附件一

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（計畫名稱）

低成本高性能高可靠度先進氧化鋅奈米線場發射元件之研究

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摘要

本實驗利用低溫水溶液成長氧化鋅奈米柱於氧化鋅/矽基板上，將成長完成之氧化鋅奈米柱經由電漿處理不同時間，可得到具備奈米尖錐的氧化鋅奈米柱陣列，氧化鋅奈米柱陣列經X-光繞射分析與掃瞄式電子顯微鏡觀察結果具備有（002）的優選成長方向，藉由電漿處理10, 30與60秒奈米尖錐場發射特性啟動電場分別為2.51, 2.22 與 3.03 V/μm，此種現象我們認為氧化鋅奈米柱於電漿處理過後，具備奈米尖錐的形貌，使得電子更容易發射，場發射特性而能顯著的提升。螢光光譜顯示出原生氧化鋅奈米柱陣列具備有一狹窄的UV峰與寬化的綠光峰值，我們藉由電漿處理的過程中通入不同的氬/氧比，將氧離子植入氧化鋅奈米柱填補本身氧空缺，使得寬化的綠光峰值消失，而得單一高強度的UV光譜。

關鍵字：氧化鋅奈米柱、電漿處理、場發射

Abstract

The ZnO nanorods on ZnO/Si substrates were synthesized by using the low temperature growth aqueous solution method. The various etching time of plasma treatments were carried on the as-grown ZnO nanorods to provide the nanorods with nanotips. The morphology and crystal structure of the ZnO nanorods were exhibit the preferred (002) orientation by scanning electron microscopy and X-ray diffraction. The field emission properties of the ZnO nanorods after plasma treatment for 10, 30 and 60 sec are: the turn-on electric fields (at the current density of 10 $\mu A/cm^2$) are about 2.51, 2.22 and 3.03 V/μm, respectively. The improved field emission properties are believed to benefit from sharp nanotips. The PL spectrum show the as-grown ZnO nanorods display narrow UV emission and broader green emission peak. It is shown that the green emission peak disappeared and only strong UV emission after plasma treatment by adjust

Ar/O_2 ratio.

Keyword: ZnO nanorods、Plasma treatment、Field emission

1. Introduction

Recently, nanoscale materials have been attracting particular interest because of its remarkable electronic transport, optical and other properties. One-dimensional (1D) nanomaterials are extensively being considerable as the candidate materials for field emission displays, optical/electrical devices and gas sensor[1-2]. One of the most important applications of the 1D nanostructures is in the field emission panel displays due to their high aspect ratio. However, many studied have been accomplish on field emission from nanorods/nanowires such as carbon nanotubes (CNTs)[3], SnO_2[4], etc. Recently, the ZnO nanorods is also considered to be one of the most prospective cold cathode materials due to their large excition binding energy, stronger radiation-oxidation resistance, and high thermal stability[5-7]. The recent field emission analysis result of the 1D ZnO nanomaterials indicates that electrons are more easily emitted from the nanostructures with sharp tips than the nanostructures with a uniform diameter. Therefore, it is necessary to control the morphologies of the nanorods for improving their field emission properties. So far, the 1D ZnO nanorods synthesized by using different technology including vapor-liquid-solid (VLS) growth[8], thermal evaporation[9], metal-origanic chemical vapor deposition (MOCVD)[10] and aqueous solution method[11]. Among the numerous growth processes, the aqueous solution synthesis has the advantages of low temperature, pressure, simple equipment and ambient being achievable for large area fabrication of different ZnO nanosturctures.

In this letter, we synthesized the ZnO nanorods by using aqueous solution and combined the plasma etching method to form nanotip from the as-grown nanorods. Effects of the etching time and Ar/O2 ratio on the morphology, electrical and optical characteristics of the ZnO nanorods were studied.

2. *Experimental method*

ZnO nanorods were grown on p-type silicon (Si) substrate by using seed-assisted aqueous solution method. The p-type Si (100) substrate was cleaned by a standard RCA cleaning method and then rinsed in acetone for 30 min to remove pollutants from the surface of Si substrate. Subsequently, the epitaxial ZnO buffer layer was deposited by rf-sputtering and follow by in-situ annealing at 750 ℃ for 30 min. After annealing, the thickness of the epitaxial ZnO buffer layer was about 100 nm, which had a highly preferred orientation along (002) (XRD not shown here). Then, the Si-substrate with ZnO seeding layer was carried out at 80℃ for 3h in a sealed kettle placed in a quartz beaker to synthesized ZnO nanorods. The solution containing of the same mole concentration of zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$, 99.9% purity) and methenamine ($C_6H_{12}N_4$, 99.9% purity). After the aqueous synthesis, the piece covered with ZnO nanorods were bound on a sputtering target by carbon tape and exposed to Ar/O_2 plasma with a rf-power of 30 W under a pressure at $5x10^{-2}$ Torr. The plasma treatment under different etching times and adjust Ar/O_2 ratio to form the nanorods with nanotips. The morphology and size distribution of the as-grown and the ZnO nanorods with nanotips were investigated by field-emission scanning electron microscope (FE-SEM, Hitchi S-4700I, Japan). The field-emission current-voltage (I-V)

curves of both as-grown ZnO nanorods and the nanorods with nanotips were measured at room temperature in the tubo pump vacuum chamber at a pressure of 2×10^{-6} Torr. A copper tip was employed to act as an anode with the tip area of 0.00709 cm^2 and P-type Si covered with ZnO emitters as an cathode with an area of $1cm^2$. We used micrometer to adjust the distance between a copper anode and tip of ZnO nanorods was 150 μm. The micrometer with the an accuracy of ± 0.1 μm. The field emission properties are affected by the anode area and anode-cathode distance based on Filips model[12]. The photoluminescence (PL) spectrum was obtained using a He-Cd laser (325nm) as excitation source at room temperature.

3. Results and discussion

3-1 Crystal structure and morphology of ZnO nanorods

Fig. (1) illustrates the XRD patterns of as-grown and plasma etched nanorods. Diffraction peaks in XRD patterns for all of the ZnO nanostructures can be indexed as wuritize hexagonal structure (ICDD-2003 No.80-0075, a=0.3253nm and c=0.5209nm) and the nanostructures of ZnO exhibit the preferred (002) orientation due to the minimal surface energy in the ZnO hexagonal wuritize structure. No characteristic diffraction peaks from impurities were detected. The XRD pattern of as-grown nanorods and plasma treated with 10 and 30 sec show the high intensity of (002) diffraction peak, which it implies the ZnO nanorods exhibit high crystal quality. In constant with plasma treated for 60 sec, the intensity of (002) peak apparent decrease, which is argon and oxygen ion created some damages to effect crystallinity.

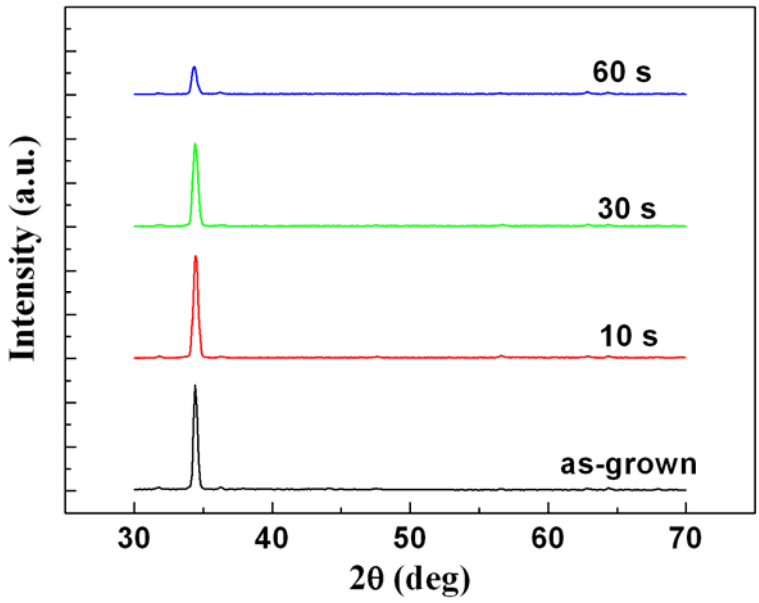

Fig. (1) X-ray diffraction patterns of the nanorod field emitters

The morphology of the as-grown and plasma etched nanorods were observed using FE-SEM and their SEM images shows in Fig. 2. As show in Fig. 2a, the as-grown ZnO nanorods arrays are vertically well-aligned with diameter in the range from 200-300 nm, several microns in length and relatively high cover density. The SEM images of the nanorods after plasma treatment for 10 sec, 30 sec and 60 sec are shown in Fig. 2b-d, respectively. While the plasma treatment for 10 sec, we can find the top of nanorods become tower-shaped morphology and increase the treatment time to 30 sec, the nanotips of the nanorods were formed. Compared with SEM images of as-grown and plasma for 10 sec and 30 sec, the tops of nanorods become nanotips morphology due to argon and oxygen ion bombardment of the edge of the nanorods and relatively high cover density will leading to the edge etching rate faster than center etching rate. As a Fig. 2d shows the plasma treatment for 60 sec, the experiment result indicated a destruction or shortening of the nanorods, which will decrease the field emission properties.

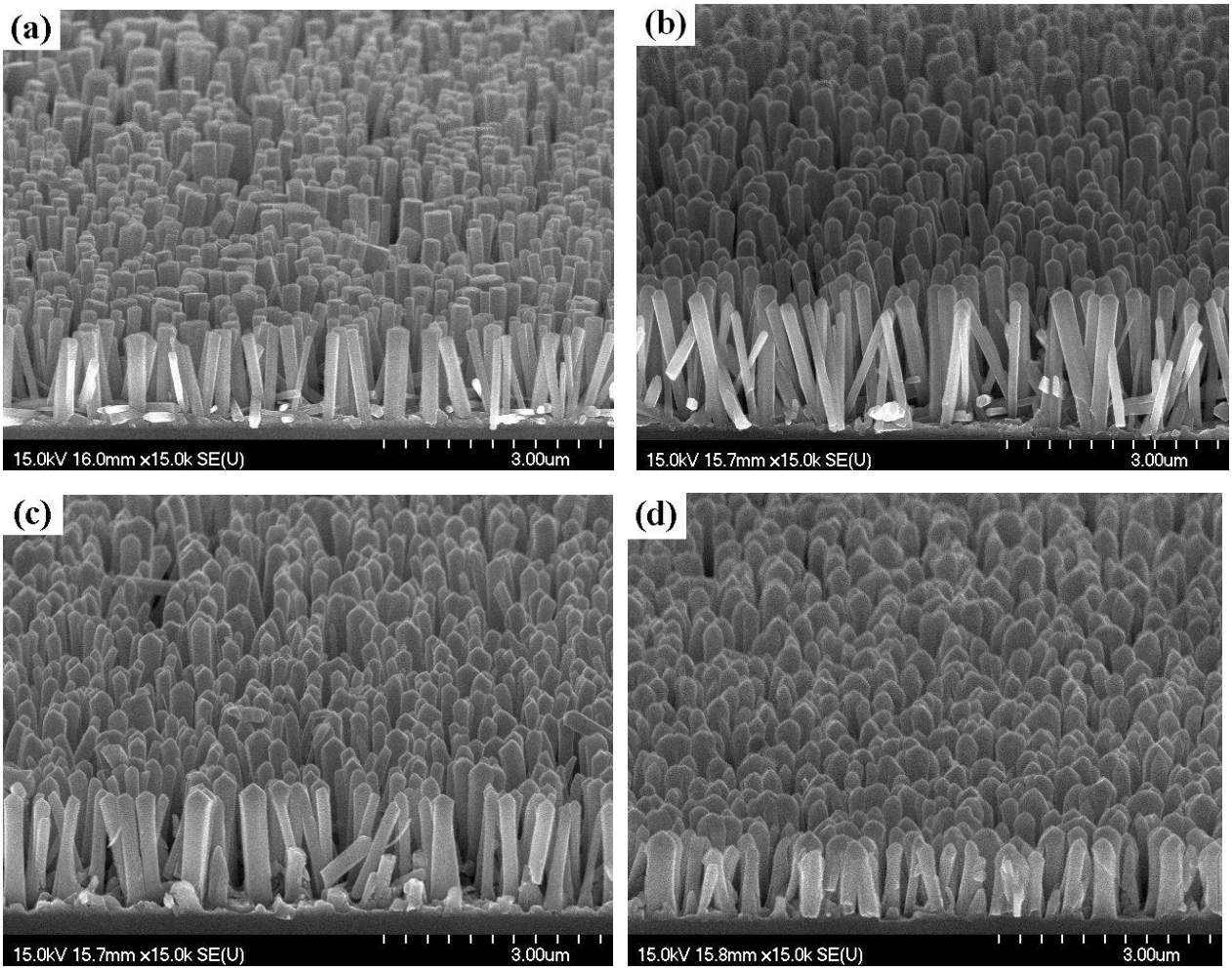

FIG. 2 (a) SEM image of as-grown ZnO nanorods. (b), (c) and (d) SEM images of plasma etching ZnO nanorods for 10, 20, 30 and 60 sec, respectively.

3-2 Field emission properties

Fig. 3a shows the result of current versus electric field (J-E curve) with the inset being the semi-logarithmic J-E plots. The figure indicating that the turn-on electric field of as-grown and plasma treatment with 10 sec, 30 sec and 60 sec are 3.25, 2.51, 2.22 and 3.03 V/μm, respectively, at current density of 10 μA/cm^2. The emission current–voltage characteristics were analyzed by using the Fowler-Nordheim (F-N) equation[13-15] for the field emission measurement.

$$J=A\left(\frac{\beta^2 E^2}{\psi}\right)\exp\left(-\frac{B\psi^{1.5}}{\beta E}\right)$$

Where J is the current density, E is the applied field, A=1.56×10^{-10} (AeV/V^2), B=6.83×10^9

($V/eV^{1.5}m$), β is a field enhancement factor and ψ is the work function of the emitter which about 5.37 eV for ZnO. When the work function of the ZnO nanorods is known, the field enhancement factor can be calculated from the slope of the F-N plots shown in Fig. 3b. The β values are about 1645, 2546, 2696 and 1610 for as-grown, plasma treatment with 10 sec, 30 sec and 60 sec, respectively. Based on Filips model, the β approximately equal $1+s\frac{d}{r}$, where s is dependent on screen effect, d is the distance between anode and cathode and r is the radius of the emitters. In our experiment, the emitters will consider with the same nanorods density of 15.55 / μm^2 from SEM images and the distance between tips and anode plate is kept const, which were compared the effect field emission properties with the different plasma etching time. Clearly, the nanorods after plasma treatment have a small tip curvature than the as-grown nanorods, when the sharp tips of nanorods become the exact emission sites and high β values will be obtained. In our case, the best condition with plasma treatment is 30 sec and it shows the lower turn-on field, uniform morphology distribution and high crystallinity. Our experiment results also indicate that an increasing treatment time may result in decrease aspect ratio and destruction of nanorods, which would degenerate the field emission properties.

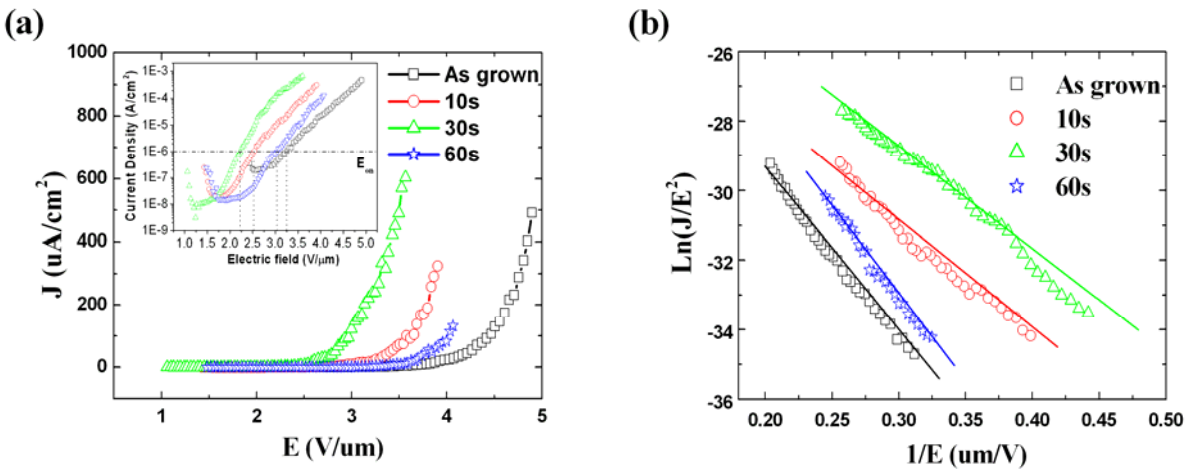

FIG. 3 (a) J-E curves of the nanorod field emitters. (b) Fowler-Nordheim plots of the nanorod

field emitters.

3-3 Optical properties

Photoluminescence (PL) spectrum is a useful technology for characterizing the optical properties of nanostructures. Fig. 4 shows the PL spectrum for as-grown ZnO nanorods and during the plasma treated for 30 sec with different Ar/O^2 ratio. For as-grown nanorods, the stronger UV emission occurs at about 377nm, which cones from recombination of excition and broader emission band is located in green emission of the visible spectrum with the emission peak about 550 nm, which occurs from oxygen vacancy of the nanorods. Previously our group research[16], we studied the as-grown ZnO nanowires annealing at various temperature in an oxygen atmosphere and the experiment result indicate the green emission will reduction by annealing in the oxygen atmosphere. In contrast with our case, we were control different Ar/O^2 ratio during plasma treatment, which employed oxygen ion implantation into ZnO nanorods and make reparation the oxygen vacancy of ZnO nanorods. From Fig. 4, when increasing the oxygen amount, as the green emission centered at about 550nm is decreased, which enhancement the UV emission optical and crystal properties shall facilitate the applications of nanotips of nanoscale high emitting device.

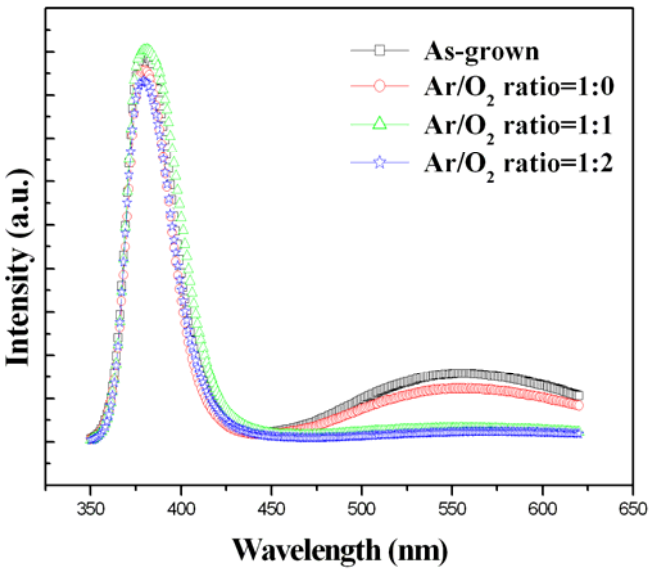

FIG. 4 Photoluminescence spectra of the as-grownZnO nanorods and under plasma treated with different Ar/O_2 ratio.

4. Conclusions

In summary, we successfully synthesized sharp tip structured ZnO nanorods employing plasma treatment. The orientation of ZnO nanorods has been proved by both the highest intensity of (002) peak in XRD patterns and SEM images. After plasma treatment, the field emission properties of vertically aligned nanorod emitters were significantly enhanced. The PL spectrum reveal that the green emission peak disappeared and only strong UV emission after plasma treatment by adjust Ar/O_2 ratio. These well-aligned nanotips of the nanorod are expected to be a multifunctional consistent for field emission and UV-laser device by one-step plasma treatment.

Acknowledgment

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97-2221-E-009-150-MY3.

References

1. C.Y. Lee, S.Y. Li, P. Lin and T.Y. Tseng, IEEE Trans. On Nanotechnology, 5 (2006) 216.
2. S.N. Bai and T.Y. Tseng, Thin solid films, 515 (2006) 872.
3. C.M. Tan, J.J. Jia, W.B. Yu, Appli. Phys. Lett., 86 (2005) 263104.
4. S.H. Luo, Q. Wan, W.L. Liu, M. Zhang, Z.F. Di, S.Y. Wang, Z.T. Song, C.L. Lin and J.Y. Dai, Nanotechnology, 15(2004) 1424.
5. L.F. Banerjee, S.H. Jo and Z.F. Ren, Adv. Mater., 16 (2004) 2028.
6. H. Zhang, D.R. Yang, X.T. Ma and D.L. Que, J. Phys. Chem. B, 109 (2005) 17055.
7. Q. Wan, K. Yu, T.H. Wang and C.L. Lin, Appl. Phys. Lett., 83 (2003) 2253.
8. S. Y. Li, C.Y. Lee and T.Y. Tseng, J. Cryst. Growth, 247 (2003) 357.
9. Z.W. Pan, Z. R. Dai and Z.L. Wang, Science, 291 (2001) 1947.
10. D.J. Lee, J.Y. Park, S.Y. Yun, S.Y. Hong, H.J. Moon, T.B. Lee and S.S. Kin, J. Cryst. Growth, 276 (2005) 458.
11. C.Y. Lee, S.Y. Li, P. Lin and T.Y. Tseng, J. Nanosci. & Nanotechnology, 5 (2005) 1008.
12. F. M. Charbonnier, W. A. Mackie, R.L. Hartman and T. B. Xie, J. Vac. Sci. Technol. B, 19 (2001) 1064.
13. L.M. Li, Z.F. Du, C.C. Li, J. Zhang and T.H. Wang, Nanotechnology, 18 (2007) 355606.
14. J. Xiao, Y. Wu, X. Bai, W. Zhang and L. Yu, J. Phys. D: Appl. Phys., 41 (2008) 135409.
15. J.P. Liu, C.X. Xu, G.P. Zhu, X. Li, Y.P. Cui, Y. Yang and X.W. Sun, J. Phys. D: Appl. Phys., 40

(2007) 1906.

16. S.N. Bai, H.H. Tsai and T.Y. Tseng, Thin solid films, 516 (2007) 155.