

## Chapter 5

### Conclusion

The growth mechanism, morphology, structure, and optical properties of the ZnO nanostructures grown on bare and gold-coated substrates using carbothermal reaction at atmospheric pressure were investigated under different growth conditions. The growth conditions of ZnO nanostructures were studied as a function of substrate location, furnace temperature, Ar gas flow rate, deposition time and ZnO powder to carbon powder mass ratio. The morphology and structure of the samples were characterized using the field-emission scanning electron microscopy (FESEM), energy dispersive x-ray spectroscopy (EDX), x-ray diffraction (XRD) and high resolution transmission electron microscopy (HRTEM). For the ZnO nanostructures grown on Si (100), the dependence of ZnO nanostructures on the substrate position to the ZnO/C source confirmed the reduction-evaporation model of ZnO formation using carbothermal route. There seem to an optimize window of distances for ZnO structures to be formed. In this work, the best distance was at 11 cm while the closest distance studied yielded ZnO film and the furthest distance yielded only Zn. It was discovered that, density of ZnO increases with increasing Ar flow rate, which may be due the supply increase of Zn, ZnO<sub>x</sub> and CO/CO<sub>2</sub> vapors delivered to substrate. In addition, by controlling such parameters aligned nanowires/rods with different diameters and lengths can be obtained. The average diameter of these nanowires was about 50-200 nm and the length was 4-8μm. The growth mechanism of ZnO nanostructures grown on Si (100) is attributed to self-catalytic (VLS). PL measurements of the nanostructures fabricated at various furnace temperatures are carried out at room temperature with an excitation wavelength of 325 nm. A relatively wide emission band was

observed at all grown samples, which ranges from 450 to 550 nm centered around 480 nm corresponding. This emission can be the resulted from zinc vacancies, interstitial zinc and lattice defects related to oxygen and zinc. Since the ZnO nanostructures were synthesized in a relatively low oxygen environment, it is reasonable to believe that the green emission band peak is related to oxygen vacancies. It is clear that the green emission band was suppressed by increasing the furnace temperatures. On other hand, the ultraviolet (NBE UV) at 381 nm near the band edge started to appear at 1100°C and 1200°C furnace temperatures. It was enhanced when the furnace temperature was increased. This might be indicate that the furnace temperature has a great influence on the concentration defects in the grown ZnO nanostructures. The dependence of post annealing on the luminescence properties of grown ZnO nanostructures was investigated. PL study shows that the green emission band peak, which is mainly due to defects in ZnO, can be lowered by annealed the grown sample for 1 h in air at 1000 °C. The reduction in the green emission intensity during annealing in the air can be understood by the diffusion of oxygen to fill the vacancies and, hence reducing the concentration of oxygen vacancies. Therefore, the post annealing reduces the growth defects in ZnO nanostructures. On the other hand, the growth process of ZnO nanostructures grown on gold-coated silicon substrates by carbothermal process at atmospheric pressure has been investigated. It has been found that the pre-annealing of gold-coated silicon substrates plays a key role on ZnO nanostructures growth density. Pre-annealing process reduces the agglomeration of catalyst droplets on the substrate surface and hence more distribution of the catalyst droplets resulting a high yield growth. In addition, it has been found that the gold droplets are responsible to trigger and guide the ZnO nanostructures growth EDX and FESEM confirmed the observations. Thus, all the investigated parameters have been found to play an important role on the formation of ZnO on gold-coated silicon substrates. The morphology of the ZnO nanostructures is

strongly dependant to the location of the substrate and to the furnace temperature. In contrast, deposition time, gas flow rate and the different ratios of reactant materials play an important role in controlling sizes of ZnO nanostructures. At best condition; (1200°C) furnace temperature, 11 cm substrate location, 40sccm Ar flow rate and 30 min deposition time, aligned nanowires have been obtained. The average diameter of these nanowires was about 50 nm to 500 nm and the length was 3-5 $\mu$ m. The growth of ZnO nanostructures grown with Au catalyst can be described by the VLS method.

The morphologies of the ZnO nanostructures with catalyst-free and using Au as catalyst were very different. For the ZnO nanostructures grown with Au catalyst, they exhibit a higher density growth than that without Au catalyst. XRD spectra showed that ZnO nanostructures grown without catalyst exhibited a peak intensity of the *c*-plane (002). The peak was over 1.5 times higher than that of the *c*-plane of ZnO nanowires grown on gold-coated silicon substrate. Therefore, it was suggested that the ZnO nanowires grown without catalyst have a better preferential orientation along the [002] orientation than that grown with gold catalyst. It also showed different optical characteristics in PL measurement. From the PL measurement, the ZnO nanostructures grown catalyst-free showed the UV-emission peak at 381 nm and low intensity of the deep-level emission from 450 to 620nm centered at 480 nm. However, the sample grown with Au catalyst showed a lower UV-emission intensity peak and the intensity of the deep-level emission was 2 times higher than UV-emission of the sample grown without Au. It demonstrated that there are more defects in the sample grown with Au catalyst than that grown with catalyst-free. The difference of the morphology, structural and optical properties of the ZnO nanostructures with and without catalysts might be due to the different growth mechanisms.

ZnO nanostructures doped with phosphorus have been carried by carbothermal reaction at atmospheric pressure. FESEM images showed that the doping process caused structural change in the ZnO shape from nanorods to nanoballs. XRD spectra implied a slightly shift in the diffracted angle towards higher angles for the P doped ZnO nanostructures. This angle shift gives a strong evidence for the structural defects is caused by P incorporation with ZnO nanostructures. In addition, PL spectra showed lower UV peak as well as broader and stronger intensity of green emission peak after the doping process. The UV peak was also shifted toward the lower energy after the doping process. Both XRD and PL results confirmed that P-ZnO nanostructures have been achieved through the carbothermal reaction at atmospheric pressure.