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Electrodeposition of aligned ZnO sheet array on ITO substrate and their field emission characteristics*

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ZnO sheet array was fabricated by a simple electrodeposition method on the transparent ITO substrate at a temperature of about 60 °C. The field emission properties of the ZnO sheet array were investigated. The fluctuation of the field emission current is less than 5% over several hours. The Fowler–Nordheim curves with a roughly linear characteristic were obtained by analysing the current density and the intensity of the electrical field. The results prove that such a simple electrochemical method can potentially meet the demands on the production of cold cathodes for field emission display.

Keywords: field emission, electrodeposition, ZnO, ITO
PACC: 7970, 8280

1. Introduction

Demands on displays of low energy cost, small volume, high performance and environmental compatibility led to the birth of flat display. Field emission display is one of the most promising candidates for the flat displays, and the research on cold cathodes has attracted great attention. There have been many reports on the field emission characteristics of different cold cathodes such as metal emitters, carbon nanotubes and oxide semiconductors. Metal emitters are highly effective but their relatively low resistance to oxidation prevents their further applications in cold cathodes.[1,2] Carbon nanotube (CNT) is a kind of good material for field emission due to its low threshold and high conductivity.[3−5] But the difficulty in purification affects the repeatability of CNT cathode. Plasma-treated thin film of diamond has been reported to have negative electron affinity.[6] However, fabrications of such cathodes are expensive. So metal oxides become promising candidates for the cold cathodes due to their high stability and good performance. Field emissions of In_2O_3,[7,8] SnO_2,[9] CuO[10,11] and ZnO[12−15] nanostructures have been reported. Among these materials, ZnO, having a relative high melting point and easy collection, can meet the demands of both long duration and low cost. Electrodeposition is a method carried out at relatively low temperatures with good accommodation to industry production, as compared with some other methods operating at high temperatures. And indium-tin oxide (ITO) substrate also meets the demands of low cost and good conductivity of the cathodes. ZnO-based cathodes synthesized by electrodeposition on transparent ITO substrate will facilitate their applications in flat display.

In this article, roughly aligned array of ZnO sheet is synthesized through electrodeposition on the ITO substrate. The field emission of the sample is investigated by varying the voltage across the electrodes of different distances. It is found that the emission current follows the Fowler–Nordheim (F–N) theory. The field enhancement factor and the turn-on field are obtained by analysing the relation between the current density (J) and the electrical field (E) characteristics.

2. Experimental details

ZnO sheet array was grown by electrodeposition on an ITO glass. The fabrication was carried out in a typical three-electrode electrochemical cell with an ITO working electrode, a graphite countering electrode and a KCl-saturated Ag/AgCl reference elec-

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trode. Clear solution of 0.05 M $ZnNO_3$ and 0.05 M KCl served as an electrolyte, in which the nitrate was the electrochemical hydroxide precursor. ZnO could be deposited from the reduction of nitrate ions according to the total reaction $Zn^{2+} + NO_3^- + 2e^- \rightarrow ZnO + NO_2^-$.[16,17] Electroreduction of nitrate to nitrite ions led to the increase of OH^- concentration at the cathode, which would result in the final formation of ZnO. The electrodeposition was performed with a similar method described in Ref.[18]. After deposition, the sample was washed with de-ionized water and annealed in air at 350 °C for an hour.

The morphology of the as-prepared sample was characterized by a scanning electron microscope (SEM, Hitachi, S-4200). The crystal structure of the annealed sample was analysed by x-ray diffraction (XRD), on a diffractometer (Rigaku, D/MAX-2400) with a graphite-monochromatized Cu Kα radiation. The field emission properties of the samples were measured using a two-parallel-plate configuration in an ultrahigh vacuum chamber at a pressure of about 3.0×10^{-7} Pa at room temperature.

3. Results and discussion

Figure 1(a) shows the SEM image of the as-prepared sample on an ITO substrate, from which it can be seen that the substrate is covered by two-dimensional (2D) sheets almost vertical to the substrate. These sheets are about 3 μm in diameter and 100–300 nm in thickness. The XRD pattern of the annealed sample is shown in Fig.1(b). All diffraction peaks, except the small peaks marked with stars, match with the standard data of ZnO with a hexagonal structure (Joint Committee on Powder Diffraction Standards file No. 36-1451). The star-marked peaks are those produced by the ITO substrate. The result of the XRD shows that the annealed sample on the ITO substrate is ZnO.

The field emission experiments of the ZnO sheet array were carried out in a vacuum chamber with a pressure of 3.0×10^{-7} Pa at room temperature. The ITO substrate with ZnO sheets was attached to a stainless-steel plate as cathode and another stainless-steel plate served as anode with an adjustable distance with respect to the cathode. The schematic diagram of the setup for field emission is shown in the inset of Fig.2(a). To obtain a good contact between the ZnO array and the cathode, a layer of Au about 150 nm was sputtered onto the back of the ITO substrate. Then the substrate was annealed in N_2 at 400 °C for 15 min. A high voltage of about 5 kV was applied to the parallel electrodes before each measurement for removal of contaminants and degassing the sample. A voltage at a sweep step of 50 V was applied between the anode and cathode to supply an electrical field that extracts the electrons out of the emitters. The emission current was monitored using a Keithley 485 picoammeter.

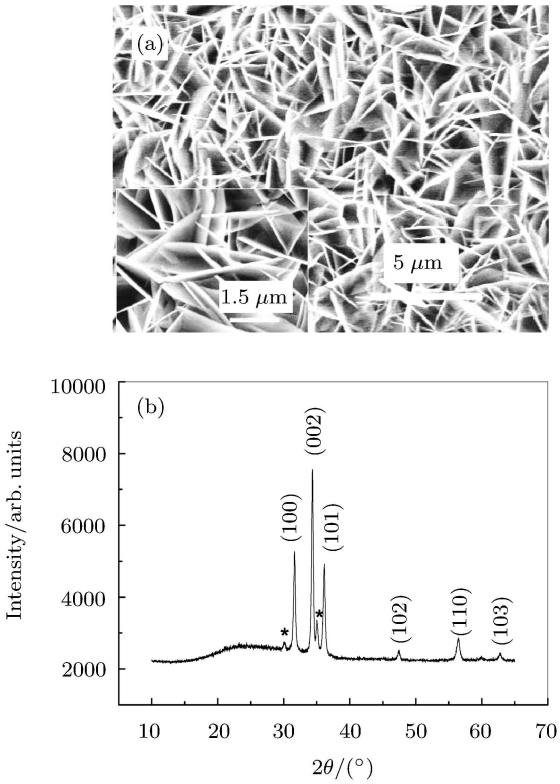


Fig.1. (a) SEM image of the as-prepared sample on an ITO glass, the inset being the enlarged image. (b) XRD pattern of the sample after annealed in air.

Figure 2(a) shows the $J - E$ characteristics of ZnO sheet arrays at different distances between the electrodes. As the voltage exceeds a certain value, the sheet array begins to emit electrons with the driving of electrical field, and from this point on the current increases with the voltage exponentially. The electrical fields at the current densities of 1 μA/cm^2 and 1 mA/cm^2 are defined as the turn-on electrical field and the threshold electrical field, respectively. The turn-on fields of the ZnO sample are 6.13, 6.67, 7.48, 8.41 and 13.50 V/μm at electrodes' separations of 500, 350, 250, 100 and 50 μm, respectively.

Figure 2(b) shows the F–N plot. The F–N curves indicated in the figure are obtained by analysing the current density and the mean field intensity. The F–N curves obtained at different distances between elec-

trodes are consistent with the F–N mechanism, exhibiting roughly linear dependence, which reveals that the emission current is caused by the quantum tunnelling effect. For metal materials, the relationship of the emission current versus the applied field has been analysed by the F–N theory, which is described as $J = A((\beta E)^2/\phi)\exp(-B\phi^{3/2}/(\beta E))$.[19] In this equation, J is the emission current density, and E is the mean electrical field between the two parallel-electrodes. A and B are constants, ϕ is the work function. For oxide semiconductors, oxygen adsorption will result in the formation of surface charge layers, which increase the barrier for the electron emission. And the field penetration has to be taken into account due to its effect on the electron emission. So, considering the differences from metal emitters, the emission current can be described by $J = A((\beta E)^2/\phi)\exp(-B\phi^{3/2}/(\beta E))\exp((-\Delta W^{\mathrm{S}} - \Delta W^{\mathrm{P}})/(2kT))$,[20] where ϕ denotes work function, which is estimated to be 5.3 eV for the ZnO sample.[21] Here, β is the field enhancement factor. ΔW^{S} and ΔW^{P} are the increase of surface potential barrier for semiconductor emitter due to surface states and the decrease of surface potential barrier due to field penetration, respectively. During the field emission, electrons overcome the work function as well as the surface barriers and tunnel through the gap between the electrodes under the function of electrical field. Generally, the surface states and field penetration will change the slope coefficient of the F–N plot and make it nonlinear as indicated in Ref.[7]. In our experiment, such a characteristic induced by surface states can be observed from the F–N plot. During the field emission, current will raise the temperature of the emitters, and the surface state induced by the oxygen adsorption will be eliminated from the emitters as the temperature rises. The lack of surface states results in the decrease of barrier for the electron emission.[7,20]

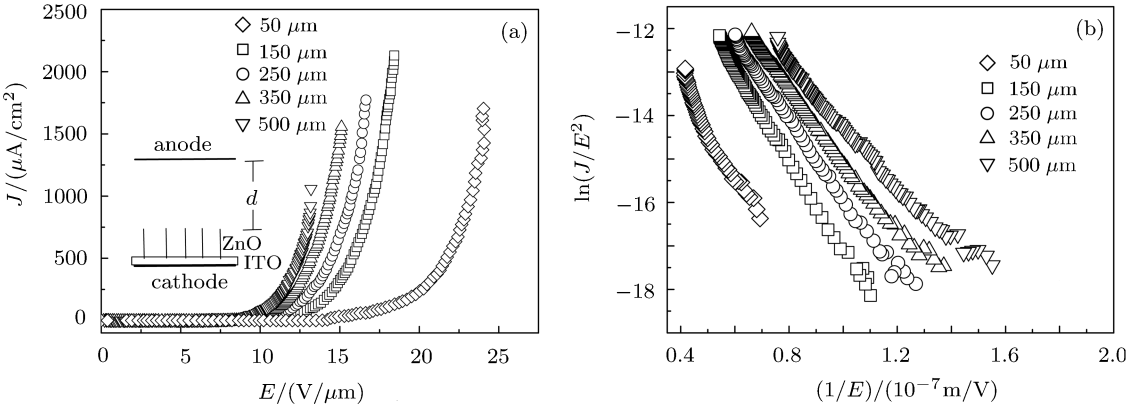


Fig.2. (a) $J-E$ curves measured at different distances between the substrate and the anode ($d = 50$, 150, 250, 350 and 500 μm). The inset in Fig.2(a) is the schematic diagram showing the field emission setup (b) the corresponding F–N plots of the field emission.

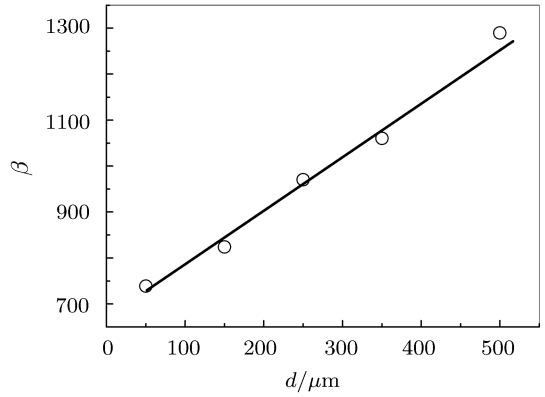


Fig.3. Relation between the enhancement factor and the distance between electrodes.

It was found that as the distance between the two electrodes becomes larger, the enhancement factor β is increased, which is a factor related to the shape and size of the emitters and can be calculated from the slope coefficient of the F–N plot. Obtained from our experiment, β has values 739, 824, 970, 1060 and 1290 when the corresponding distances are 50, 150, 250, 350 and 500 μm, respectively. The field intensity enhanced by the space structure of the emitters is equal to the product of β and the mean field intensity, and the enhanced field drives the electrons off the emitters. The roughly linear relation between the enhance factor and the distance between the electrodes shown in Fig.3 matches the case mentioned in

Ref.[22]. Because the buffer space between the local field intensity and the mean field intensity shrinks as the electrodes' distance increases, which increases the enhancement effectively, the turn-on field will decrease as the distance increases.

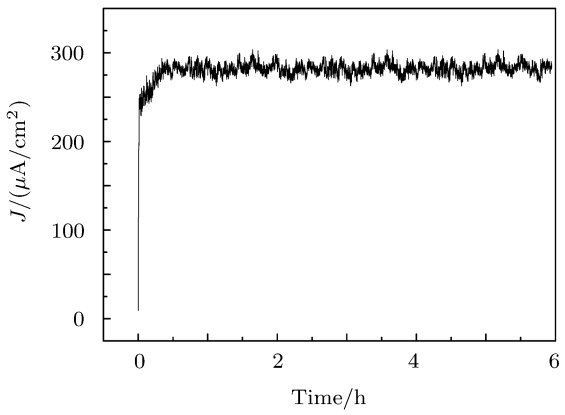


Fig.4. The stability curve of the ZnO sheet over a period of six hours.

The stability of field emission from the ZnO sheet array has been measured after aging for 20h to eliminate the surface states and the characteristic is shown in Fig.4. The curve is obtained at the current density of about 280 μA/cm^2 and the fluctuation around the mean value is less than 5% over a period of six hours of investigation.

4. Conclusion

ZnO sheet array has been synthesized on the ITO substrate by electrodeposition. The field emission characteristic of the ZnO sheet array was investigated and revealed by the F–N plot, indicating that it follows the rules revealed by F–N theory. By analysing the nonlinear region of the F–N curve, the effect of surface states induced by oxygen adsorption has been revealed. The fluctuation of the emission current is less than 5%. Synthesis of ZnO sheet with electrochemical method on transparent ITO substrate was carried out at low temperatures and the experiment with this kind of ZnO sheet is compatible to the industrial production. Good performance of field emission from the ZnO sheet facilitates its potential application in flat display.

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