Improving Field Electron Emission Properties of ZnO Nanosheets with Ag Nanoparticles Adsorbed by Photochemical Method

Sheng-Joue Young,* Yi-Hsing Liu, and Jen-Tse Chien

ABSTRACT: Zinc oxide is a low cost and practical II–VI chemical material, which is utilized to absorb silver (Ag) nanoparticles (NPs) on zinc oxide nanosheets (ZnO NSs). Using the Ag NP-decorated ZnO NSs can improve the electrical characteristics of zinc oxide. Field electron emission characteristics of ZnO NSs and Ag–ZnO NSs indicate the turn-on fields were 5.3 and 3.2 V/μm in the dark, whereas the turn-on field were 4.3 and 2 V/μm under UV light, respectively. In addition, the field electron emission characteristics of ZnO NSs and Ag–ZnO NSs indicate the enhanced field enhancement factors were 3002 and 3420 in the dark and 3276 and 4815 under UV light, respectively.

I. INTRODUCTION

The field emission inter-related electronic devices must have favorable electron emission characteristics, mainly determined by their material nanostructures. The excellent field emission properties provide high conductivity, shrill-tip morphology nanostructures, high stabilities, and low work function, as investigated. The various component material nanostructures of the field emission inter-related electronic devices have greatly attracted substantial attention, such as ZnO, SiC, CNT, GaN, and graphene.1−5 Among these materials, zinc oxide (ZnO) was widely studied as a result of its exhibiting excellent properties from electronic devices and optoelectronic devices for application. It is well known that ZnO has a wide band gap as a semiconductor and large exciton binding energy of 3.37 eV and 60 meV, respectively, at room temperature.6 Generally, in the case of undoped material, the ZnO exhibits n-type semiconductor properties, with a hexagonal wurtzite structure, with the lattice constant \( a = 3.24 \text{ Å}, \) \( c = 5.20 \text{ Å} \).7 Currently, a variety of nanostructures of ZnO material have been developed, for example, nanorods, nanowires, nanopins, nanotubes, nanoplates, nanodisks, and nanosheets (NSs), by various methods.8−14 On the other hand, various geometrical morphologies of ZnO nanostructures have been developed by various grown methods, for example, hydrothermal method, electrochemical deposition, chemical solution method, and chemical vapor deposition.15−18 The chemical solution method to synthesize ZnO nanostructures exhibits distinct advantages of uniform morphology, simple process, homogeneous size, low temperature, and low cost. It is known that the excellent field emission properties are attributed to high conductivity, shrill-tip morphology nanostructures, high stabilities, and low work function; hence, the NS structure was suitable for achieving excellent properties in a field emission device. On the other hand, there are many methods to ameliorate the field electron emission property of emitters based on ZnO nanostructures, such as metal doping, exposing with UV light, and decoration of nanoscale noble metal particles on nanostructure surface.19−21

In this work, the emitter based on ZnO or Ag nanoparticle (NP)-adsorbed ZnO used glass substrate by low-temperature chemical solution method is used so that complex manufacturing processes can be avoided and give effect to lower costs. The field emission characteristics of an emitter based on ZnO or Ag NP-adsorbed ZnO were researched. In addition, the field emission characteristics and reliability in the dark or on exposure to UV light of emitter based on ZnO or Ag NP-adsorbed ZnO were also measured. The results of this article demonstrate that decorating with Ag on ZnO nanostructured surface can enhance field emission; moreover, the illumination by UV enhanced emission characteristics from ZnO NSs and Ag–ZnO NSs.

II. RESULTS AND DISCUSSION

Figure 1a−d reveals the field emission scanning electron microscope (FE-SEM) images of ZnO and Ag–ZnO NSs. The figures verify pure and Ag–ZnO NSs were vertically grown and interwoven with each other on the glass substrate. The average diameter and length of ZnO NSs and Ag–ZnO NSs were ~16 and ~20 nm and ~1.82 and ~1.83 μm, respectively. In the FE-SEM image, it can be observed that the surface of ZnO NSs was effectively decorated with Ag nanoparticles of around 120–180 Å. Figure 1e shows the energy dispersive X-ray
EDX images of Ag-adsorbed ZnO NSs, it can be found that these NSs consisted of 46.31, 52.31, and 1.36% of Zn, O, and Ag, respectively. The EDX images can indicate that the ZnO NSs contain Ag NPs.

Figure 2 shows the photoluminescence spectra of the ZnO and Ag-adsorbed ZnO NSs. It can be found that there are two emission bands of UV and visible region, demonstrating a typical luminescence characteristic of ZnO. The ∼380 nm peak of UV emission can correspond with near band edge emission and free-excitonic recombination. The ∼540 nm peak of visible region emission can correspond with nature-generated defects or intrinsic oxygen vacancies of ZnO structure. In addition, it can also be found that the UV emission peak is much stronger and visible region emission intensity was reduced by Ag particle adsorption on ZnO nanosheet surface.

Figure 3 shows the X-ray diffraction (XRD) spectrum of ZnO NSs and Ag−ZnO NSs. On the basis of JCPDS Card: 3601451, the result indicates that these diffraction peaks correspond with (002), (102), (103), and (112). The diffraction peak indicated the hexagonal wurtzite structures of the ZnO NSs and Ag−ZnO NSs. The (002) diffraction peak is relatively higher than the other diffraction peaks; it can be indicated ZnO NSs crystals mainly grow was along c-axis direction. Furthermore, the diffraction peaks of Ag were found in Figure 3b. On the basis of JCPDS Card: 04-0783, the result indicates that the peaks conformed to (111) and (200), meaning the Ag is successfully adsorbed into the ZnO structure.
Figure 4 shows the transmission electron microscope (TEM) images, high-resolution transmission electron microscope (HR-TEM) images, and EDX spectroscopic images of Ag−ZnO NSs. A sample locational with stochastically chosen Ag nanoparticles deposited on the surface of the ZnO NSs. It can be found that the surfaces display rugged of the Ag-adsorbed ZnO NSs as a result of the Ag nanoparticle adsorption on the surface; moreover, the average diameter of Ag nanoparticles was around 6−9 nm. From the mapped images of Ag-decorated ZnO NSs, it can be found that the Zn, O, and Ag atoms were evenly scattered at all places. The Ag-decorated ZnO NSs detail 12.116 atom % Ag, as determined in the EDX spectrum; this can further indicate that the Ag nanoparticles were adsorbed on the ZnO nanosheet surface.

To further understand the field emission performance of the ZnO and Ag−ZnO NSs, the measured current density electric field \( (J-E) \) curves were analyzed by the Fowler–Nordheim (F−N) equation

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

\( (1) \)

\( E \) defines the applied field between cathode and anode, \( J \) defines the current density, \( A \) is constant \( (A = 1.56 \times 10^{-10} \ A \ V^{-2} \ eV) \), \( B \) is constant \( (B = 6.83 \times 10^9 \ V \ eV^{-3/2} \ \mu m^{-1}) \), \( \phi \) defines the work function of emitting material (the work function was ~5.3 eV of ZnO\(^{23} \)), and \( \beta \) defines the effective field enhancement factor. The measurements of field electron
emission were processed in high vacuum for ZnO and Ag–ZnO NSs in a homemade cavity. The anode and cathode used indium-tin oxide glass (ITO glass) and as-prepared samples (ZnO and Ag–ZnO NSs). The working area of the as-prepared sample is 25 mm²; the spacing between anode and cathode is at about 160 μm. Figure 5a,b shows the J–E curves of field electron emission measurements from the ZnO and Ag–ZnO samples. From the J–E curves, it can be found that the turn-on fields were 5.3 and 3.2 V/μm of ZnO and Ag–ZnO NSs in the dark and under UV irradiation, respectively. The turn-on field is defined as the electric field that corresponds to a current density of 10⁻⁶ A/cm². To further probe the effective field enhancement factor, the Fowler–Nordheim equation was more simplified:

$$\ln \left( \frac{J}{E^2} \right) = \ln \left( \frac{A \times \beta^2}{\varepsilon} \right) - \frac{B \times \varepsilon^{3/2}}{E \times \beta}$$

The slope of F–N plot is a function of both β and φ; it can be expressed as

$$\text{slope} = B\Phi^{3/2}/\beta$$

This function could be calculated by β or φ.

Figure 5. (a, b) show the J–E curves of field electron emission measurements and (c, d) show F–N plot with (1/E) versus ln(J/E²) curves of field electron emission measurements from ZnO and Ag-adsorbed ZnO samples.

Figure 6. Schematic band diagram of ZnO nanosheets and Ag nanoparticle-adsorbed ZnO nanosheets in darkness and under UV illumination with a strong external field.

ACS Omega

DOI: 10.1021/acsomega.8b01041
ACS Omega 2018, 3, 8135–8140
happen in this situation. Figure 7 presents the reliability of Ag-adsorbed ZnO NS samples when measured with an applied field of 3.2 V/μm for 60 min. From Figure 7, it was found that Ag-adsorbed ZnO NS samples show good stability during the measurement period.

III. CONCLUSIONS

Our samples were successfully synthesized on a glass substrate via hydrothermal method. From the J–E curves, it can be found that for the pure and Ag-adsorbed ZnO samples, the turn-on fields were 5.3 and 3.2 and 4.3 and 2 V/μm in the dark and under UV light, respectively. The Ag NPs adsorbed on ZnO surface can enhance the electrical conductivity. In addition, the Ag nanoparticles adsorbed can increase emitter points on ZnO NSs surface. The results of this article demonstrate that decoration with platinum on ZnO nanostructured surface can enhance field emission; moreover, the illumination by UV light enhanced emission characteristics from ZnO and Ag–ZnO NSs.

IV. EXPERIMENTAL SECTION

First, an ultrasonic oscillator was used to wash the glass substrates (Corning 1737) with deionized water, acetone, and methanol. First, the ZnO film was deposited as a seed layer for 25 nm by radio frequency magnetron sputtering on a glass substrate. The size of the target was 3 in. ZnO (99.99%) and the base pressure and radio frequency power of the chamber were 3.75 × 10⁻⁸ Pa and 100 W, respectively. During sputtering, the pressure gases were kept at 5 mTorr and the Ar and O₂ gas flows into the chamber were kept 18 and 2 sccm, respectively. The aqueous solution was sodium hydroxide (0.4 M) and zinc nitrate hexahydrate (0.1 M) dissolved in deionized water. Subsequently, the size of the seed layer coated on the substrate was steeped in solution for 1 h at room temperature. The reaction was completed, and the sample was rinsed in deionized water and subsequently dried at room temperature. The rapid thermal annealing system was used to anneal the sample in oxygen environment for 5 min at 400 °C. Thereafter, the sample of the NSs/seed layer/glass was steeped in solution for 15 min at room temperature; the solution is 0.1 mM silver nitrate (AgNO₃ Sigma-Aldrich) under UV light (254 nm, 0.025 W/cm²). The field emission element based on Ag-decorated ZnO NSs was finished.

The field electron emission scanning electron microscope (FE-SEM, Hitachi S-4800I) was used to measure and check the surface morphology of the ZnO NSs and Ag–ZnO NSs. The high-resolution transmission electron microscope (HR-TEM, Philips Tecnai F20 G2 FEG-TEM) and Bruker D8 X-ray diffractometer (XRD) were used to measure and check the crystalline structure of the ZnO and Ag–ZnO NSs. The field emission characteristics of our samples were measured by Keithley 2410 equipment in a homemade cavity (the pressure condition was maintained below 37.5 × 10⁻⁹ Pa in the vacuum cavity). The anode and cathode used ITO glass with 30 mm width and 5 mm length and out samples. The distance between the cathode and anode is 160 μm. The electron beam evaporator is used to deposit Pt contact electrode (about 100 nm thick) in our samples. The field emission characteristics were measured using Keithley 2410 system for providing voltages (the voltages were provided from 0 to 1100 V, with each stage increasing by 10 V).

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: shengjoueyoung@gmail.com.

ORCID

Sheng-Joue Young: 0000-0003-3164-2949

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the Ministry of Science and Technology under contract numbers MOST 107-2622-E-150-002-CC2, 106-2221-E-150-041-MY3, 106-2622-E-150-005-CC3, and 106-2622-E-150-017-CC2. We also acknowledge the assistance of the Common Laboratory for Micro/Nano Science and Technology of the National Formosa University for some of the measurement equipment used in this study and the Center for Micro/Nano Science and Technology of National Cheng Kung University for device characterization.

■ REFERENCES

(1) Su, X. F.; Chen, J. B.; He, R. M.; Li, Y.; Wang, J.; Wang, C. W. The preparation of oxygen-deficient ZnO nanorod arrays and their enhanced field emission. Mater. Sci. Semicond. Process. 2017, 67, 55–61.
(2) Cui, Y. K.; Chen, J.; Di, Y. S.; Zhang, X. B.; Lei, W. High performance field emission of silicon carbide nanowires and their applications in flexible field emission displays. AIP Adv. 2017, 7, No. 125219.
(3) Lim, Y. D.; Grabov, D.; Hu, X. L.; Kong, Q. Y.; Tay, B. K.; Labunov, V.; Miao, J. M.; Coquet, P.; Aditya, S. Enhanced field emission properties of carbon nanotube bundles confined in SiO₂ pits. Nanotechnology 2018, 29, No. 075205.
(4) Mancini, L.; Moyon, F.; Houard, J.; Blum, I.; Lefebvre, W.; Vurpillot, F.; Das, A.; Monroy, E.; Rigutti, L. Multi-excitonic emission from Stranski-Krastanov GaN/AlN quantum dots inside a nanoscale tip. Appl. Phys. Lett. 2017, 111, No. 243102.
(5) SanKaran, K. J.; Ficek, M.; Kunuku, S.; Panda, K.; Yeh, C. Y.; Park, J. Y.; Sawczak, M.; Michalowski, P. P.; Leou, K. C.; Bogdanowicz, R.; et al. Self-organized multi-layered graphene-boron-doped diamond hybrid nanowalls for high-performance electron emission devices. Nanoscale 2018, 10, 1345–1355.
(6) Yang, C. C.; Yu, H. C.; Su, Y. K.; Chuang, M. Y.; Hsiao, C. H.; Kao, T. H. Noise Properties of Ag Nanoparticle-Decorated ZnO Nanorod UV Photodetectors. IEEE Photonics Technol. Lett. 2016, 28, 379–382.
(7) Qasmi, T. Synthesis of Zn (x) Co3-x O-4 spinels at low temperature and atmospheric pressure. J. Mater. Sci. 2018, 53, 3250–3266.

(8) Shabania, R. High-sensitivity UV photodetector based on oblique and vertical Co-doped ZnO nanorods. Mater. Lett. 2017, 214, 254–256.

(9) Wu, J.; Chen, L. F.; Li, S. Y.; Du, C.; Zhang, Q. Z.; Zheng, C. L.; Xu, J. M.; Song, K. X. Improved field emission performance for graphene/ZnO nanowires/graphene sandwich composites. Mater. Lett. 2018, 2045, 391–393.

(10) Yin, S.; Chen, Y. Q.; Su, Y.; Jia, C.; Zhou, Q. T.; Li, S.; Xin, M. J.; Kong, W. H.; Zhang, X. H.; Lu, Y. S. Controllable synthesis and photoluminescence properties of ZnO nanorod and nanopin arrays. J. Nanosci. Nanotechnol. 2008, 8, 993–996.

(11) Oh, S.; Ha, K.; Kang, S. H.; Yohn, G. J.; Lee, H. J.; Park, S. J.; Kim, K. K. Self-standing ZnO nanotube/SiO2 core-shell arrays for high photon extraction efficiency in III-nitride emitter. Nanotechnology 2018, 29, No. 015301.

(12) Yu, W. C.; Sebastian, N.; Chagun, W. C.; Tsia, C. Y.; Lin, C. M. Electrochemical Deposition of ZnO Porous Nanoplate Network for Dye-Sensitized Solar Cells. J. Nanosci. Nanotechnol. 2018, 18, 56–61.

(13) Patra, P.; Mitra, S.; Das Gupta, A.; Pradhan, S.; Bhattacharya, S.; Ahir, M.; Mukherjee, S.; Sarkar, S.; Roy, S.; Chattopadhyay, S.; Adhikary, A.; Goswami, A.; Chattopadhyay, D. Simple synthesis of biocompatible biotinylated porous hexagonal ZnO nanodisc for targeted doxorubicin delivery against breast cancer cell: In vitro and in vivo cytotoxic potential. Colloids Surf., B 2015, 133, 88–98.

(14) Khan, S. A.; Azam, S.; Kanoun, M. B.; Murtaza, G.; Rani, M.; Gounni Said, S. Tailoring the electronic structure and optical properties of cadmium-doped zinc oxides nanosheet. Cogent Phys. 2017, 4, No. 1391734.

(15) Zhang, Z. Y.; Xu, M. Z.; Liu, L.; Ruan, X. F.; Yan, J. F.; Zhao, W.; Yun, J. N.; Wang, Y. N.; Qin, S. J.; Zhang, Y. Novel SnO2@ZnO hierarchical nanostructures for highly sensitive and selective NO2 gas sensing. Sens. Actuators, B 2018, 257, 714–727.

(16) Rahmanian, R.; Mozaffari, S. A.; Amoli, H. S.; Abedi, M. Development of sensitive impedimetric urea biosensor using DC sputtered Nano-ZnO on TiO2 thin film as a novel hierarchical nanostructure transducer. Sens. Actuators, B 2018, 256, 760–774.

(17) Goktas, A. High-quality solution-based Co and Cu co-doped ZnO nanocrystalline thin films: Comparison of the effects of air and argon annealing environments. J. Alloys Compd. 2018, 735, 2038–2045.

(18) Sossi, H.; Jabra, S.; Souissi, A.; Lusson, A.; Gallier, P.; Meftah, A.; Sallet, V.; Queslati, M. Effect of in situ Al doping on structure and optical properties of ZnO nanowires grown by MOCVD. Mater. Res. Express 2018, 5, No. 015003.

(19) Singh, A.; Senapati, K.; Kumar, M.; Som, T.; Sinha, A. K.; Sahoo, P. K. Role of work function in field emission enhancement of Au island decorated vertically aligned ZnO nanotapers. Appl. Surf. Sci. 2017, 411, 117–123.

(20) Liu, X.; Yang, J.; Zhao, W.; Wang, Y.; Li, Z.; Lin, Z. A Simple Route to Reduced Graphene Oxide-Doped Nanocomposites with Markedly Enhanced Visible-Light Photocatalytic Performance. Small 2016, 12, 4077–4085.

(21) Liu, X.; Iocozzia, J.; Wang, Y.; Cui, X.; Chen, Y.; Zhao, S.; Li, Z.; Lin, Z. Noble metal–metal oxide nanohybrids with tailored nanostructures for efficient solar energy conversion, photocatalysis and environmental remediation. Energy Environ. Sci. 2017, 10, 402–434.

(22) Ding, J. J.; Chen, H. X.; Ma, L.; Fu, H. W.; Wang, X. J. Field emission of graphene oxide decorated ZnO nanorods grown on Fe alloy substrates. J. Alloys Compd. 2017, 739, 538–544.

(23) Gu, C. P.; Huang, H. H.; Huang, J. R.; Jin, Z.; Zheng, H. X.; Liu, N.; Li, M. Q.; Liu, J. H.; Meng, F. L. Chlorobenzene sensor based on Pt-decorated porous single-crystalline ZnO nanosheets. Sens. Actuators, A 2016, 252, 96–103.

(24) Chen, T. P.; Young, S. J.; Chang, S. J.; Hsiao, C. H.; Huang, C. S. Field-Emission and Photoelectrical Characteristics of ZnO Nanosheets Photodetectors Prepared on Flexible Substrate. J. Electrochem. Soc. 2012, 159, J153–J157.

(25) Zheng, Y. H.; Chen, C. Q.; Zhan, Y. Y.; Lin, X. Y.; Zheng, Q.; Wei, K. M.; Zhu, J. F. Photocatalytic activity of Ag–ZnO heterostructure nanocatalyst: Correlation between structure and property. J. Phys. Chem. C 2008, 112, 10773–10777.

(26) Park, H. H.; Zhang, X.; Lee, L. W.; Sohn, A.; Lim, D. W.; Kim, J.; Song, J. W.; Choi, S. Y.; Lee, H. K.; Jung, S. H.; Lee, I. G.; Cho, Y. D.; Shin, H. B.; Sung, H. K.; Park, K. H.; Kang, H. K.; Park, W. K.; Park, H. H. Selective photochemical synthesis of Ag nanoparticles on position-controlled ZnO nanosheets for the enhancement of yellow-green light emission. Nanoscale 2015, 7, 20717–20724.

(27) Choi, H.; Ko, S. J.; Choi, Y.; Joo, P.; Kim, T.; Lee, B. R.; Jung, J. W.; Choi, H. J.; Cha, M.; Jeong, J. R.; Hwang, I. W.; Song, M. H.; Kim, B. S.; Kim, J. Y. Versatile surface plasmon resonance of carbon-dot-supported silver nanoparticles in polymer optoelectronic devices. Nat. Photonics 2013, 7, 732–738.