전계방출 소자 응용을 위해 solution method 를 이용하여 선택적으로 성장된 1D ZnO 나노구조

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Selective Area Growth of 1D ZnO Nanostructures via Expedient Solution Method for Field Emission Device Applications

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Introduction

Nanostructured Zinc oxide (ZnO) has attracted much attention due to its suitable physical properties and also utilized in different fields for diverging applications. In this view, a huge number of reports have been originated by describing its properties and applications [1-4]. However, the synthesis of perfectly aligned as well as well-ordered ZnO nanorods is one of the critical and considerable tasks for the development of novel ZnO based nanodevices. There are various methods have been developed to achieve the above goal including physical vapor deposition (PVD), metal organic chemical vapor deposition (MOCVD), chemical vapor deposition (CVD), and solution growth methods. Among them, the solution growth method is one of the most attractive technique because it is a simple, cost-effective technique and scalable to large areas. By using conventional photolithography, some groups successfully synthesized well-aligned ZnO nanorods in a selected area on pre-patterned ZnO/Si substrates. However, to achieve this task they also used a complex and multi-step process to grow ZnO seed layer on Si substrate and they obtained patterned substrate by using expensive metal mask. To overcome these problems, we prepared well adherent ZnO seed layer, in single-step, on Si substrates using the atomic layer deposition (ALD) technique and the ZnO/Si substrate was patterned using an inexpensive photo polymer (polyethylene terephthalate) mask. In this paper, we present the synthesis and characterization of the selectively grown well-aligned ZnO nanorods using solution method on pre-patterned ZnO/Si substrates. The device performance of the selectively grown ZnO nanorod arrays, studied first time with the help of field emission measurements, has been reported and discussed the observations by comparing the recent results reported by other groups. Finally, the electron beam lithography (eBL) was employed to pattern ZnO/Si substrate, and individual or two nanorods grown periodically for the first time by solution method by decreasing the size of pattern to sub 100 nm.

Experimental

The ZnO/Si substrates were patterned by lithography. For preparing ZnO nanostructures on patterned ZnO/Si substrates, zinc nitrate hexahydrate and water-soluble

hexamethylene tetraammine were used as reagents. In a typical reaction, 0.01M aqueous solution) of zinc nitrate hexahydrate ($Zn(NO_3)_2$ $6H_2O$) and hexamethylene tetraammine ($C_6H_{12}N_4$) were transferred into a three-neck round-bottom flask and kept on a heating mantle. The pre-patterned ZnO/Si substrates were immersed in the solution. Then the flask was heated to a temperature of 70-90ºC and kept constant during the reaction period for 6 hrs. After the successful completion of the process, the system was cooled slowly to room temperature. The re-collected samples from the aqueous solution were rinsed with distilled water and allowed them to dry for a long time at room temperature.

Result and discussion

FESEM images of ZnO nanorods grown on pre-patterned ZnO/Si substrates represent low magnified FESEM images of ZnO nanorods grown in selected areas of squares, on ZnO/Si substrates shown in figure 1. Each square and circle has size of 60 and 30 μm, respectively. The inter-distance between the two squares is about 40 μm and between the two circles is about 50 μm. These pictures also show that the synthesized ZnO nanorods are well-aligned and grown perpendicular to the surface of the substrate with an average diameter and length of ~45±5 and ~600±50 nm, respectively.

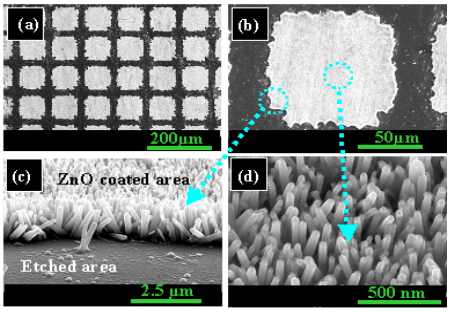

Figure 1. FESEM image of ZnO nanorods arrays grown on prepatterned ZnO/Si

The PL spectrum of ZnO nanorods and thin film is compared and shown in figure 2. It indicates that the selectively grown ZnO nanorods have a strong UV emission at 381 nm and a broad deep level visible emission at 580 nm compared to the ZnO film**.** The UV emission is the band-edge emission resulting from the recombination of excitonic centers. The green emission results from the recombination of electrons in singly occupied oxygen vacancies with photo-excited holes. The sharp excitonic UV emission peak compared to ZnO films represents ZnO nanorods are perfectly single crystalline than ZnO thin films. These optical properties of ZnO nanorods demonstrate that the as-grown ZnO nanostructures might show considerable good performance than other nanostructures.

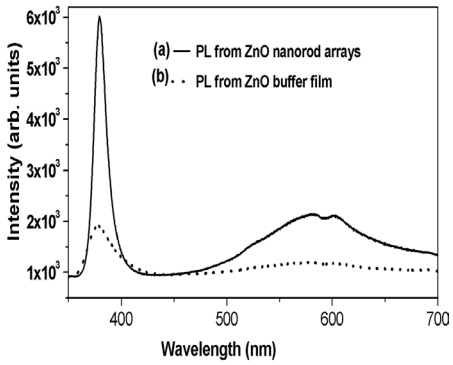

Figure 2. PL spectra of (a) selectively grown ZnO nanorods and (b) ZnO film.

The emission current density (J) versus macroscopic electric field (E) plot of selectively grown ZnO nanorods on (square shaped) ZnO/Si substrates with an anode sample separation of 150 μm is shown in figure 3. In addition, the uniform fluorescence image was recorded. The emission current density of ZnO nanorods sharply reached ~0.052 mA/cm^2 at a macroscopic field of 3.2 V/ m. The turn-on field, it is the field where the emission current density can be districted from the background noise, of the present field emission device is found to be 2.85 V/ m. The present study results indicate that the selectively grown well-aligned ZnO nanorod arrays at low temperature could be offering a promising candidature for the future device applications particularly as flat panel displays and electron emitters.

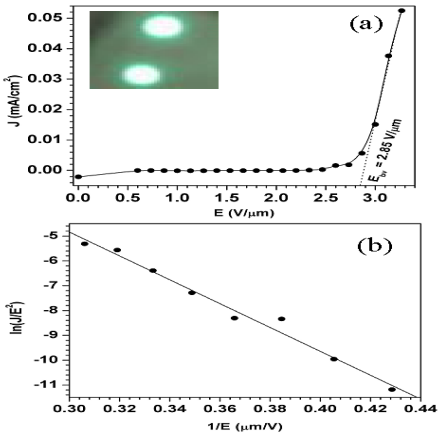

Figure 3. Field emission current density versus electric field plot for selectively grown ZnO nanorods on square shaped patterned sample, corresponding F-N (Fowler and Nordeihm) plot.

The feasibility of patterned growth using electron beam lithography on ZnO/Si substrates is determined. Figure 4 shows the periodically grown nanorod arrays on 2 μm, 500 nm and 100 nm size prepatterned ZnO/Si substrate respectively. The interdistance between each pattern spot was about 1μm. The length and diameter of as-grown nanorod is about 1-1.5μm and 60±10 nm respectively. These vertically grown nanorods arrays exhibits remarkable uniformity in terms of diameter and length. Controlling the size of pattern simultaneously controlled the density of nanorods arrays. Growth of bunch-like nanorods arrays with

excellent long-range order has been observed when pattern size was kept 2 μm, and 500 nm respectively. The successful synthesis of periodic individual, or two nanorods is achieved by decreasing pattern size to sub 100 nm. The occasionally missing spots in the 100 nm patterns are likely caused by either poor electron beam patterning or during the removal of electron beam resist material.

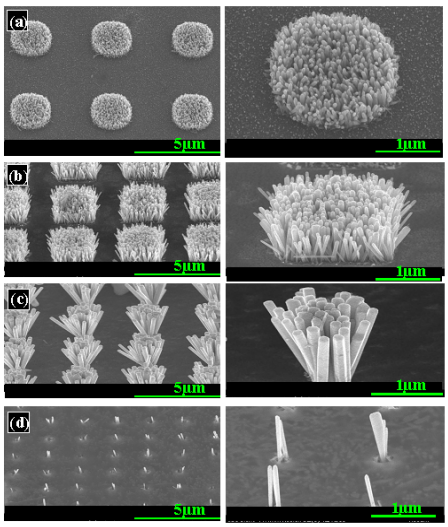

Figure 4. Low and high magnification FESEM images of ZnO nanorod arrays grown on pre-patterned ZnO/Si substrate with diameter of (a-d) 2 μm, (e,f) 500 nm, and (g,h) 100 nm respectively.

Conclusion

We have developed a straightforward and simple strategy for large-scale selective area growth of well-aligned ZnO nanorods at a temperature of 70-90ºC. Room temperature photoluminescence analysis showed a strong ultra violet emission at 381 nm and a broad deep level visible emission at 580 nm. The field emission properties of ZnO nanorods grown on square shaped pattern showed high β value, low turn-on field and large emission efficiency. The periodic growth of nanorods arrays is achieved at very low temperature.

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