Featured Letter

Highly efficient field emission from indium-doped ZnO nanostructure on nanographene/macroporous electric conductive network

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\textbf{Abstract}
Indium-doped ZnO nanoparticles coated on nanographene/MECN enhance the field emission properties by avoiding electrostatic screen, providing more emitters, as well as introducing nanographene and indium doping. A simple hydrothermal method is developed to fabricate In-doped ZnO field emitters with different ratios of In and ZnO (5%, 10%, and 20%). The 10% In-ZnO shows a turn-on electric field as low as $1 \text{ V}\mu\text{m}^{-1}$ at a current density of $10 \mu\text{A}\text{cm}^{-2}$, and the threshold field is $5.8 \text{ V}\mu\text{m}^{-1}$ at $1 \text{ mA}\text{cm}^{-2}$. The largest current density is $2.88 \text{ mA}\text{cm}^{-2}$, and the estimated $b$ is 27918. The emission currents are very stable at high, medium, and low current densities with an average deviation of only 2.5%. The outstanding field emission performance indicates that In-doped ZnO coated on nanographene/MECN is an efficient field emitter and has large potential in displays, lightings, and sensors.

\textbf{1. Introduction}
High-quality field emitters offer many advantages and are sometimes preferred scanning electron microscopes, and flat panel displays \cite{1}. ZnO is one of most extensively studied metal oxides as nanostructured field emitters due to its unique physical properties such as large exciton binding energy (60 meV), direct wide band gap (3.37 eV), low electron affinity, and high thermal stability \cite{2–4}. In particular, the graphene and ZnO hybrid nanostructures show promise in field emission because of the excellent electrical conductivity, mechanical flexibility, as well as chemical/thermal stability rendered by graphene. A three-dimensional structure provides more edges and avoids electrostatic shielding and so the ZnO-graphene hybrid structure prepared on a patterned 3D substrate has excellent field emission characteristics \cite{5}. It is also well known that group-III dopants such as Al \cite{6}, Ga \cite{7}, and In \cite{8} are efficient donors in ZnO and enhance the carrier concentrations for better conductivity \cite{9}. In this work, the doping effects on the field emission properties of ZnO \cite{10} are investigated by preparing and studying In doped ZnO coated on 3D nanographene/macroporous electric conductive network (MECN) \cite{11}.

\textbf{2. Experimental details}
The 3D substrate composed of Si-MCPs (microchannel plates) was prepared by a microelectromechanical system (MEMS) process \cite{12}. A nickel film was coated on the Si-MCPs to obtain a macroporous electric conductive network (MECN) by electroless deposition \cite{13} and the nanographene was coated on the MECN by a hydrothermal carbonization process and annealing \cite{14}. The samples were immersed into 20 mM zinc acetate [Zn(CH$_3$COO)$_2$\text{H$_2$O}] solution and then annealed at 300 $^\circ\text{C}$ for 1 h under Argon atmosphere to form ZnO template. Indium chloride (InCl$_3$), 25 mM zinc nitrate hexahydrate [Zn(NO$_3$)$_2$\text{6H$_2$O}], and 25 mM hexamethylenetetramine (HMT) was mixed up under hydrothermal process. The ratios of In and Zn were 5%, 10% and 20%, respectively. The sample with ZnO template was put in a 25 ml Teflon-sealed stainless steel autoclave with hydrothermal solution and heated to 90 $^\circ\text{C}$ for 4 h \cite{10}. After washing and drying, indium-doped-ZnO/nanographene/MECN was obtained. The samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive X-ray spectrometer (EDS), as well as...
Fig. 1. (a) Top-view SEM image of 10% In-ZnO; (b) Magnified image of (a); (c) XRD patterns of 5%, 10%, and 20% In-ZnO; (d) EDS pattern of 10% In-ZnO.

Fig. 2. XPS spectra: (a) Survey spectrum of 10% In ZnO; (b) High-resolution In 3d spectrum; (c) High-resolution Zn 2p spectrum; (d) High-resolution C 1 s spectrum.
X-ray photoelectron spectroscopy (XPS). The field emission properties were determined on a diode structure in vacuum chamber at 5 × 10⁻⁵ Pa. The distance between the sample and anode was 100 μm and the sample area was 0.5 cm².

3. Results and discussions

Fig. 1a displays the top-view SEM images of the 10% In In-ZnO sample which has the best field emission properties. Fig. 1b is the magnified image of the Fig. 1a revealing a square array with 5 × 5 μm pores and In-doped ZnO nanoparticles coated on the nanographene/MECN uniformly and densely. These nanoparticles offer many edges to improve the field emission characteristics. Fig. 1c presents the XRD patterns of the three samples. The strongest peak (4 0 0) at 69.1° is indexed to silicon and the sharp peaks of (1 1 1) at 44.6°, (2 0 0) at 51.9°, and (2 2 0) at 76.6° arise from Ni. The peaks (1 0 0) at 31.7°, (0 0 2) at 34.4°, and (1 0 1) at 36.2° are indexed to the ZnO [15]. However, In is almost invisible because of the small concentration and so is the graphene (0 0 2) peak. To confirm indium doping, the EDS spectrum shows the presence of In by red box in Fig. 1a. The examined area is marked as Fig. 1d. The XPS spectra of Zn 2p, O 1 s, In 3d, and C 1 s are displayed in Fig. 2a and b shows peaks at 452.2 eV and 444.75 eV corresponding to In 3d⁵/₂ and In 3d³/₂ respectively [10] and the small satellite peaks corroborate indium doping in the ZnO nanoparticles. Fig. 2c exhibits two peaks at 1045.3 eV and 1022.1 eV corresponding to Zn 2p and In 3d peaks are 23.2 eV and 7.45 eV consistent with the reference value of 22.97 eV and 7.5 eV, respectively. The In 3d peaks show a positive shift in comparison to the standard value of In possibly caused by electron transfer from ZnO to In due to the strong electronic interaction between In and oxide. The Zn 2p peaks show a negative shift due to the electronegativity (χ) difference between In (χ = 1.78) and Zn (χ = 1.65) [17]. Fig. 2d shows a big peak at 284.75 eV and small peak at 289.1 eV corresponds to C sp² and C-OO [18]. The high intensity of C sp² represents the nanographene.

The field emission properties measured from 5% In-ZnO, 10% In-ZnO, 20% In-ZnO and pure ZnO reported in ref [5] are presented in Fig. 3. The turn-on fields (defined as the E corresponding to the J of 10 μA cm⁻²) are 0.75, 1, 0.8 and 0.5 V cm⁻¹. The threshold field (defined as the E where J arrives at 1 mA cm⁻²) of 10% In-ZnO and 20% In-ZnO is 5.8 and 3.7 V cm⁻¹. In comparison, the field of 5% In-ZnO is 2.66 V μm⁻¹ at 526 μA cm⁻² which cannot reach the threshold current density. This phenomenon is similar to it observed from pure ZnO field emitter. Although the turn-on and threshold fields of 20% In-ZnO are less than those of 10% In-ZnO, the current density of 10% In-ZnO increases more rapidly where the E high and the largest current density is 2.88 mA cm⁻², indicating that the field emission properties of 10% In-ZnO is better than that of the others samples. The emission current-voltage characteristics of the samples are analyzed by the Fowler-Nordheim (F-N) equation as follows [19],

\[
J = \frac{A\beta^2E^2}{\Phi} \exp\left(-\frac{B\Phi^{3/2}}{\beta E}\right)
\]

where \(A = 1.54 \times 10^{-10} \text{AV}^{-2} \text{eV}, B = 6.83 \times 10^{-9} \text{V}^{-1} \text{eV}^{-3/2}, \) and \(\Phi\) is the work function, which is about 5.2 eV for ZnO. Here, the concentration of In is much less than that of ZnO so that the work function is dictated by ZnO. \(\beta\) is the field enhancement factor which reflects the ability of the emitters to enhance the local electric field and can be delineated from the slope of \(-B\Phi^{3/2}/(\beta E)\) at high electric fields. Fig. 3b shows the linear dependence of the In/J/E² vs. 1/E (F-N) plots of 5%, 10%, 20% In-ZnO, and pure ZnO. The average values of \(\beta\) are 24059, 27918, 23382, and 25550, respectively, indicating that 10% In-ZnO is the most suitable dopant concentration. These values are bigger than those of indium-doped ZnO reported by other groups. All in all, 10% In-ZnO possesses the best field emission properties as manifested by large current density and field enhancement factor. The long-term emission current sustainability and stability of 10% In-ZnO is measured at low, medium, and high current densities for 120 min as shown in Fig. 3c. The average deviations of the current densities are 2.6%, 2.5%, and 1.9% at current densities of 38, 125, and 260 μA cm⁻², respectively and the largest fluctuations are 5.4%, 5.8%, and 6.7%, respectively, demonstrating the good stability. Moreover, the average electric fields of 10% In-ZnO at three current densities are 1.8, 2.8, and 4 V μm⁻¹ which are almost consistent with the J–E curve in Fig. 3a demonstrating great repeatability.

4. Conclusion

5%, 10%, and 20% In-doped ZnO nanoparticles are prepared on nanographene/MECN and 10% In-ZnO shows a turn-on electric field of 1 V μm⁻¹ and threshold field of 5.8 V μm⁻¹. The largest current density is 2.88 mA cm⁻² and \(\beta\) of 10% In-ZnO is 27918. The emission currents are very stable at high, medium, and low current densities with an average deviations of only 2.5%. The outstanding field emission properties stem from the 3D MECN sub-strate providing many sharp edges and patterned porous structure.
avoiding electrostatic shielding due to the uneven lattice surface. Nanographene is introduced to enhance the field emission performance and indium improves the carrier concentration and resistance to oxidation. The results demonstrate a simple approach for the large scale production of nanomaterials with efficient field bonding well for field-emission devices such as displays, lightings, and sensors.

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References