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Effects of O_2 and Ar reactive ion etching on the field emission properties of aligned CuO nanowire films

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Abstract

The effects of oxygen (O_2) reactive ion etching (RIE) on the field emission (FE) properties of aligned CuO nanowire films are investigated systematically. It is found that the FE performance of the films is largely enhanced after initial exposure to reactive oxygen ions but degrades after extended treatment. As comparison, Ar RIE is also used to treat CuO nanowires, which, however, results in the deterioration of FE properties. The enhanced FE after O_2 RIE is attributed to the shaper morphology, cleaner surface and better conductivity. On the other hand, increased work function and non-crystallized surface structure cause the deterioration of FE of CuO nanowires after Ar RIE treatments.

Introduction

Recently, electron field emitters based on one-dimensional (1D) nanomaterials attract much attention because of their high aspect ratio, which can effectively enhance the local field and lower the turn-on voltage. Excellent field emission (FE) properties have been obtained from various 1D nanostructures, such as carbon nanotubes [1], ZnO nanowires [2], SiC nanowires [3], Mo and its oxide nanowires [4], Co nanowires [5], WO_x nanorods [6] and so on. At the same time, to further improve and to reach a better control of the FE properties, numerous post-treatment methods are developed. These include chemical doping [7], laser irradiation [8], ion beam irradiation [9], surface coating [10] and plasma treatment [11]. On the other hand, as a commonly used dry etching method, reactive ion etching (RIE) has been used to generate 1D nanostructures [12] or to fabricate field emitters with sharp apex [13]. However, there are few reports on the effects of RIE on the morphology and FE properties of nanowires [14]. Since aligned CuO nanowires can be readily synthesized by heating Cu in ambient conditions [15] and have shown uniform FE images [16], O_2 or Ar RIE is used to treat CuO nanowires in this work. It is observed that proper O_2 RIE effectively sharpens the nanowires and enhances the FE properties. In contrast, Ar RIE deteriorates the field emission. Possible mechanisms are discussed.

Experiment

The growth of vertically aligned CuO nanowire films have been described elsewhere [16]. After growth, as-grown samples were placed inside the chamber of a SAMCO RIE-10N Reactive Ion Etching Unit to be treated. Different samples were exposed to the reactive ions produced from O_2 (35 sccm) or Ar (16 sccm) gas. The detailed RIE process and parameters were same with our previous report [17]. As-grown and treated samples were characterized by scanning electron microscopy (SEM, JEOL JSM-6400F), transmission electron microscopy (TEM, JEOL JEM-2010F) and Fourier transform infrared spectroscopy (FTIR, Shimadzu, IRPrestige-21). The

measurements of FE properties were carried out using a two-parallel-plate configuration in a vacuum chamber with a pressure of about 5×10^{-7} Torr. To minimize the effects other than RIE treatment, the field emission of same sample was measured before and after treatments.

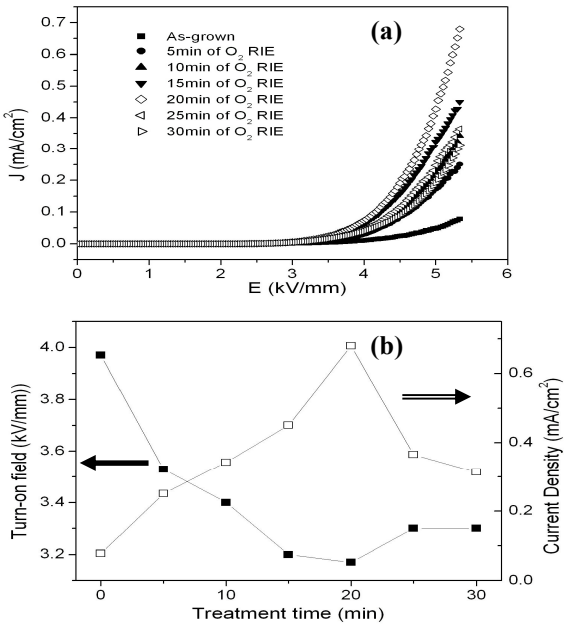

Fig. 1 (a) *J-E* curves of CuO nanowires before and after O_2 RIE. (b) The dependence of turn-on field and maximal current density on O_2 RIE durations.

Results and Discussion

Fig. 1(a) shows the field emission current density (*J*) versus applied field (*E*) curves of a typical sample before and after O_2 RIE. The treatment durations increased from 5 minutes to 30 minutes with a step of 5 minutes. We can see that both the turn-on field (corresponding to J = 10 $\mu A/cm^2$) and maximal current density (under the field of about 5.3 kV/mm) depend on the RIE durations, as shown in Fig. 1 (b). 20 minutes of O_2 RIE reduces the turn-on field from 4 kV/mm to 3.2 kV/mm and the maximal current density increases from 0.1 to 0.7 mA/cm^2 at the same time. After extended O_2 RIE, the field emission performance becomes worse. This optimal O_2 RIE duration depends on samples, but generally falls in 10 ~ 20 minutes. On the other hand, only 1 minute of Ar RIE deteriorates the field emission of CuO nanowires by reducing the maximal current density from 0.14 to 0.06 mA/cm^2. The turn-on field also increases from 2.5 to 2.7 kV/mm for a typical sample. Further measurements show that by changing the Ar RIE duration to 30 seconds or several minutes or reducing the Ar flow rate to 8 sccm, the FE of nanowires was still deteriorated. So, to improve the FE properties of CuO nanowires, short duration of O_2 RIE is preferred over Ar RIE.

To study the mechanisms behind such O_2 RIE enhanced field emission, SEM was used to compare the morphological changes of the same individual nanowires before and after RIE. To realize this, some channels were created by focused laser pruning [18], as shown in Fig. 2(a). Some individual nanowires nearby the channel were chosen and their diameters were carefully compared before and after O_2 RIE, as shown in Fig. 2(b) and (c) with marked nanowires. It is clearly observed that after 10 minutes of O_2 RIE, some nanowires like nanowire 1, 2 and 3, are bent, possibly induced by ions bombardments. Nanowire 4 becomes thinner even in the low-magnification images.

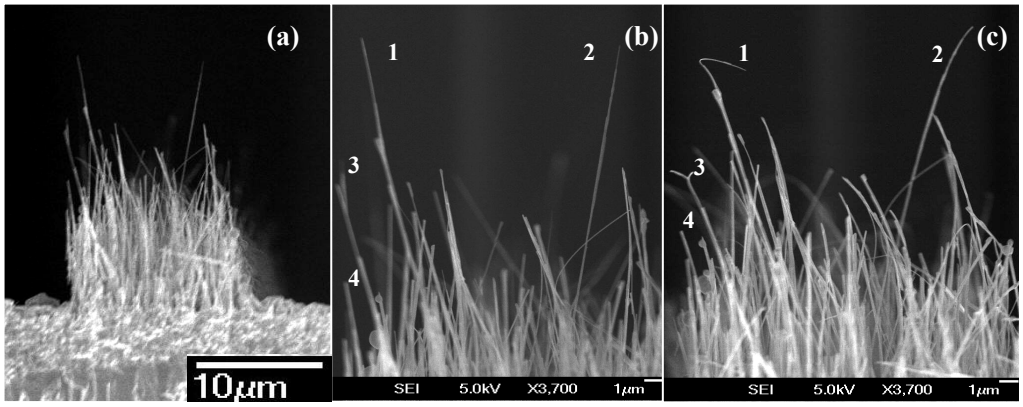

Fig. 2 (a) Aligned CuO nanowires between two channels made by laser pruning. Same part of nanowires before (b) and after (c) 10 minutes of O_2 RIE.

10 minutes of O_2 RIE decreased the diameters of nanowires by an average value of 9 nm. Such bent or/and thinner nanowires will increase the effective emission area of nanowires since the side walls of emitters also contribute to the FE current [16, 19]. On the other hand, after 1 minute of Ar RIE, there were no apparent changes in the morphologies of CuO nanowires under SEM. Furthermore, longer time of treatment broke the nanowires.

Fig. 3 shows the TEM and high resolution TEM (HRTEM) images of an as-grown CuO nanowire and those after RIE treatments. Generally the as-grown CuO nanowires have flat heads covered by an amorphous layer of several nanometers, which could be formed during cooling, as shown in the inset of Fig. 3(a). However, after 10 minutes of O_2 RIE, the tips of most nanowires are sharpened, as shown in Fig. 3(b). At the same time, the surface of nanowires becomes cleaner and the original amorphous layer disappears. After 10 minutes of Ar RIE, most nanowires have been broken and many fragments were found under TEM. Fig. 3(c) is a nanowire with an etching terminal face, which also shows sharp tip and cleaner surface compared with the as-grown one. But from the inset of Fig. 3(c) we can see that the new surface is still covered by an amorphous layer, which could be induced by the bombardment of heavier Ar ions. Previous studies have shown that the amorphous layer on the surface of nanowires can increase the transport electron scattering and hamper the FE properties [20]. Here, after O_2 RIE, cleaner surface helps to enhance the field emission by reducing electron scattering; but Ar RIE creates new amorphous phase on the surface. Ultraviolet photoelectron measurements on Ar ions treated nanowires shown that the work function value of CuO nanowires increased by about 1 eV, which is believed to be the main reason for deteriorating the field emission.

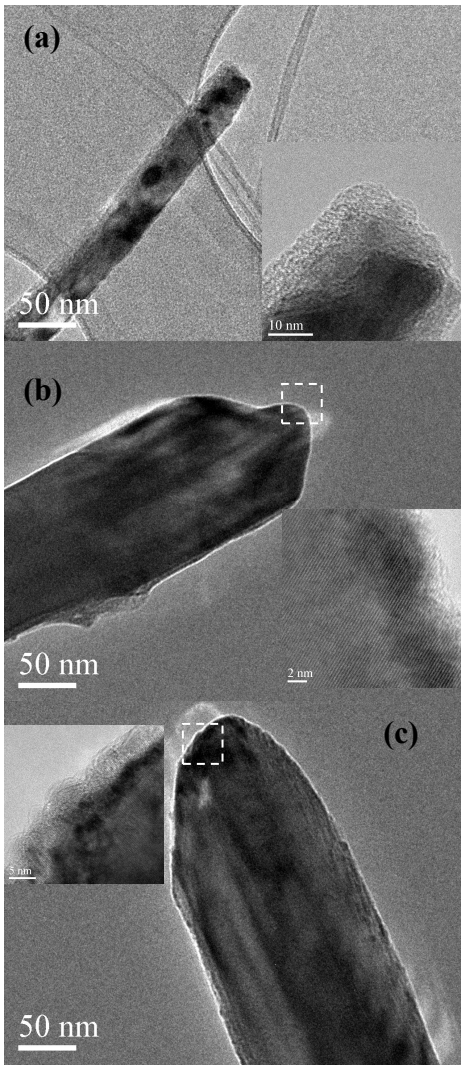

Fig. 3 Typical TEM and HRTEM images of (a) an as-grown CuO nanowire, (b) a nanowire after 10 minutes of O_2 RIE and (c) a nanowire after 10 minutes of Ar RIE.

Another possible explanation for enhanced FE by O_2 RIE is supplied by FTIR measurements, as demonstrated in Fig. 4. We can see that in shown region, after RIE a band nearby 617 cm^{-1} disappears and three bands allocated at 660, 738 and 1010 cm^{-1} are strengthened. Other ranges of FTIR spectra remain unchanged. Among the bands, 660 cm^{-1} band results from CuO [21]; 617 cm^{-1} band can be attributed to $CuO(O_2)$ [22], which may be induced by the O_2 adsorption on CuO nanowires. And the bands at 738 and 1010 cm^{-1} are related to some

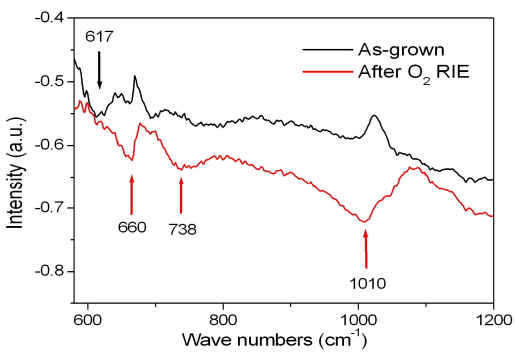

Fig. 4 FTIR results of CuO nanowire films before and after 10 minutes of O_2 RIE treatments. Reflected intensity was collected.

superoxide and complex [22]. Previous study shown that oxygen plasma could generate CuO_x (x = 2, 3, 4) and enhance the conductivity of CuO_x coated indium-tin-oxide (ITO) electrode. Here, after O_2 RIE the weak oxygen adsorption could be replaced by some superoxides on the surface of CuO nanowires, which may improve the field emission by the similar mechanism with Ref [21]. After extended treatments, the surface crystalline structures could be destroyed or even the nanowires broke, which resulted in the degradation of field emission.

Summary

O_2 RIE has been used to etch aligned CuO nanowires. It is observed that suitable duration of treatments enhance the field emission of the nanowires, which related to the sharpened morphology, cleaner surface and generation of superoxides. On the contrary, Ar RIE deteriorates the field emission because of larger work function induced by surface bombardments by inert Ar reactive ions. Such method provides a simple way to control the morphology and to improve the field emission properties of the nanowires more than CuO nanowires.

References

[1] N. De Jonge and J.M. Bonard: Phil. Trans. R. Soc. Lond. A 362 (2004), 2239

[2] D. Banerjee, S.H. Jo and Z.F. Ren: Adv. Mater. 16 (2004), 2028

[3] Z. Pan, H.-L. Lai, F.C.K. Au, X. Duan, W. Zhou, W. Shi, N. Wang, C.-S. Lee, N.-B. Wong, S.-T. Lee and S. Xie: Adv. Mater. 12 (2000), 1186

[4] J. Zhou, N.S. Xu, S.Z. Deng, J. Chen, J.C. She and Z.L. Wang: Adv. Mater. 15 (2003), 1835

[5] L. Vila, P. Vincent, L.D.-De Pra, G. Pirio, E. Minoux, L. Gangloff, S.D. -Champagne, N. Sarazin, E. Ferain, R. Legras, L. Piraux and P. Legagneu: Nano Lett. 4 (2004), 521

[6] J. Liu, Z. Zhang, Y. Zhao, X. Su, S. Liu and E. Wang: Small 1 (2005), 310

[7] J. Xu, J. Mei, X.H. Huang, X. Li, Z. Li, W. Li and K. Chen: Appl. Phys. A 80 (2005), 123

[8] O. Yavas, N. Suzuki, M. Takai, A. Hosono and S. Kawabuchi: Appl. Phys. Lett. 72 (1998), 2797

[9] W.M. Tsang, S.P. Wong and J.K.N. Lindner: Appl. Phys. Lett. 84 (2004), 3193

[10] W. Yi, T. Jeong, S.G. Yu, J. Heo, C. Lee, J. Lee, W. Kim, J.-B. Yoo and J. Kim: Adv. Mater. 14 (2002), 1464

[11] C.Y. Zhi, X.D. Bai, and E.G. Wang: Appl. Phys. Lett. 81 (2002), 1690

[12] C.-H. Hsu, H.-C. Lo, C.-F. Chen, C. T. Wu, J.-S. Hwang, D. Das, J. Tsai, L.-C. Chen and K.-H. Chen: Nano Lett. 4 (2004), 471

[13] I.W. Rangelow: Microelectronics Engineering 23 (1994), 369

[14] F.C.K. Au, K.W. Wong, Y.H. Tang, Y.F. Zhang, I. Bello and S.T. Lee: Appl. Phys. Lett. 75(1999), 1700

[15] X.C. Jiang, T. Herricks and Y.N. Xia: Nano Lett. 2 (2002), 1333

[16] Y.W. Zhu, T. Yu, F.C. Cheong, X.J. Xu, C.T. Lim, V.B.C. Tan, J.T.L. Thong and C.H. Sow: Nanotechnology 16 (2005), 88

[17] Y.W. Zhu, F.C. Cheong, T. Yu, X.J. Xu, C.T. Lim, J.T.L. Thong, Z.X. Shen, C.K. Ong, Y.J. Liu, A.T.S. Wee and C.H. Sow: Carbon 43 (2005), 395

[18] K.Y. Lim, C.H. Sow, J. Lin, F.C. Cheong, Z.X. Shen, J.T.L. Thong, K.C. Chin and A.T.S. Wee: Adv. Mater. 15 (2003), 300

[19] R.C. Che, L.M. Peng and M.S. Wang: Appl. Phys. Lett. 85 (2004), 4753

[20] Y.Z. Jin, W.K. Hsu, Y.L. Chueh, L.J. Chou, Y.Q. Zhu, K. Brigatti, H.W. Kroto and D.R.M. Walton: Angew. Chem. Int. Ed. 43 (2004), 5670

[21] W. Hu, M. Matsumura, K. Furukawa and K. Torimitsu: J. Phys. Chem. B 108 (2004), 13116

[22] G.V. Chertihin, L. Andrews and C.W. Bauschlicher: J. Phys. Chem. B 101 (1997), 4026