Field Emission from Selectively-patterned ZnO Nanorods Synthesized by Solution Chemistry Route

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Abstract An effective wet-chemical approach is demonstrated for growing large-area, selectively-patterned, and low-temperature-synthesized ZnO nanorods (ZNRs). The growth of ZNRs was enhanced on a Co layer. The selectivity and density were readily controlled by the control of the temperature when the substrate transfers into aqueous solution. The cross-sectional transmission electron microscopy image shows that single crystalline ZNRs grown along [0001] have good adhesion at interface between ZNRs/substrate. The turn-on field was 4 V/μm at the emission current density of 1 μA/cm^2. The stable emission was obtained at 0.11 mA/cm^2 under 7.2 V/μm over 10 hr. These results suggest that selectively-patterned ZNRs have the potential for use as field emitters in large-area field emission displays.

Key words zinc oxode, nanorod, field emission, selective patterning.

1. Introduction

ZnO nanomaterials are one of most important functional oxide nanostructures, stimulating a wide range of research interest such as UV-emission nanolasers,[1] photodetectors,[2] field emitters,[3,4] vacuum and gas sensor,[5,6] solar cell,[7] and piezoelectric actuator,[8] etc. The growth of selectively-patterned ZnO nanorods (ZNRs), is potentially promising for applications in field emitters, sensor, and optoelectronics. Recently, the selectively-patterned ZNRs were grown by vapor-liquid-solid (VLS) method and metalorganic chemical-vapor deposition[9] over 800°C, which significantly limit the choice of possible substrate materials.[10] The wet chemical synthesis of ZNRs has been recently reported.[11-14] However, to my best knowledge, until now, there is no report on the growth of the selectively-patterned ZNRs by wet chemical method and their field emission properties. Here I demonstrate the growth of selectively-patterned growth of ZNRs on Co-deposited substrates and controlling growth kinetics at low temperature below ~100°C. In addition, field emission properties and luminescent pattern were investigated for application as field emitter arrays. This process and field emission properties can be readily applied to large-area field emission displays (FEDs).

2. Experimental

A 5 nm-Co catalyst was deposited on the Si substrates through a shadow mask by a magnetron sputter. The ZNRs were synthesized on the Co-coated Si substrates by using a wet chemical growth method. The zinc nitrate hexahydrate [Zn(NO$_3$)$_2$·6H$_2$O] (0.001M) and methenamine (C$_6$H$_{12}$N$_4$) (0.001M) were used as reactants. The aqueous solution was then prepared by mixing reactants with 230 mL of deionized water in a glass container, which was transferred into a conventional laboratory oven. The temperature condition for transferring substrates into a glass container including aqueous solution was split into two main conditions. One substrate set (ZNR-1) was transferred at room temperature and the other (ZNR-2) was transferred at 75°C after heating aqueous solution into a glass container. The growth temperature was maintained at 85°C for 1 hr after increasing 2°C/min from initial substrate transferring temperature for both sets of substrates. For field emission measurements, hemispherical copper with a 1.0 mm diameter was used as the anode electrode, which was designed so as to be movable in the x–y–z directions. The spacing between the cathode and the anode electrodes was maintained at about 250 μm. Field emission measurements were carried out in a vacuum with a background pressure of 5×10^7 Torr at room temperature.

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3. Results and Discussion

Fig. 1 shows scanning electron microscopy (SEM) images of ZNRs grown in aqueous solutions. The substrate transferring temperature significantly affects the growth selectivity of ZNRs, as shown in Fig. 1(a) and 1(d). In ZNR-1 samples, the ZNRs were grown on Si substrates both with and without Co layer, as shown in Fig. 1(a). I previously confirmed that ZNRs can be grown on diverse bare substrates without the Co layer such as Si, glass, and plastic substrate, when these substrates transferred at the room temperature into aqueous solutions. However, the growth of ZNRs on the Co layer [Fig 1(b)] was shows a higher density of ZNRs than that grown without Co layer [Fig. 1(c)]. The Co thin-film is very effective for growing high-dense ZNRs [Fig. 1(b)] without the need of pre-formed ZnO nanoparticles on the substrate.[14] Fig. 1(b) and 1(c) were magnified SEM images from indicated regions by the black and white arrow in Fig. 1(a), respectively. By controlling the substrate transferring temperature into aqueous solution at 75°C (ZNR-2 sample), we can clearly

see the selective growth of ZNRs, as show in Fig 1(d) and 1(e), in which the ZNRs were only grown on the patterned Co layer. Fig. 1(e) and 1(f) magnified SEM images in the regions of the black dotted circle and the white dotted circle in Fig. 1(d) and Fig 1(e), respectively. The detailed structure of ZNRs grown on the selectively-deposited Co layer is shown in Fig. 1(f). Meanwhile, no nanorods were grown on the bare Si surface without the Co layer as shown in region of the white dotted square of Fig 1(e). The diameters of ZNRs range from 50 to 150 nm. The density of ZNRs in ZNR-2 samples was significantly reduced even on the Co layer compared to that of Fig. 1(b), as shown in Fig. 1(f). The substrate experienced from room temperature to growth temperature showed that ZNRs were grown on both regions with and without Co layer and have a relatively higher density on Co layer. In my more detailed experiments, it was found that the ZNRs can be grown even on regions without Co layer, when it was transferred below about ~70°C. However, the growth of ZNRs was significantly suppressed on the substrate without Co layer for ZNR-2 samples. Therefore, it is concluded that the substrate transferred
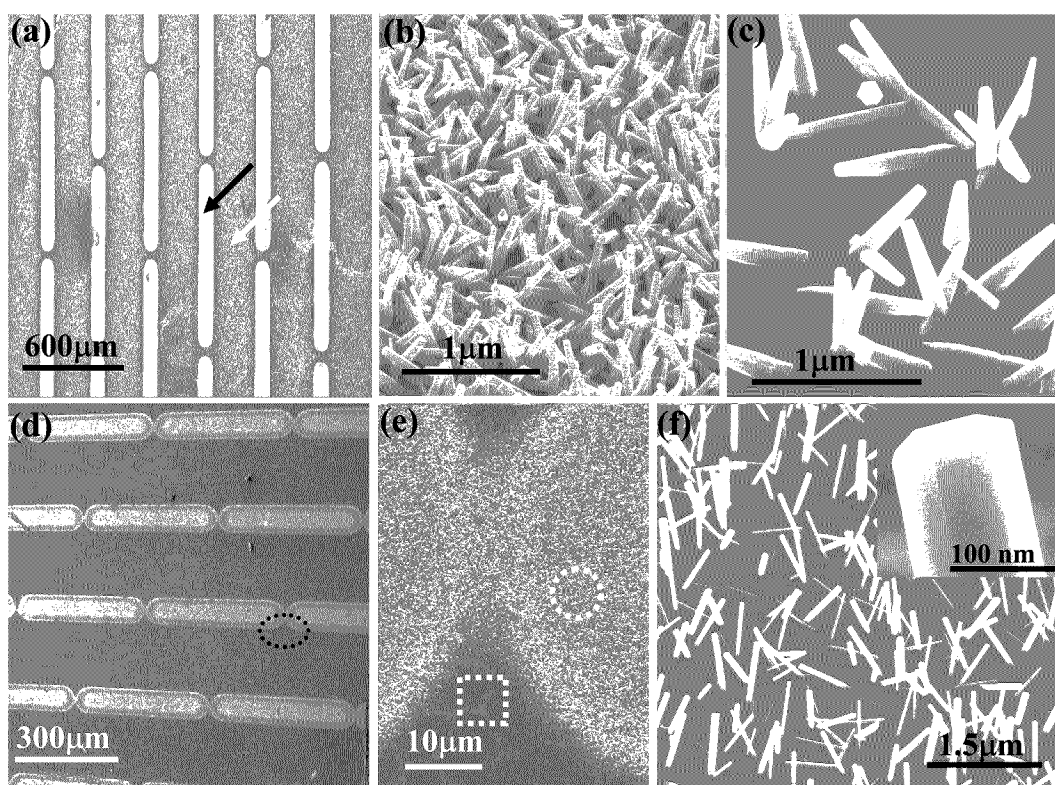

Fig. 1. SEM micrographs of ZNRs grown (a) on Co-patterned substrate transferred into the aqueous solution at room temperature (b) on region indicated by the black arrow. (c) on the region indicated by the white arrow. (d) on Co-patterned substrate transferred into the aqueous solution at 75°C. (e) SEM images in black dotted region in Fig. 1(d). (f) the magnified SEM image in white dotted region in Fig. 1(e). The inset shows the hexagon-shaped at the end of ZNR.

above 75°C could not induce the stable nucleation on sub-strate, which is a main reason for achieving the high selectivity in the patterned growth and also the reduction of nucleation site density on Co layer as well. The reduction in the density of ZNRs on Co layer in ZNR-2 samples [Fig. 1(f)] is a useful result, because the low density control is a very important issue in field emitter applications, in order to avoid mutual field-shield effect in high density nanorods.[3] Therefore, this experimental result provides important information as the effective conditions for controlling the nucleation and selectively-growing of ZNRs by adjusting substrate transferring temperature.

Prior to field emission measurement, I have investigated the cross-sectional transmission electron microscopy (TEM) of ZNRs grown by wet chemical method in order to characterize the crystalline state and the interface between ZNRs/Co-deposited substrate, which is important for stable electron emission with reliable electrical contact. The ZNRs showed a good adhesion with the substrate, as shown in Fig. 2(a). The chemical composition of ZnO was confirmed by energy dispersive spectroscopy (EDS) (, in which the carbon peak originated by TEM grid) [Fig. 1(b)]. The high resolution TEM (HRTEM) shows that the nanorods are single crystalline, showing clear lattice fringe [Fig. 1(c)]. The selected-area electron diffraction pattern (SAED) indicates that the nanorods grow along [0001] and its side surfaces are defined by $\{2\bar{1}\bar{1}0\}$.

Fig. 3(a) shows the characteristics of emission current

Fig. 3. (a) The measured current density as a function of the macroscopic electric field for ZNRs. The inset shows the FN plots (obtained from the data shown in the inset of Fig. 3(a)). (b) Stability of electron emission as a function of time at a fixed anode voltage.
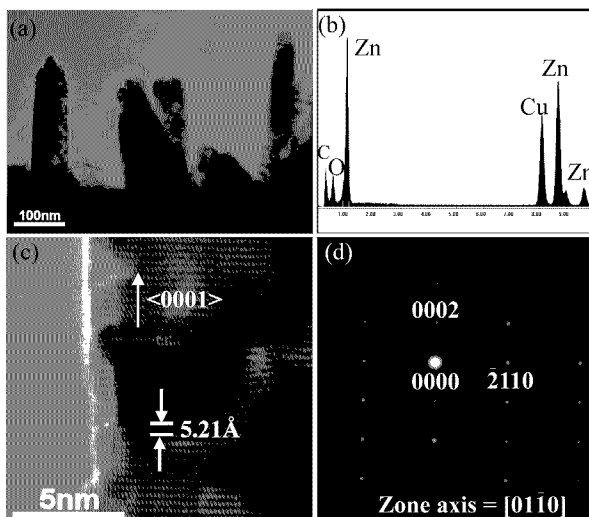

Fig. 2. TEM image of ZNRs. (a) cross-sectional TEM image. (b) EDS results, indicating the nanorods consist of Zn and O. (c) HRTEM image of a single nanorod. (d) SAED pattern of nanorod.
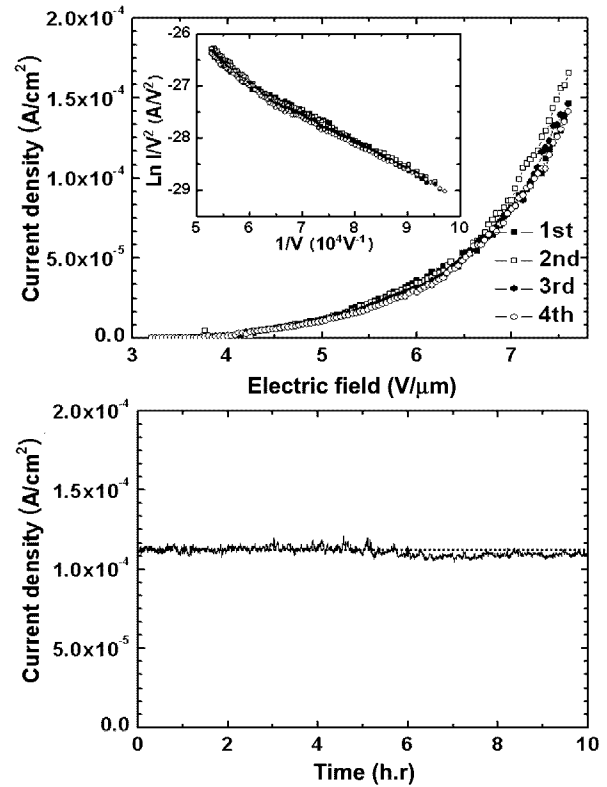
density versus applied electric field for the several times of bias voltage sweeps. The turn-on field, defined as the electric field which is required to produce a current density of 1 μA/cm^2, is estimated to be about 4 V/μm. The emission current density of the ZNRs reached 0.1 mA/cm^2 under an applied field of 7.1 V/μm. The field emission from the ZNRs exhibits nonlinearity in F-N behavior, showing a mainly two linear slope in the F-N plot (Fig 3b). The conventional field emission of electrons can be described by F-N theory.[15] The current density (J), which is related to the local field (E) at the emitter surface can be expressed as $J = aE^2\exp(-b\phi^{3/2}/E)$, where a and b are constants used to fit the data. The E [V/m] is the local field at the field emitter surface and is generally related to the applied voltage, such as $E = \gamma V/d$, where γ (geometric enhancement factor) is dimensionless and can be determined from the slope (-6.44 $\times 10^9\phi^{3/2}d/r$) of an F-N plot. The average γ values of low field (LF) and high field (HF) region in the two regimes of F-N plots were found to be about 1600 and 3000, respectively, assuming the work function of the ZNRs to

be 5.2 eV.[16] The reduction of γ value (with a larger linear slope) at the HF region in the field emission of ZNRs is reverse nonlinearity in F-N behavior compared to carbon nanotubes.[17-19] However, similar phenomenon have been observed during the field emission from other semiconducting nanowires,[20,21] and could be explained by the variety in the field enhancement factor induced by the diverse morphology and density of nanowires.[20] The ZNRs grown by wet chemical method showed a large diameter distribution [Fig. 1(f)]. Therefore, the electrons could be mostly emitted from the ZNRs with small diameter with high γ at LF and, while at the HF, the ZNRs with relatively larger diameter nanorods with low γ also emit electrons and contribute the total emission current. Another possibility can be suggested that it is attributed to the different donation of the sharp vertex (with high γ) and facets or sides (with low γ) in hexagon-shaped end of ZNRs [Fig. 1(e)] to total emission currents as increasing the applied field. The emission stability of the sample was tested at a constant anode voltage of 1800 V, as shown in Fig 3(b). The average current density of 0.11 mA/cm^2 was determined and its fluctuation was about 7%. No obvious degradation in current density was observed over approximately a 10 hr period. The ZNRs synthesized by wet chemical method showed efficient field emission properties. Moreover, it is easily synthesized at low temperature (~100°C) and this simple method has no fundamental limitations in being scaled-up to a FEDs with a large area.

4. Conclusion

In conclusion, I have presented an effective approach for growing large-area, selectively-patterned, and low-temperature-synthesized ZNRs by the means of solution chemistry route. The growth of ZNRs could be favored on the Co surface versus the bare substrate. High growth selectivity and density control were obtained by controlling the growth kinetics from adjusting the initial substrate transferring temperature into aqueous solutions. The turn-on field was 4 V/μm at the emission current density of 1 μA/cm^2 and the stable emission was obtained at 0.11 mA/cm^2 (under the applied field of 7.2 V/μm) over 10 hr. This approach opens the possibility of creating selective patterns

of ZNRs for applications as field emitter arrays for FEDs.

References

1. M. H. Huang, S. Mao H. Feick, H. Yan, W. Wu, H. Kind, E. Weber, R. Russo and P. Yang, Science, **292**, 1897 (2001).
2. H. Kind, H. Yan, B. Messer, M. Law and P. Yang, Adv. Mater., **14**, 158 (2002).
3. S. H. Jo, J. Y Lao, Z. F. Ren, R. A. Farrer, T. Baldacchini and J. T. Fourkas, Appl. Phys Lett., **394**, 4821 (2003).
4. C. J. Lee, T. J. Lee, S. C. Lyu, Y. Zhang, H. Ruh and H. J. Lee, Appl. Phys. Lett., **81**, 3648 (2002).
5. D. -H. Kim and H. R. Lee, J. Korean Phys. Soc., **45**, L803 (2004).
6. Q. Wan, Q. H. Li, Y. J. Chen, T. H. Wang, X. L. He, J. P. Li and C. L. Lin, Appl. Phys. Lett., **84**, 3654 (2004).
7. K. Keis, E. Magnusson, H. Lindstorm, S. E. Lindquist and A. Hagfeldt, Sol. Energy Mater., **73**, 51 (2002).
8. M. H. Zhao, Z. L.Wang and S. Mao, Nano Lett., **4**, 587 (2004).
9. W. I. Park, J. Y. Yoo and G.-C. Yi, J. Korean Phys. Soc., **46**, L1067 (2005).
10. W. X. Wang, C. J. Summers and Z. L. Wang, Nano Lett., **4**, 423 (2004).
11. B. Liu and C. J. Zeng, J. Am. Chem. Soc., **125**, 4430 (2003).
12. L. Guo. S. H. Yang., C. L. Yang, J. N. Wang and W. K. Ge, Chem. Mater., **12**, 2268 (2000).
13. S. Yamabi and H. J. Imai, Mater. Chem., **12**, 3773 (2002).
14. L. Vayssieres, Adv. Mat., **15**, 464 (2003).
15. R. H. Fowler and L. Nordheim, Proc. R. Soc. London Ser., A **119**, 173 (1928)
16. X. Bai, E. G. Wang, P. Gao and Z. L. Wang, Nano Lett., **3**, 1147 (2003).
17. P. G. Collinse and A. Zettl, Phys. Rev., B **79**, 2811 (1997).
18. J. M. Bonard, F. Maier, T. Stocjli, A. Chatelain, W.A. de Heer, J. M. Salvetat and L. Forro, Ultramicroscopy, **73**, 7 (1998).
19. D. -H. Kim, H. -R. Lee, M. -W. Lee, J. -H. Lee, Y. -H. Song, J. -G. Jee and S. -Y. Lee, Chem. Phys. Lett., **355**, 53 (2002).
20. J. Chen, S. Z. Deng, J. C. She, N. S. Xu, W. Zhang, X. Wen and S. Yang, J. Appl. Phys., **93**, 1774 (2003).
21. C. T. Hsieh, J. M. Chen, H. H. Lin and H. C. Shih, Appl. Phys. Lett., **83**, 3383 (2003).