

ZnO-based MIS photodetectors

S.J. Young^a, L.W. Ji^b, S.J. Chang^{a,*}, S.H. Liang^a, K.T. Lam^c, T.H. Fang^b,
K.J. Chen^a, X.L. Du^d, Q.K. Xue^d

^a Institute of Microelectronics & Department of Electrical Engineering, National Cheng Kung University, Tainan 70101, Taiwan

^b Institute of Electro-Optical and Materials Science, National Formosa University, Yunlin 632, Taiwan

^c Department of Information Communication Leader University, Tainan 701, Taiwan

^d Beijing National Laboratory of Electron Microscopy for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100080, PR China

Received 3 August 2006; received in revised form 26 August 2006; accepted 2 October 2006

Available online 7 November 2006

Abstract

We report the fabrication of ZnO-based metal–insulator–semiconductor (MIS) and metal–semiconductor–metal (MSM) photodetectors. With 5 V applied bias, it was found that photocurrent to dark current contrast ratios of the ZnO MSM and MIS photodetectors were 2.9×10^2 and 3.2×10^4 , respectively. It was also found that measured responsivities were 0.089 and 0.0083 A/W for the ZnO MSM and MIS photodetectors, respectively, when the incident light wavelength was 370 nm. Furthermore, it was found that ultraviolet (UV) to visible rejection ratios for the fabricated ZnO MSM and MIS photodetectors were 2.4×10^2 and 3.8×10^3 , respectively.

© 2006 Elsevier B.V. All rights reserved.

PACS: 81.05.Dz; 81.15.Gh; 78.66.Hf; 85.60.Gz

Keywords: ZnO; Semiconducting II–VI materials; Photodiodes

1. Introduction

In recent years, much research has been focused on high performance solid state ultraviolet (UV) photodetectors [1]. Photodetectors operating in the UV region are important devices that can be used in various commercial and military applications. For example, visible-blind UV photodetectors can be used in space communications, ozone layer monitoring and flame detection. Currently, light detection in the UV spectral range still uses Si-based optical photodiodes. Although, Si-based photodiodes are sensitive to visible and infrared radiation, the responsivity in the UV region is low since the room temperature bandgap energy of Si is only of 1.2 eV. With the advent of optoelectronic devices fabricated on wide direct band gap materials, it becomes possible to produce high performance solid-state photodetectors that are sensitive in the UV region. For example, GaN-based UV photodetectors are already commercially available [2,3]. ZnSe-based UV photodetectors have also been demonstrated [4].

ZnO is another wide direct bandgap material that is sensitive in the UV region [5,6]. The large exciton binding energy of 60 meV and wide bandgap energy of 3.37 eV at room temperature make ZnO a promising photonic material for applications such as light emitting diodes, laser diodes and UV photodiodes. Indeed, ZnO has attracted much attention in recent years [7–9]. High quality ZnO epitaxial layers can be grown by metalorganic chemical vapor deposition [5], molecular beam epitaxy (MBE) [10] and pulsed laser deposition [11] on top of ZnO substrates [6], sapphire substrates [12] and epitaxial GaN layers [13]. ZnO Schottky diodes and metal–semiconductor–metal (MSM) photodetectors detecting in the UV region have also been demonstrated [8]. MSM photodetectors consist of two interdigitated Schottky contacts deposited on top of an active layer. The reduced parasitic capacitance of this structure, as well as the low dark current and noise values, and its linearity with optical power, make MSM detectors the most promising candidates for high-speed photodetection [14–16]. To achieve high performance MSM UV photodetectors, it is important to improve crystal quality and to achieve large Schottky barrier height at metal–semiconductor interface. A large barrier height leads to small leakage current and high breakdown voltage

* Corresponding author. Tel.: +886 6 2757575x62391; fax: +886 6 2761854.
E-mail address: changsj@mail.ncku.edu.tw (S.J. Chang).

which could result in improved responsivity and photocurrent to dark current contrast ratio. To achieve a large Schottky barrier height on ZnO, one can choose metals with high work functions [17]. However, many of the high work function metals are not stable. In other words, severe inter-diffusion might occur at metal–ZnO interface. To solve this problem, one can insert an insulating layer between metal and the underneath ZnO [18]. With the insulating layer, we can also effectively suppress leakage current of the photodetectors. In this paper, we report the fabrication of ZnO-based metal–insulator–semiconductor (MIS) UV photodetectors. Optical and electrical properties of the fabricated photodetectors will also be discussed.

2. Experiments

Samples used in this study were all grown by radio frequency (rf) plasma-assisted MBE (Omni Vac) on sapphire (0001) substrates. The base pressure in the growth chamber was $\sim 1.4 \times 10^{-11}$ Pa. The source material of Zn was elemental Zn (6N) evaporated from a commercial Knudsen cell (Crea Tech). Active oxygen and nitrogen radicals were separately produced by two rf-plasma systems (SVTA). The flow rate of oxygen/nitrogen gas was controlled by a mass flow controller (ROD-4, Aera). Prior to the growth, we first degreased sapphire substrates in trichloroethylene and acetone. These sapphire substrates were then etched in $\text{H}_2\text{SO}_4:\text{H}_3\text{PO}_4 = 3:1$ at 110°C for 30 min followed by rinsing in de-ionized water. The sapphire substrates were then loaded into the growth chamber. We then exposed the sapphire substrates to oxygen radicals for 30 min at 180°C with 350 W rf power and 2.5 sccm oxygen flux so as to form oxygen-terminated sapphire surface. After this treatment, we exposed the sapphire substrates to nitrogen radicals for 1 h at 180°C with 480 W rf power and 3.0 sccm nitrogen flux for nitridation. It should be noted that the formation of a uniform O-terminated surface prior to nitridation is crucial for the formation of the N-polar AlN and the suppression of the Zn-polar inversion domains (the Zn-polar domains in an O-polar ZnO matrix, for instance). It should also be noted that nitridation involves the diffusion of nitrogen atoms into sapphire and the substitution for oxygen. We can thus achieve N-polar AlN thin layer due to atom substitution [19] and subsequently achieve uniform O-polar ZnO films. From the reflection high energy electron diffraction patterns, it was found that a very thin AlN layer (~ 2 nm) was formed with a 30° in-plane rotation of its lattice with respect to that of sapphire substrates after nitridation. We subsequently grew a 1000 nm-thick unintentionally doped ZnO epitaxial layer with conventional two-step growth method, i.e., a low temperature buffer layer grown at 400°C and a high temperature layer grown at 650°C . After the growth, we in-situ annealed the ZnO epitaxial layer at 750°C . At this moment, we observed 3×3 reconstruction pattern which indicates O-polar of our ZnO films [20]. From room temperature Hall measurements, it was found that carrier concentration of the as-grown ZnO films was $2.8 \times 10^{16} \text{ cm}^{-3}$. Room temperature photoluminescence (PL) and X-ray diffraction (XRD) measurements were also performed to evaluate quality of the as-grown samples.

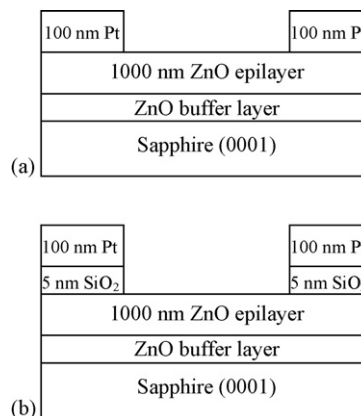


Fig. 1. Structure of (a) ZnO MSM photodetector, (b) ZnO MIS photodetector.

ZnO MSM and MIS photodetectors were then fabricated. Prior to metal deposition, we cleaned the ZnO samples by acetone and methanol. For MSM photodetectors, we deposited 100 nm-thick Pt film onto the sample surface by electron beam evaporation to serve as metal contacts. Standard lithography and etching were then performed to define the interdigitated contact pattern. For MIS photodetectors, we first deposited 5 nm-thick SiO₂ by plasma enhanced chemical vapor deposition (PECVD) followed by the same Pt film deposition and photolithography. The fingers of the Pt contact electrodes were $10 \mu\text{m}$ wide and $180 \mu\text{m}$ long with a spacing of $10 \mu\text{m}$. The active areas of the fabricated MSM and MIS photodetectors were all kept at $200 \times 200 \mu\text{m}^2$. The schematic structures of the MSM and MIS photodetectors fabricated in this study were shown in Fig. 1(a) and (b), respectively. Room temperature current–voltage (I – V) characteristics of the devices were then measured by an HP 4145 semiconductor parameter analyzer under both darkness and illumination. For photocurrent measurements, a He–Cd laser was used as the light source. A 250 W xenon arc lamp was used as the light source for spectral responsivity measurements. The monochromatic light, calibrated with UV-enhanced Si photodetectors and an optical power meter, was collimated onto each photodetector via an optical fiber.

3. Results and discussion

Fig. 2 shows room temperature PL spectrum of our ZnO epitaxial films. It was found that we observed a strong excitonic related PL peak at 379 nm (3.27 eV). It was also found that full-width-half-maximum (FWHM) of the excitonic related PL peak was only 74 meV [12]. It should be noted that no oxygen vacancy related defect peaks could be found in the spectrum. These results all indicate good crystal quality of our ZnO epitaxial layers [12]. The inset of Fig. 2 shows measured XRD spectrum of the 1000 nm-thick ZnO epitaxial film prepared on sapphire substrate. The peak located at $2\theta = 41.9^\circ$ in the spectrum was originated from the (006) plane of sapphire substrate. We also observed a ZnO (002) XRD peak at $2\theta = 34.3^\circ$ with a FWHM of 0.11° . Such a result indicates that the ZnO film was preferentially grown in c -axis direction. The small FWHM of

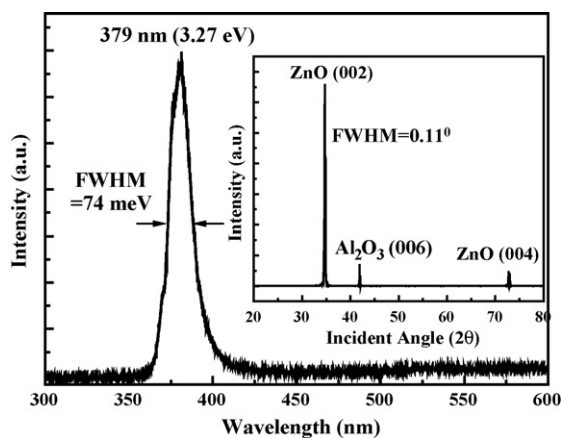


Fig. 2. Room temperature PL spectrum of epitaxial ZnO films. The inset shows XRD spectrum of the epitaxial ZnO films prepared on sapphire substrate.

the ZnO (002) XRD peak again indicates good crystal quality of our samples.

Fig. 3 shows I - V characteristics of the two fabricated ZnO photodetectors measured in darkness (dark current) and under 370 nm illumination (photocurrent) while the incident optical power was 100 mW. The dark current is originated from thermionic emission of carriers. It can be seen clearly that dark currents measured from MIS photodetector were much smaller than that measured from MSM photodetector. With 5 V applied bias, it was found that measured dark currents were 4.11×10^{-7} and 2.22×10^{-10} A for the fabricated MSM and MIS photodetectors, respectively. In other words, we can reduce dark current by more than three orders of magnitude by inserting the 5 nm-thick SiO₂. Such a significant reduction could be attributed partially to the insulating nature of SiO₂ and partially to the effective passivation of ZnO surface states by the SiO₂ layer. Compared with the photocurrent of ZnO MSM photodetector, it was found that photocurrent measured from ZnO MIS photodetector was small. With 5 V applied bias, it was also found that measured photocurrents were 1.2×10^{-4} and 7.12×10^{-6} A for the ZnO MSM and MIS photodetectors, respectively. Furthermore, photocurrent to dark current contrast ratios for these two photodetectors can be determined from the measured dark currents and photocurrents, as shown in Fig. 4. With 5 V applied

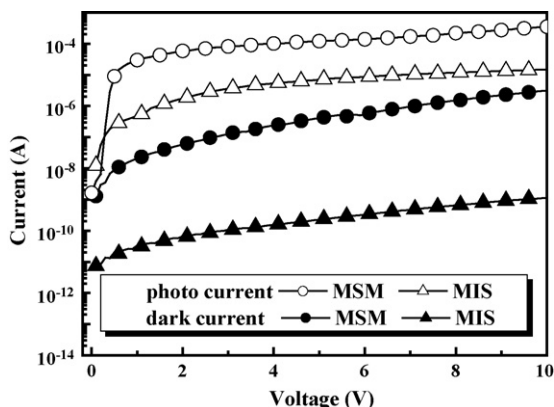


Fig. 3. I - V characteristics of the two fabricated ZnO photodetectors measured in dark and under 370 nm illumination.

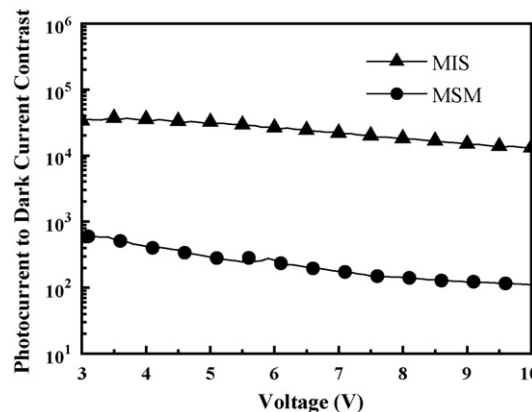
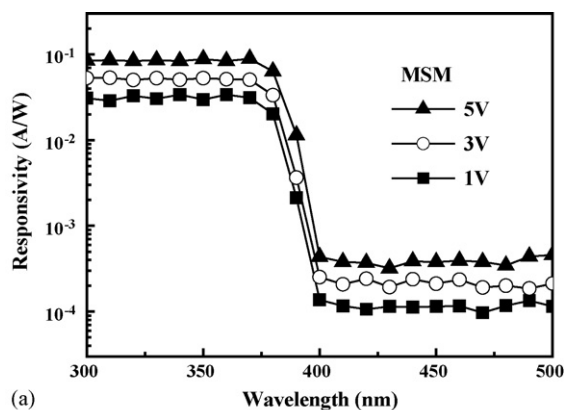


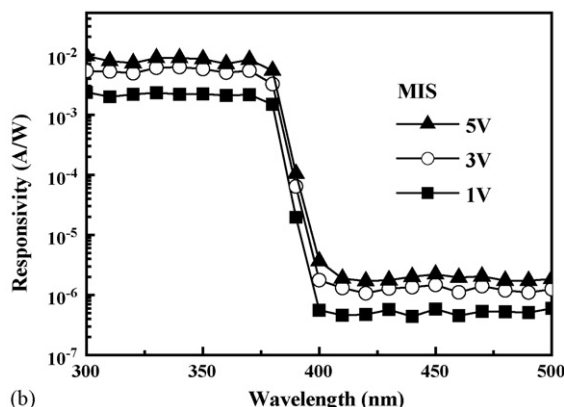
Fig. 4. Photocurrent to dark current contrast ratios for these two photodetectors.

bias, it was found that photocurrent to dark current contrast ratios of the ZnO MSM and MIS photodetectors were 2.9×10^2 and 3.2×10^4 , respectively. In other words, we can achieve much larger photocurrent to dark current contrast ratio from the ZnO MIS photodetector.

Fig. 5(a) and (b) show measured optical responsivities of the ZnO MSM and MIS photodetectors, respectively. It was found that sharp cutoff occurred at around 370 nm for both detectors. With incident light wavelength of 370 nm and 5 V applied bias, the measured responsivities were 0.089 and 0.0083 A/W for the ZnO MSM and MIS photodetectors, respectively. The smaller



(a)



(b)

Fig. 5. Measured spectral responsivities of the (a) ZnO MSM and (b) MIS photodetectors.

responsivity observed from ZnO MIS photodetector can again be attributed to the insertion of highly resistive SiO₂ layer. It was found that responsivity in the long wavelength stop band was also smaller for ZnO MIS photodetector, as compared to that measured from ZnO MSM photodetector. This agrees well with the smaller dark current for ZnO MIS photodetector. Here, we define UV to visible rejection ratio as the responsivity measured at 370 nm divided by the responsivity measured at 450 nm. With such definition and 5 V applied bias, it was found that UV to visible rejection ratios for the fabricated ZnO MSM and MIS photodetectors were 2.4×10^2 and 3.8×10^3 , respectively. These values indicate that we can also significantly enhance UV to visible rejection ratio by inserting a SiO₂ into our ZnO photodetectors. The large 3.8×10^3 UV to visible rejection ratio also suggests ZnO MIS photodetectors are potentially useful for practical applications.

4. Summary

In summary, ZnO epitaxial films were grown on sapphire (000 1) substrates by MBE. ZnO MSM and MIS UV photodetectors were fabricated. It was found that we can achieve smaller dark current, larger photocurrent to dark current contrast ratio and larger UV to visible rejection ratio from the ZnO MIS UV photodetector.

Acknowledgement

This work was supported by National Science Council under contract number NSC-94-2215-E-150-009.

References

- [1] M. Razeghi, A. Rogalski, Semiconductor ultraviolet detectors, *J. Appl. Phys.* 79 (1996) 7473–7844.
- [2] C.H. Chen, S.J. Chang, Y.K. Su, G.C. Chi, J.Y. Chi, C.A. Chang, J.K. Sheu, J.F. Chen, GaN metal–semiconductor–metal ultraviolet photodetectors with transparent indium–tin–oxide Schottky Contacts, *IEEE Photon Technol. Lett.* 13 (2001) 848–850.
- [3] D.V. Kuksenkov, H. Temkin, A. Osinsky, R. Gaska, M.A. Khan, Low-frequency noise and performance of GaN p–n junction photodetectors, *J. Appl. Phys.* 83 (1998) 2142–2146.
- [4] S.J. Chang, T.K. Lin, Y.K. Su, Y.Z. Chiou, C.K. Wang, S.P. Chang, C.M. Chang, J.J. Tang, B.R. Huang, Homoepitaxial ZnSe MSM photodetectors with various transparent electrodes, *Mater. Sci. Eng. B* 127 (2006) 164–168.
- [5] T.M. Barnes, J. Leaf, S. Hand, C. Fry, C.A. Wolden, A comparison of plasma-activated N₂/O₂ and N₂O/O₂ mixtures for use in ZnO:N synthesis by chemical vapor deposition, *J. Appl. Phys.* 96 (2004) 7036–7044.
- [6] H. Kato, M. Sano, K. Miyamoto, T. Yao, Homoepitaxial growth of high-quality Zn-polar ZnO films by plasma-assisted molecular beam epitaxy, *Jpn. J. Appl. Phys.* 42 (2003) L1002–L1005.
- [7] Y.I. Alivov, E.V. Kalinina, A.E. Cherenkov, D.C. Look, B.M. Ataev, A.K. Omaev, M.V. Chukichev, D.M. Bagnall, Fabrication and characterization of n-ZnO/p-AlGaIn heterojunction light-emitting diodes on 6H-SiC substrates, *Appl. Phys. Lett.* 83 (2003) 4719–4721.
- [8] S.J. Young, L.W. Ji, S.J. Chang, Y.K. Su, ZnO metal–semiconductor–metal ultraviolet sensors with various contact electrodes, *J. Cryst. Growth* 293 (2006) 43–47.
- [9] A. Mang, K. Reimann, St. Rübenacke, Band gaps, crystal-field splitting, spin-orbit coupling, and exciton binding energies in ZnO under hydrostatic pressure, *Solid State Commun.* 94 (1995) 251–254.
- [10] A. Setiawan, Z. Vashaei, M.W. Cho, T. Yao, H. Kato, M. Sano, K. Miyamoto, I. Yonenaga, H.J. Ko, Characteristics of dislocations in ZnO layers grown by plasma-assisted molecular beam epitaxy under different Zn/O flux ratios, *J. Appl. Phys.* 96 (2004) 3763–3768.
- [11] E.M. Kaidashev, M. Lorenz, H. von Wenckstern, A. Rahm, H.C. Semmelhack, K.H. Han, G. Benndorf, C. Bundesmann, H. Hochmuth, M. Grundmann, High electron mobility of epitaxial ZnO thin films on c-plane sapphire grown by multistep pulsed-laser deposition, *Appl. Phys. Lett.* 82 (2003) 3901–3903.
- [12] K. Sakurai, D. Iwata, S. Fujita, S. Fujita, Growth of ZnO by molecular beam epitaxy using NO₂ as oxygen source, *Jpn. J. Appl. Phys.* 38 (1999) 2606–2608.
- [13] H.J. Ko, Y.F. Chen, S.K. Hong, T. Yao, MBE growth of high-quality ZnO films on epi-GaN, *J. Cryst. Growth* 209 (2000) 816–821.
- [14] R.P. Joshi, A.N. Dharamsi, J. McAdoo, Simulation for the high-speed response of GaN metal–semiconductor–metal photodetectors, *Appl. Phys. Lett.* 64 (1994) 3611–3613.
- [15] E. Monroy, F. Calle, J.L. Pau, E. Munoz, F. Omnes, B. Beaumont, P. Gibart, Application and performance of GaN based UV detectors, *Phys. Status Solidi A* 185 (2001) 91–97.
- [16] J.C. Carrano, T. Li, P.A. Grudowski, C.J. Eiting, R.D. Dupuis, J.C. Campbell, Comprehensive characterization of metal–semiconductor–metal ultraviolet photodetectors fabricated on single-crystal GaN, *J. Appl. Phys.* 83 (1998) 6148–6160.
- [17] F.D. Auret, S.A. Goodman, M. Hayes, M.J. Legodi, H.A. van Laarhoven, D.C. Look, Electrical characterization of 1.8 MeV proton-bombarded ZnO, *Appl. Phys. Lett.* 79 (2001) 3074–3076.
- [18] A. Chini, J. Wittich, S. Heikman, S. Keller, S.P. DenBaars, U.K. Mishra, Power and linearity characteristics of GaN MISFETs on sapphire substrate, *IEEE Electron Device Lett.* 25 (2004) 55–57.
- [19] Z.X. Mei, Y. Wang, X.L. Du, M.J. Ying, Z.Q. Zeng, H. Zheng, J.F. Jia, Q.K. Xue, Z. Zhang, Controlled growth of O-polar ZnO epitaxial film by oxygen radical preconditioning of sapphire substrate, *J. Appl. Phys.* 96 (2004) 7108–7111.
- [20] Y.F. Chen, H.J. Ko, S.K. Hong, T. Yao, Layer-by-layer growth of ZnO epilayer on Al₂O₃ (0 0 0 1) by using a MgO buffer layer, *Appl. Phys. Lett.* 76 (2000) 559–561.

Biographies

S.J. Young received his BS degree from Department of Physics, National Changhua University of Education, Changhua, Taiwan in 2003, MS degree from Institute of Electro-Optical Science and Engineering, National Cheng Kung University (NCKU) in 2005. Currently, he is working toward his PhD degree in the Institute of Microelectronics, NCKU, Tainan, Taiwan.

L.W. Ji received his PhD degree from the Institute of Microelectronics, National Cheng Kung University, Tainan, Taiwan in 2004. Currently, he is an associate professor with the Institute of Electro-Optical and Materials Science, National Formosa University, Yunlin, Taiwan.

S.J. Chang was born in Taipei, Taiwan on January 17, 1961. He received his BSEE degree from National Cheng Kung University (NCKU), Tainan, Taiwan in 1983, MSEE degree from State University of New York, Stony Brook in 1985 and PhDEE from University of California, Los Angeles in 1989. He was a research scientist in NTT Basic Research Laboratories, Musashino, Japan from 1989 to 1992. He became an Associate Professor in EE Dept. NCKU in 1992 and was promoted to full Professor in 1998. Currently, he also serves as the Director of Semiconductor Research Center in NCKU. He was a Royal Society Visiting Scholar in University of Wales, Swansea, UK from January 1999 to March 1999, a Visiting Scholar in Research Center for Advanced Science and Technology, University of Tokyo, Japan from July 1999 to February 2000, a Visiting Scholar in Institute of Microstructural Science, National Research Council, Canada from August 2001 to September 2001, a Visiting Scholar in Institute of Physics, Stuttgart University, Germany from August 2002 to September 2002 and a Visiting Scholar in Waseda University, Japan from July 2004 to September 2004. He is also a honorary professor of Changchun University of

Science and Technology, China. He received outstanding research award from National Science Council, Taiwan in 2004. His current research interests include semiconductor physics and optoelectronic devices.

S.H. Liang received his BS degree from National Changhua University of Education, Changhua, Taiwan in 2005. Currently, he is working toward his MS degree in the Institute of Nanotechnology and Nanosystems Engineering, National Cheng Kung University, Tainan, Taiwan.

K.T. Lam received his PhD degree from Department of Mechanical Engineering, National Sun Yat-Sen University, Kaohsiung, Taiwan. Currently, he is an associate professor with the Department of Information Communication, Leader University, Tainan, Taiwan.

T.H. Fang received his PhD degree from Department of Mechanical Engineering, National Cheng Kung University, Tainan, Taiwan. Currently, he is an

associate professor with the Institute of Electro-Optical and Materials Science, National Formosa University, Yunlin, Taiwan.

K.J. Chen received his MS degree from Department of Mechanical Engineering, Southern Taiwan University of Technology, Tainan, Taiwan in 2006. Currently, he is working toward his PhD degree in the Institute of Microelectronics, National Cheng Kung University, Tainan, Taiwan.

X.L. Du received his PhD from Beijing Institute of Technology, Beijing, China in 1999. Currently, he is a Research Scientist with the Institute of Physics, Chinese Academy of Sciences, Beijing, China.

Q.K. Xie received PhD degree from Institute of Physics, Chinese Academy of Sciences, Beijing, China in 1994. Currently, he is the professor and head of Surface Physics Lab., Institute of Physics, Chinese Academy of Sciences, Beijing, China.