Appl Phys A (2011) 103:951–954
DOI 10.1007/s00339-011-6390-4

Applied Physics A
Materials Science & Processing

RAPID COMMUNICATION

Synthesis and characterization of Ag-doped p-type ZnO nanowires

Guoping Wang · Sheng Chu · Ning Zhan · Huimei Zhou · Jianlin Liu

Received: 13 January 2011 / Accepted: 8 March 2011 / Published online: 31 March 2011
© Springer-Verlag 2011

Abstract P-type ZnO nanowires with silver (Ag) doping were synthesized via a chemical vapor deposition process. The incorporation of Ag was confirmed by selected-area energy-dispersive x-ray spectroscopy. The formation of acceptor states was demonstrated by temperature and excitation power-dependent photoluminescence measurements. Characterization of field-effect transistors using Ag-doped ZnO nanowires as channels showed p-type conductivity of the nanowires with a hole concentration of 4.9×10^{17} cm^{-3} and a carrier mobility of approximately 0.18 cm^2 V^{-1} s^{-1}.

ZnO, a wide-band-gap semiconductor with large exciton binding energy of 60 meV at room temperature [1, 2], is a promising candidate for optoelectronic devices such as blue-light emitting diodes [3, 4], ultraviolet laser diodes [5, 6], and photodiodes [7, 8]. It is well known that one of the biggest challenges toward good ZnO-based optoelectronic devices is the difficulty of reliably fabricating p-type ZnO due to the self-compensating effect from native defects (for example, oxygen vacancy V_o and zinc interstitial Zn_i) and/or H incorporation [9]. There has already been a great deal of efforts on the fabrication of p-type ZnO films by doping group I (Na, Ag) [10, 11] and group V elements (N, P, As, Sb) [12–15] as p-type dopants. In contrast, there have been only a few reports on p-type ZnO nanowires (doped with N, P, and Na) [16–18]. Recently, researchers are interested in developing optoelectronic devices based on ZnO nanowires such as biosensors, ultraviolet detectors, ultraviolet light emitting diodes, and electrically driven nanowire lasers. The growth of p-type ZnO nanowires with good stability will be an essential step for the applications of nanowires in nanoelectronics and optoelectronics. Ag, a group Ib element, was predicted to be an acceptor in ZnO when incorporated into substitutional Zn sites [19]. Indeed, researchers experimentally demonstrated reliable fabrication of p-type ZnO thin films doped with Ag on sapphire substrate [11] with hole concentrations up to 6×10^{17} cm^{-3} and also demonstrated the possibility of achieving Ag-doped p-type ZnO nanowires [20, 21]. However, the electrical and optical properties of single-crystalline Ag-doped ZnO nanowires have not been comprehensively studied yet. In this paper, we report the synthesis and characterization of single-crystalline Ag-doped p-type ZnO nanowires. P-type ZnO nanowires were grown from a mixture of zinc powder and silver (I) oxide using chemical vapor deposition (CVD). The incorporation of Ag was confirmed by selected-area energy-dispersive x-ray spectroscopy (SAEDX) and photoluminescence (PL) studies. Single-nanowire field effect transistors were subsequently fabricated, which exhibited hole conduction channels, confirming the p-type conductivity of the Ag-doped ZnO nanowires.

The growth of nanowires was performed at 730°C for 15 minutes with a gas mixture, containing 600 sccm nitrogen and 300 sccm argon/oxygen (99.5:0.5). The mixture source of zinc powder and silver (I) oxide (1:2 in mass) in a quartz boat was placed in the center of the quartz tube. The silicon substrate was closely attached to the quartz boat on the downstream side.

Figures 1(a) and (b) show the scanning electron microscopy (SEM) image of the nanowires from the top and regular transmission electron microscopy (TEM) image of an individual nanowire, respectively. The length

G. Wang · S. Chu · N. Zhan · H. Zhou · J. Liu (✉)
Quantum Structures Laboratory, Department of Electrical Engineering, University of California at Riverside, Riverside, CA 92521, USA
e-mail: jianlin@ee.ucr.edu

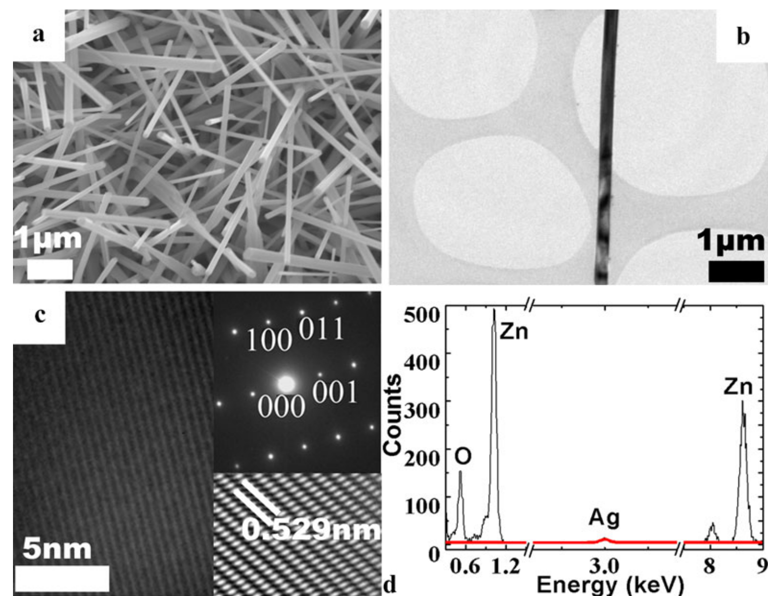

Fig. 1 (**a**) Top-view SEM image of as-grown ZnO nanowires. (**b**) TEM image of a single ZnO nanowire. (**c**) HR-TEM image of the nanowire. *Inset images* are (*top*) the SAED pattern and (*bottom*) a Fourier-filtered HR-TEM image. SAED pattern indicates the single-crystalline characteristic of the nanowire. The lattice spacing between two atomic layers is measured to be 0.529 nm. (**d**) SAEDX spectrum of the individual nanowire shown in (**b**)

and diameter of the ZnO nanowires are on average 5 µm and 250 nm, respectively. The single-crystalline nature of the ZnO nanowires is revealed by high-resolution TEM (HR-TEM) image (Fig. 1(c)) and the selected area electron diffraction (SAED) pattern analysis (the top inset of Fig. 1(c)). The lattice constant is determined to be 0.529 nm as shown in the bottom inset of Fig. 1(c), which also indicates the [001] growth direction of the nanowire. Figure 1(d) presents the SAEDX spectrum of the individual nanowire shown in Fig. 1(b), confirming the incorporation of Ag. The average atomic content of Ag was estimated to be ∼0.1 atom%.

To confirm the formation of acceptor levels by Ag doping, low-temperature PL measurements were performed with a 325 nm He–Cd laser operated at 89 µW. The laser beam impinged against the sample surface with an angle of approximately 60°. The excited PL emission was measured with an Oriel monochromator, which was aligned perpendicular to the sample surface. Figure 2(a) shows the temperature-dependent PL spectra of the Ag-doped sample at the temperatures ranging from 14 to 300 K. The emissions at 3.328 eV, 3.376 eV, 3.277 eV, and 3.226 eV under the temperature of 14 K can be assigned to be neutral-acceptor-bound exciton (A°X), ground state of A free exciton ($FX_A^{n=1}$), free electron to acceptor level (FA) and donor-acceptor pair (DAP) transitions, respectively [22]. The appearance of different states of free excitons reflects the good optical property of the ZnO nanowires. The DAP emission at 3.226 eV shows a slightly progressive blueshift with an increase of temperature from 14 to 100 K, which is a result of thermal ionization of donors at higher temperatures and has been consistently reported as a typical characteristic of the DAP transition for ZnO [23, 24].

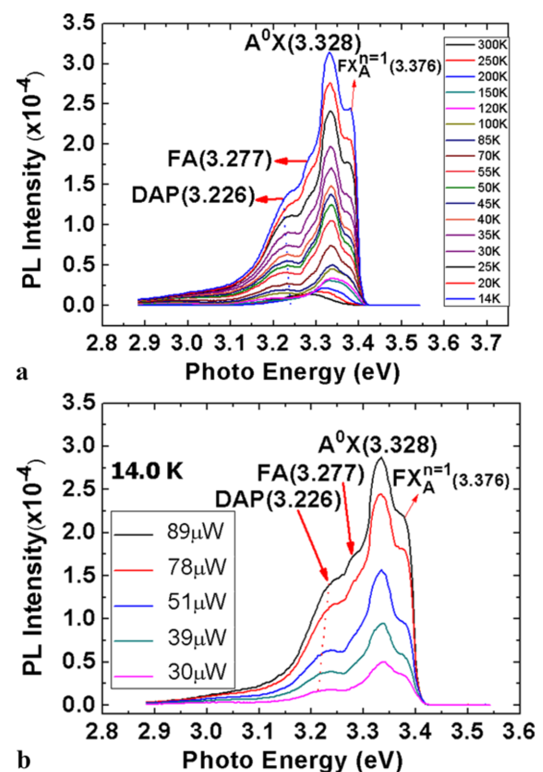

Fig. 2 Low-temperature PL spectra of (**a**) Ag-doped ZnO nanowires at temperatures ranging from 14 to 300 K. (**b**) Ag-doped ZnO nanowires under different excitation power at 14 K

In Fig. 2(b), the excitation power-dependent PL measurement results show the evolution of the DAP emission. The experiments were conducted at 14 K with different laser excitation power. With a decrease of the excitation power, the 3.226 eV emission exhibits an evident redshift. The peak

energy of such transition is given by the following equation [12]:

$$E_{DAP} = E_{gap} - E_D - E_A + e^2/4\pi\varepsilon R_{DAP} \tag{1}$$

where E_{DAP}, E_{gap}, E_D, E_A, e, ε and R_{DAP} are DAP transition energy, band gap energy, donor ionization energy, acceptor ionization energy, elementary charge constant, dielectric constant, and donor-acceptor pair distance, respectively. As the excitation intensity (power/area) decreases, the number of photo excited donor-acceptor pairs decreases, resulting in a longer donor-acceptor pair distance (R_{DAP}). Therefore, a DAP transition shifts to a lower energy.

Based on the FA peak position in Fig. 2(a), the acceptor binding energy (E_A) at 14 K can be calculated with [25]:

$$E_A = E_{gap} - E_{FA} + k_B T/2 \tag{2}$$

where E_{FA} is the temperature-dependent transition with an energy of 3.277 eV at 14 K, E_{gap} is the intrinsic band gap energy, which is approximately equal to 3.437 eV at 14 K, and k_B is Boltzmann constant. Thus, the value of E_A is calculated to be 0.158 eV.

In order to further prove p-type conductivity of the Ag-doped ZnO nanowires, electrical measurements on back-gated nanowire field effect transistors (NWFETs) were carried out. ZnO NWFETs were fabricated by standard photolithography. Ag-doped ZnO nanowires were first dispersed in isopropyl alcohol, and subsequently transferred to a p^+-silicon wafer with a 300 nm thick silicon oxide on the surface. Microcontact windows were defined on the ends of the nanowires, and then the Ni/Au electrodes were formed by e-beam deposition and subsequent lift-off. The p^+-silicon substrate served as the back-gate electrode of the transistor. The inset in Fig. 3(a) shows the SEM image of the NWFET. The drain current (I_d) versus gate voltage (V_g) curve under a drain bias (V_d) of 10 V and I_d versus V_d curves under different gate voltages are shown in Fig. 3(a) and Fig. 3(b), respectively. The drain current decreases as the increase of the gate voltage from −30 V to 30 V, suggesting that the Ag-doped ZnO nanowires exhibit p-type behavior. The hole concentration (P) in nanowires can be estimated by using the following equation [26]:

$$P = \left(\frac{V_{th}}{q}\right) \times \left(\frac{2\pi\varepsilon_r\varepsilon_0}{\ln(4h/d)}\right) \times \left(\frac{1}{\pi d^2/4}\right) \tag{3}$$

where ε_r, ε_0, h, d, V_{th}, and q are the effective dielectric constant ($\varepsilon_r = 3.9$ for SiO_2), dielectric constant of vacuum, thickness of dielectric layer (300 nm), nanowire diameter (250 nm), threshold voltage of the ZnO NWFET (∼28 V) and elementary charge constant, respectively. From (3), the hole concentration is calculated to be 4.9×10^{17} cm^{-3}. The mobility can be calculated by using [26]:

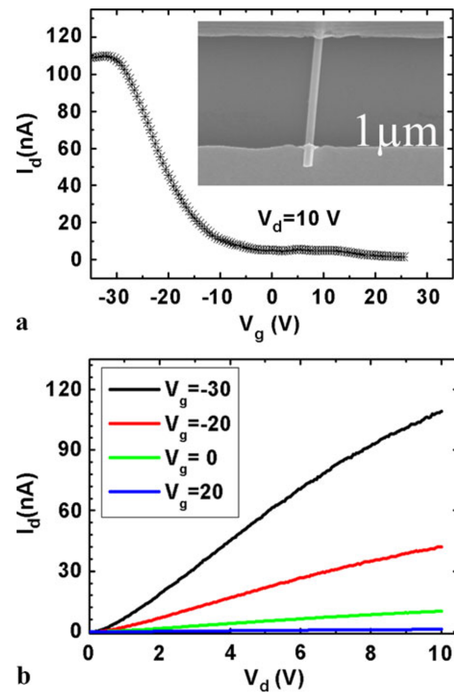

Fig. 3 (**a**) I_d–V_g curve of the ZnO NWFET under $V_d = 10$ V. Inset shows the SEM image of the NWFET. (**b**) I_d–V_d curves of the ZnO NWFET recorded at different gate voltages

$$\mu = \left(\frac{dI}{dV_g}\right) \times \left(\frac{\ln(\frac{4h}{d})}{2\pi\varepsilon_r\varepsilon_0}\right) \times \left(\frac{L}{V_d}\right) \tag{4}$$

where μ, L, and V_d is the mobility, channel length (∼3 μm in the NWFET) and drain bias (10 V), respectively. $\frac{dI}{dV_g} = 7.16\text{e}{-}009$ A/V can be extrapolated from the linear region of the I_d–V_g curve. From (4), the hole mobility is calculated as approximately 0.18 cm^2 V^{-1} s^{-1}.

In summary, Ag-doped ZnO nanowires have been grown via CVD process. The PL spectrum of the Ag-doped nanowires shows an Ag-related peak at 3.328 eV at 14 K, which can be attributed to neutral-acceptor-bound excitons (A°X). Temperature- and excitation power-dependent PL spectra confirm shallow acceptor level of 0.158 eV. The electrical measurement results suggest that the conductivity of Ag-doped ZnO nanowires is p-type and the hole mobility is approximately 0.18 cm^2 V^{-1} s^{-1}. After 5 months (by the time of the publication this paper), however, originally p-type Ag-doped ZnO nanowires turned into n-type judging from NWFET measurements. Therefore, long-term p-type stability of Ag-doped ZnO nanowires is still an issue.

Acknowledgement This research was partly supported by NSF (EECS-0900978).

References

1. E.O. Kane, Phys. Rev. B **18**, 6849 (1978)
2. C. Klingshirn, Phys. Status Solidi B **244**, 3027 (2007)
3. D.C. Look, Mater. Sci. Eng. B **80**, 383 (2001)
4. S. Chu, J.H. Lim, L.J. Mandalapu, Z. Yang, L. Li, J.L. Liu, Appl. Phys. Lett. **92**, 152103 (2008)
5. S.F. Yu, C. Yuan, S.P. Lau, W.I. Park, G. Yi, Appl. Phys. Lett. **84**, 3241 (2004)
6. L.K. van Vugt, S. Ruhle, D. Vanmaekelbergh, Nano Lett. **6**, 2707 (2006)
7. L.J. Mandalapu, F.X. Xiu, Z. Yang, D.T. Zhao, J.L. Liu, Appl. Phys. Lett. **88**, 112108 (2006)
8. L.J. Mandalapu, Z. Yang, F.X. Xiu, D.T. Zhao, J.L. Liu, Appl. Phys. Lett. **88**, 092103 (2006)
9. C.G. Van de Walle, Phys. Rev. Lett. **85**, 1012 (2000)
10. S.S. Lin, H.P. He, Y.F. Lu, Z.Z. Ye, J. Appl. Phys. **106**, 093508 (2009)
11. H.S. Kang, B.D. Ahn, J.H. Kim, G.H. Kim, S.H. Lim, H.W. Chang, S.Y. Lee, Appl. Phys. Lett. **88**, 202108 (2006)
12. D.K. Hwang, H.S. Kim, J.H. Lim, J.Y. Oh, J.H. Yang, S.J. Park, K.K. Kim, D.C. Look, Y.S. Park, Appl. Phys. Lett. **86**, 151917 (2005)
13. K.K. Kim, H.S. Kim, D.K. Hwang, J.H. Lim, S.J. Park, Appl. Phys. Lett. **83**, 63 (2003)
14. T.S. Jeong, M.S. Han, C.J. Youn, Y.S. Park, J. Appl. Phys. **96**, 175 (2004)
15. F.X. Xiu, Z. Yang, L.J. Mandalapu, D.T. Zhao, J.L. Liu, W.P. Beyermann, Appl. Phys. Lett. **87**, 152101 (2005)
16. B. Xiang, P.W. Wang, X.Z. Zhang, S.A. Dayeh, D.P. Aplin, C. Soci, D.P. Yu, D.L. Wang, Nano Lett. **7**, 323 (2007)
17. G.D. Yuan, W.J. Zhang, J.S. Jie, X. Fan, J.A. Zapien, Y.H. Leung, L.B. Luo, P.F. Wang, C.S. Lee, S.T. Lee, Nano Lett. **8**, 2591 (2008)
18. W. Liu, F.X. Xiu, K. Sun, Y.H. Xie, K.L. Wang, Y. Wang, J. Zou, Z. Yang, J.L. Liu, J. Am. Chem. Soc. **132**, 2498 (2010)
19. Y. Kanai, Jpn. J. Appl. Phys. **30**, 2021 (1991)
20. Y.W. Song, K. Kim, J.P. Ahn, G.E. Jang, S.Y. Lee, Nanotechnology **20**, 275606 (2009)
21. M.A. Thomas, J.B. Cui, J. Phys. Chem. Lett. **1**, 1090 (2010)
22. Ü. Özgür, Ya.I. Alivov, C. Liu, A. Teke, M.A. Reshchikov, S. Doğan, V. Avrutin, S.-J. Cho, H. Morkoç, J. Appl. Phys. **98**, 041301 (2005)
23. K. Tamura, T. Makino, A. Tsukazaki, M. Sumiya, S. Fuke, T. Furumochi, M. Lippmaa, C.H. Chia, Y. Segawa, H. Koinuma, M. Kawasaki, Solid State Commun. **127**, 265 (2003)
24. K. Thonke, T. Gruber, N. Teofilov, R. Schonfelder, A. Waag, R. Sauer, Physica B **308**, 945 (2001)
25. Y.R. Ryu, T.S. Lee, H.W. White, Appl. Phys. Lett. **83**, 87 (2003)
26. R. Martel, T. Schmidt, H.R. Shea, T. Hertel, Ph. Avouris, Appl. Phys. Lett. **73**, 2447 (1998)