Chapter 5: ZnO Nanodot Arrays

5.1 General Introduction of ZnO nanostructure

The wurtzite crystal structure of Zinc oxide (ZnO) in Fig. 5-1(a) is a versatile material that has achievable applications in photo-catalysts, varistors, sensors, piezoelectric transducers, solar cells, transparent electrodes, electroluminescent devices, and ultraviolet laser diodes, as a result, it stimulates fairly extensive researches.[1-7] ZnO is a crystal of hexagonal structure with the lattice constant of a=3.249Å, c=5.207 Å. Compared with other wide band gap materials, ZnO has a very large exciton binding energy of 60 meV which results in efficient excitonic emission which is much larger than that of GaN and thermal energy at room temperature , and therefore enables stable existence of excitions at temperature even up to 550 ℃. In this regard, ZnO has been recognized as a promising photonic material in the blue-UV region. It is known that ZnO nanocrystals or quantum dots (QDs) have superior optical properties to the bulk crystals owing to quantum confinement effects. In the past decade, various methods have been employed to produce ZnO quantum QDs.[8–10] For instance, Guo et al.[8] in Fig. 5-1(b) experimentally established that the third-order nonlinear susceptibility of ZnO nanoparticles is almost 500 times larger than that of bulk ZnO. Vanmaekelbergh and co-workers [11] discovered the optical transitions in artificial atoms consisting of one to ten electrons occupying the conduction levels in ZnO nanocrystals. Fonoberov et al. [12] have theoretically investigated that, depending on the fabrication technique and ZnO QD surface quality, the origin of UV photoluminescence (PL) in ZnO QDs is either recombination of confined excitons or surface-bound ionized acceptor–exciton complexes. More and more unique behaviors are continuously being explored. Understanding the electronic and optical properties of ZnO QDs and nanoparticles is important from both

fundamental science and proposed photonic applications points of view. Absorption spectra were general widely used to investigate the band edge emission from ZnO QDs.[14-20] However, direct observation of the band gap variation upon particle size from PL is relatively rare.[10]

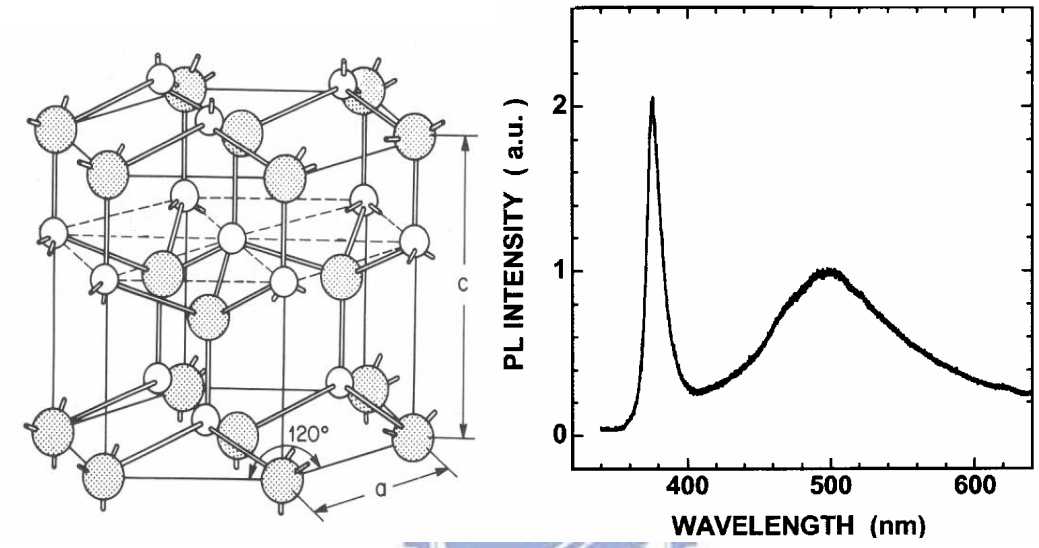

Fig. 5-1 (a) Wurtzite structure. (b) ~ 30nm ZnO nanodot arrays show an exciton PL line at 375 nm with FWHM of 113 meV at room temperature [8].

Since free-excitons in ZnO can emit UV light, it is possible to use a nanometric ZnO dot as a light emitter in the nanophotonic integrated circuits with excitonic properties further enhanced by quantum or confinement effects in nanodots [13]. In addition, applications of ZnO nanodots can also lead to novel electrical and magnetic properties. ZnO nanodots have been fabricated through sol–gel [14], hydrothermal synthesis [15], thermal oxidation [16], and metal-organic chemical vapor deposition (MOCVD) [17]. Nevertheless, as we mentioned above, lack of size uniformity and spatial ordering in ZnO nanostructures would limit their uses in various nanodevices. Recently, well-ordered ZnO nanodots have been fabricated by prepatterning the substrates periodically through focused ion beam [18], or by PLD under PAM mask

[19].

To date, most of the work on ZnO nanostructure has focused on the synthesis methods. For application of nano-photonic and electronics, it is needed to create ZnO nanodots that are selective area growth, highly aligned and orientation-ordered on substrate. The functional optical properties, including the origin of luminescence, carrier-carrier interaction, stimulated emission and lasing are also needed to understand.

5.2 Structure and Morphology of ZnO Nanodot Arrays

We focused on the condition which was anodized at 40V applied voltage in 0.3M oxalic acid electrolyte. The current as a function of anodization time was recorded in order to better understand the anodization process. Representative current versus time plot are show in Figure 5-2. Unlike TaOx specimen, there are more two current peaks before anodic completion. The current started high, decreased as an oxide layer was formed on the surface, and reached a steady level. When anodic process was turned off at point A in Figure 5-2, normal ZnO arrays like TaOx was showed. If the anodic process was gone on, a minor peak appeared right away which was defined as process II. Then a high peak came and tended towards the end of all anodization, which means process III.

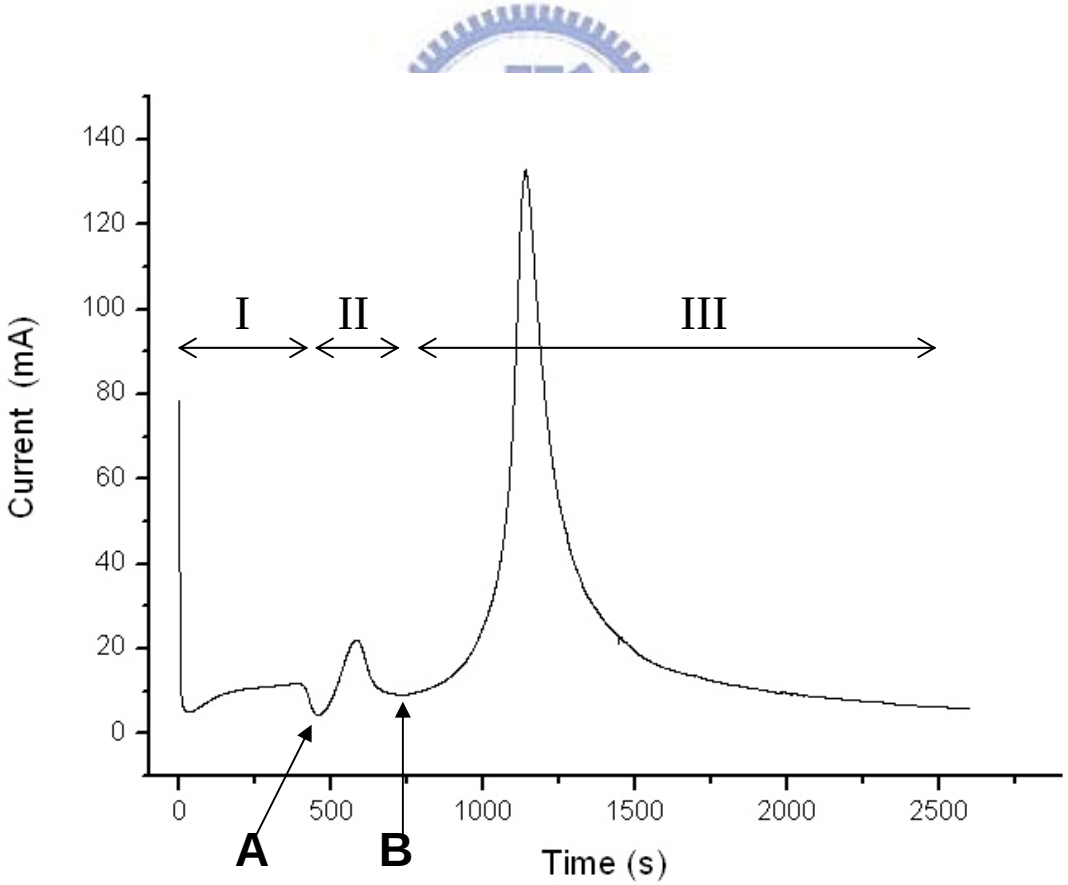

Figure 5-2 Current versus time behaviours during anodising of the Zn/Al bilayer in 0.3 M $C_2H_2O_4$ at constant 40V.