100) substrate was cleaned by a standard RCA cleaning method and rinsed in acetone for 30 min. to remove native oxide from the surface of Si substrate. Subsequently, the epitaxial ZnO buffer layer was deposited by rf-sputtering (100W, 450^{o}C at 5 mtorr for 60 min.) and in-situ annealing at 450^{o}C for 30 min. After annealing, the thickness of the epitaxial ZnO buffer layer was about 100 nm, which had a dominant orientation along (002). A thin copper layer of 70 Å in thickness was deposited on ZnO (002)/Si (100) substrate by rf-sputtering under 10 mtorr pressure at 60 W power for 15 sec. The ZnO nanowires were synthesized by VLS process[231] at temperature of 750~950 ^{o}C under flowing (rates of 20.0~100.0 sccm) high purity Ar (99.998%) gas. We characterized the crystal structure, surface morphology, chemical composition and optical properties of the ZnO nanowires using X-ray diffraction (XRD, MAC Science, MXP18, Japan), field-emission scanning electron microscopy (FE-SEM, Hitachi S-4700I, Japan), transmission electron

microscopy (TEM, Philips tecani-20, U.S.A.), Analytical Transmission Electron Microscope (AEM/EDS, JEOL, JEM-2010, Japan) X-ray photoelectron spectroscopy (XPS, VG Scientific ESCALAB-250, UK), Auger Electron Microprobe (AEM, VG Scientific, Microlab 350, UK) and photoluminescence analyzer (PL, Hitachi F-4500, Japan), respectively.

5.3 Results and Discussion

The XRD pattern in Figure 5.1(a) shows two peaks: one is oriented along (0002) and another one is weakly oriented along (100) of ZnO nanowires. Vertical growth of ZnO nanowires on Si substrate is difficult because of the lattice mismatch between Si and ZnO (~18.6%). The random distribution of ZnO nanowires grown on Si substrate can be verified from the SEM picture shown in Figure 5.2(a). However, the ZnO nanowires have single vertical growth orientation along (0002) when synthesized on ZnO (002) thin film/Si(100) substrate, as evidenced by the XRD pattern in Figure 5.1(c). The vertical growth of ZnO nanowires is obvious from the SEM image (Figure 5.2(b)), which is attributed to the fact that the epitaxial (002) ZnO buffer layer (Figure 5.1(b)) compensates for the lattice mismatch between Si substrate and ZnO nanowires. The length and diameter of ZnO nanowires vertically grown on 100 nm thick ZnO (002) buffer layer/Si(100) substrate, which are about 1.5 ~ 5.0 μm in length and about 30~70 nm in diameter, depend upon growth time, as shown in Figures 5.2(c) and (d). Comparing Figures 5.2(c) and (d), which correspond to nanowires grown within 3 min. and 6 min., respectively, it can be inferred that the longer the duration for the synthesis, the longer the length of the ZnO nanowires.

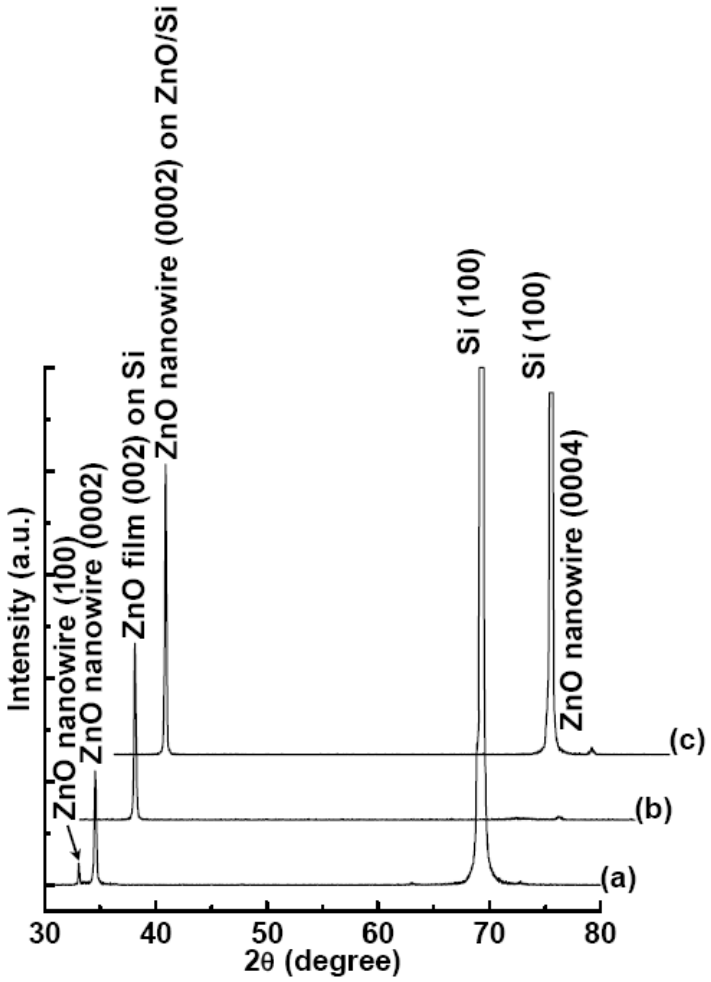

Figure 5.1 XRD patterns recorded for the (a) ZnO nanowires on Si (100) substrate, (b) ZnO thin film on Si (100) substrate, and (c) ZnO nanowires on ZnO thin film/Si (100) substrate.

The XPS method has been used to determine the chemical composition of the ZnO nanowires. The binding energies of Zn_{2p1}, Zn_{2p3} and O_{1s} are 1050.30, 1028.00 and 537.33 eV, respectively, as shown in Figure 5.3(a). The ratio of Zn:O is 1:1 after area integral calculation, which implies that the ZnO nanowires have the expected chemical composition. The AES of the ZnO nanowires (Figure 5.4) also indicate that the peak corresponding to oxygen is 510 eV, and the peaks of zinc correspond to 833, 913, 991 and 1013 eV, respectively. The weak peak of C at 273 eV can be attributed to the

contamination from the unreacted powder mixture.

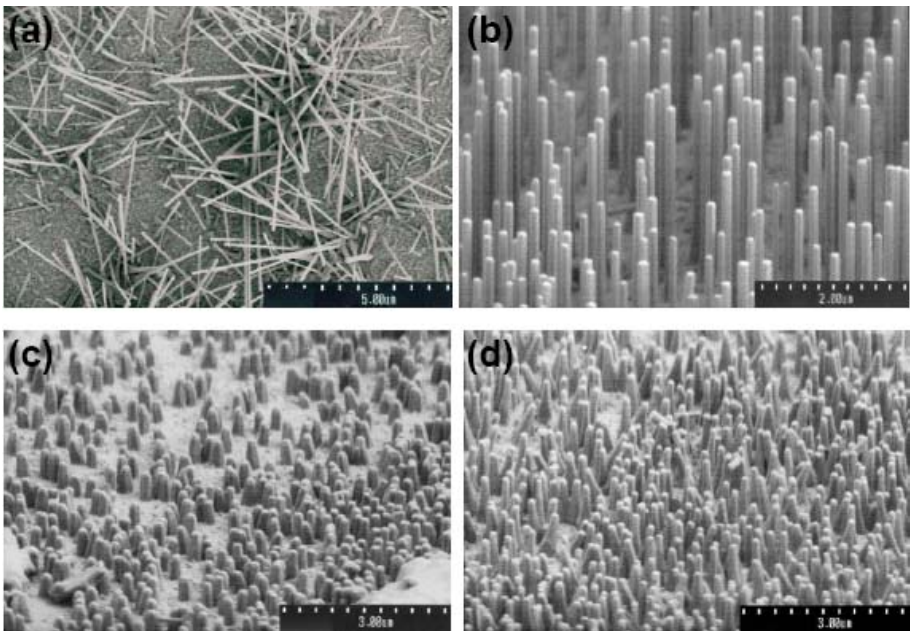

Figure 5.2 SEM micrographs of (a) ZnO nanowires grown randomly on Si substrate, (b) ZnO nanowires vertically grown on ZnO film/Si substrate, (c) vertical ZnO nanowires grown for 3 min., and (d) vertical ZnO nanowires

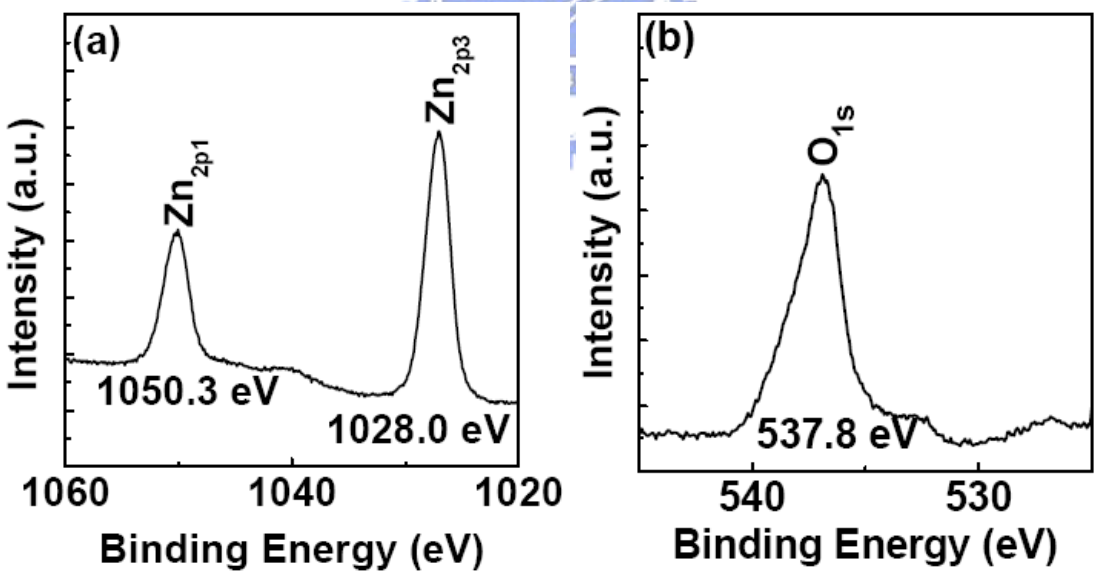

Figure 5.3 XPS spectra of ZnO nanowires of (a) peaks of Zn, and (b) a peak of O. grown for 6 min.

Figure 5.5 shows the energy dispersive spectra (EDS) of the ZnO nanowires, which reveal the presence of the Zn, O, Cu and Si in the nanowires. Copper and

Si signals should be the contribution of the copper grid and the ends of ZnO nanowires. Thus, Zn and O are the major elements comprising the ZnO nanowires. The quantitative analysis of EDS line scanning spectra indicates that the atomic composition (Zn/O) is uniform (inset of Figure 5.5) and the ratio of Zn:O is 49:51, which is in good agreement with the XPS result.

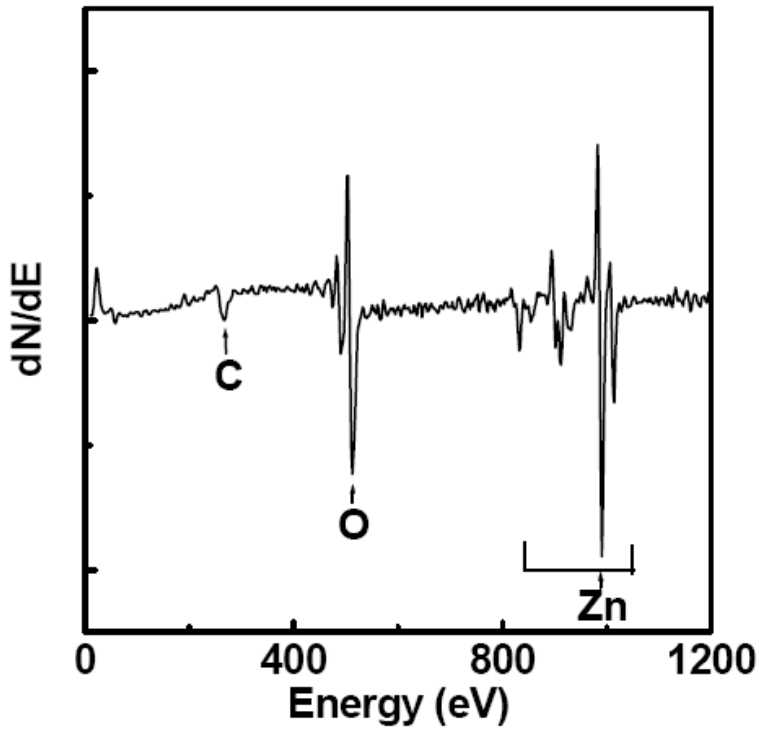

Figure 5.4 AES profiles of ZnO nanowires.

The HR-TEM image and corresponding electron diffraction patterns of the ZnO nanowires are shown in Figure 5.6, indicating the clear lattice images and well-crystallized structure of ZnO nanowires. The d-spacing of the ZnO nanowire lattice is about 5.21 Å along the [0002] direction, which is identical to the d-spacing of the wurtzite structure. The TEM image of the ZnO nanowires, as shown in Figure 5.6(b), depicts that the ratio of the diameter to the length at approximately 1:50. The broad white and black lines of ZnO nanowires indicated in Figure 5.6(b) correspond to the electron diffraction effect. The selected area electron diffraction (SAED) pattern, Figure 5.6(c),

also indicates that the ZnO nanowires have grown along [0002] direction with a wurtzite structure (HCP structure).

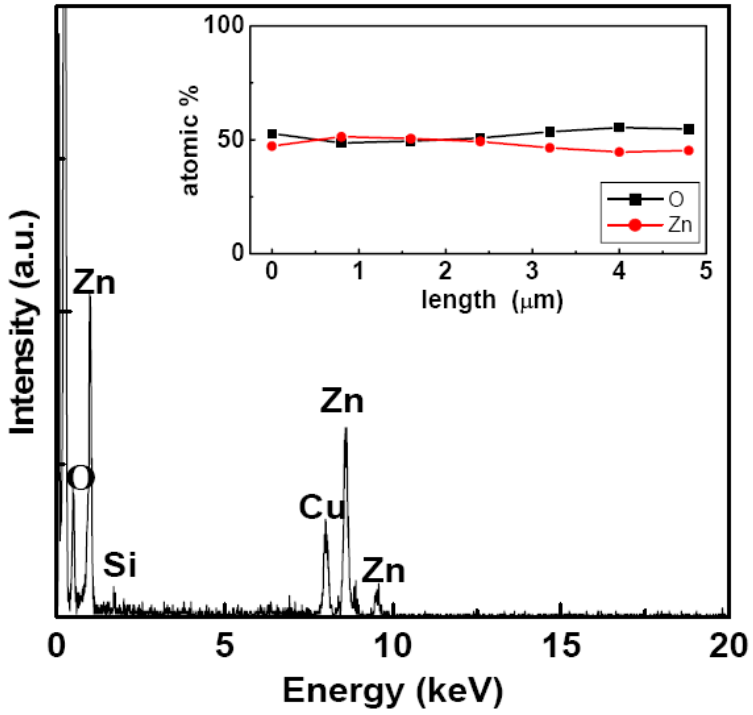

Figure 5.5 EDS spectra of the ZnO nanowires. The inset shows the line scanning Zn/O ratio of ~49/51 along the longitudinal direction.

Figure 5.7 shows the room temperature PL spectra of the ZnO nanowires and ZnO thin film on various substrates. The highest intense peak appears at 380 nm, curve (a) of Figure 5.7, which corresponds to the UV emission from the (0002) ZnO nanowires grown on ZnO film(002)/Si (100) substrate. Curves (b) and (c) of Figure 5.7 indicate that the UV emission peak of ZnO nanowires grown on Si(100) and ZnO thin film(002)/Si(100) substrates is around ~340 nm. The strong UV emission of (0002) ZnO nanowires at around 380 nm is due to the near band-edge emission of the wide band-gap ZnO. Therefore, it is suggested that, in our epitaxial ZnO nanowires, there is a low concentration of oxygen vacancies.

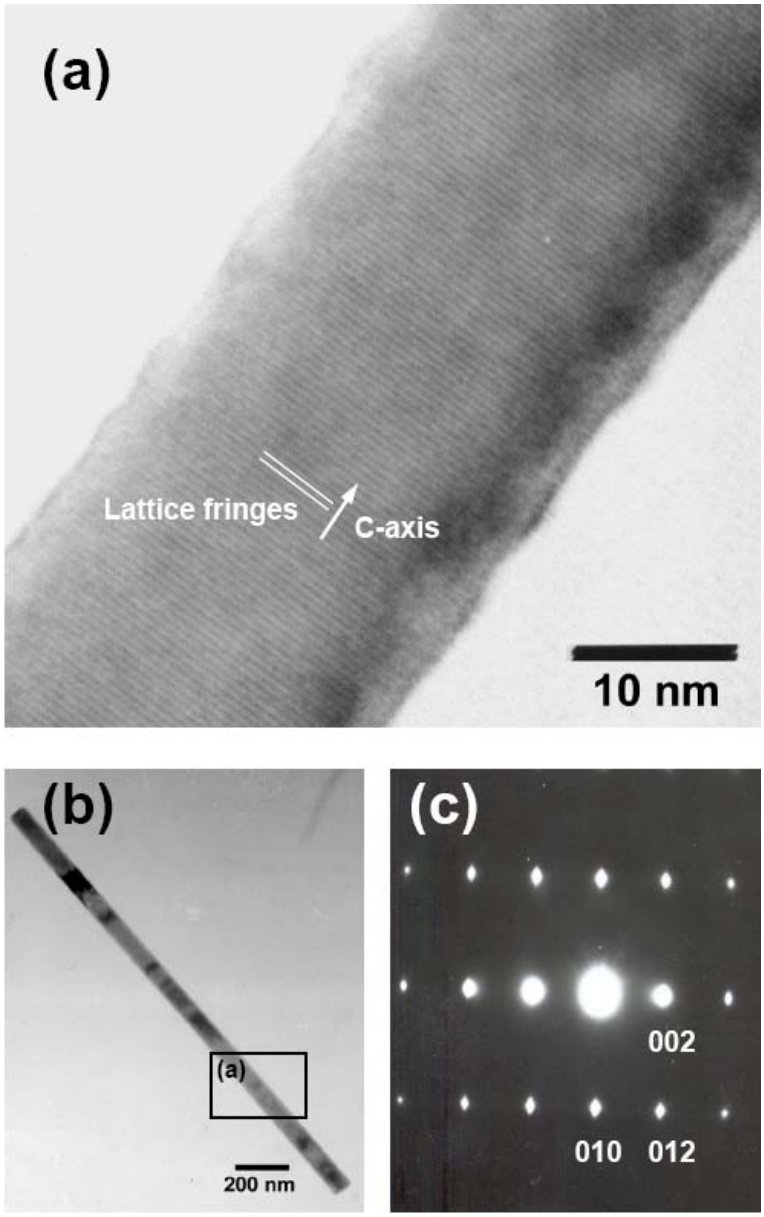

Figure 5.6 HR-TEM micrographs of ZnO nanowires of (a) the TEM image of a single crystalline ZnO nanowire showing the lattice fringes, (b) the TEM picture of ZnO nanowires showing the geometrical parameters, length and diameter, and(c) the SAED pattern along $(10\bar{1}0)$ direction.

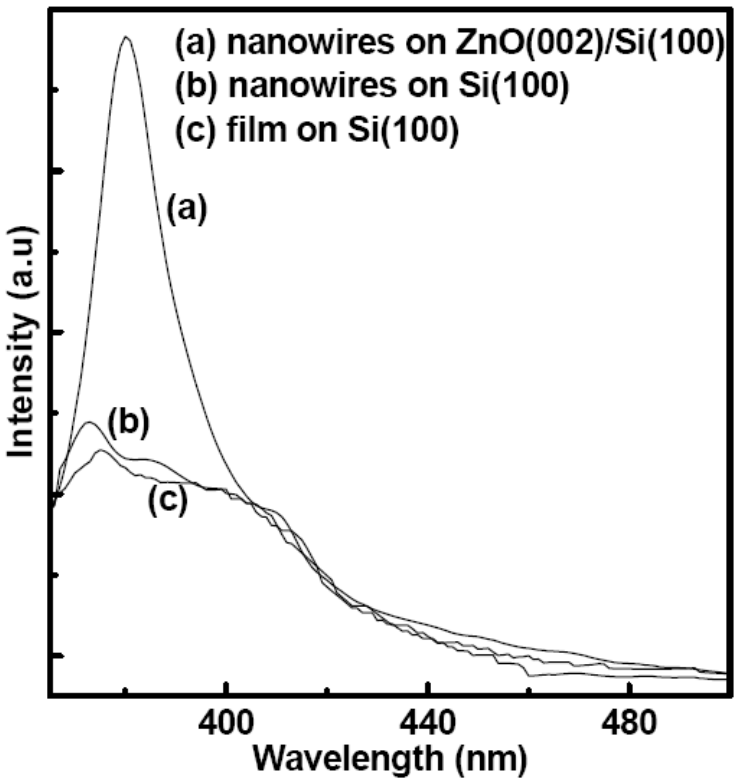

Figure 5.7 PL emission spectra of ZnO nanowires and film on various substrates using incident Xe lamp excitation at room temperature.

5.4 Summary

The new nanostructure ZnO nanowires/ZnO(002) thin film/Si(100) has been successfully fabricated in a single vertical growth direction. The compositional studies, including EDS, XPS and AES, supported the theory that the ZnO nanowires have stoichiometric composition. TEM characterization confirmed the ZnO nanowires have hexagonal crystal structure. Room temperature PL spectrum of the nanowires on ZnO(002)/Si showed a much stronger near band-edge UV emission at 380 nm compared to those on Si.