Sensors and Actuators B 198 (2014) 110–113

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Highly sensitive mixed-potential-type NO_2 sensor with YSZ processed using femtosecond laser direct writing technology

Yingzhou Guan [a], Chunhao Li [a], Xiaoyang Cheng [a], Biao Wang [c], Ruize Sun [a], Xishuang Liang [a,*], Jihong Zhao [a], Hong Chen [b], Geyu Lu [a,**]

[a] State Key Laboratory on Integrated Optoelectronics, College of Electronic Science and Engineering, Jilin University, 2699 Qianjin Street, Changchun 130012, China

[b] College of Communication Engineering, Department of Control Science and Engineering, Jilin University, Changchun 130012, China

[c] State Key Laboratory of Luminescence and Application, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033, China

ARTICLE INFO

Article history:
Received 9 December 2013
Received in revised form 6 February 2014
Accepted 27 February 2014
Available online 18 March 2014

Keywords:
YSZ
Femtosecond laser direct writing
Mixed-potential
NO_2 sensor
Three-phase-boundary

ABSTRACT

High performance mixed-potential-type NO_2 sensors using yttria-stabilized zirconia (YSZ) electrolyte with $NiCr_2O_4$ sensing-electrode were fabricated. The femtosecond laser direct writing technology was used to process YSZ-substrate to construct structured surface. The results of scanning electron microscope (SEM) revealed that porous micron-sized groove was formed on the surface of YSZ-substrate by the radiation of 800-nm femtosecond laser. The sensor using processed YSZ-substrate outputted larger signal than the sensor using unprocessed YSZ-substrate in NO_2 containing atmosphere at 800 °C which might be attributable to the enlargement of TPB (three-phase-boundary). In addition, the sensor maintained good response-recovery transients, repeatability and cross-sensitivity.

1. Introduction

The emission of nitrogen oxides (NOx) has caused serious pollution problems such as acid rain and photochemical smog. In order to monitor the emission of NOx, high performance NOx sensors are urgently demanded. At present, special attentions have been paid to YSZ-based gas sensors owing to their simple structure, attractive sensitivity and sustainability in hostile condition [1–6].

In order to improve the performance of YSZ-based NOx sensors, many studies have been focused on exploring new electrode materials [7–13]. In recent years, modification of structure of the electrode proves to be another effective method to improve the performance. For example, Park et al. formed three-dimensional TPB by mixing NiO with YSZ as the sensing electrode [14]. Liang et al. obtained YSZ-substrate with larger surface by hydrofluoric acid corrosion method [15]. These methods can significantly improve the response to NOx. However, the randomness of above methods makes it difficult to repeat the same structure in each experiment. In this case, a method of constructing structured surface which can ensure reproducibility is urgently needed.

Laser direct writing technology which can accurately control the surface structure has been widely used in 3D-fabrication. So far, there are few reports about constructing structured surface of YSZ-substrate by this technology. In this work, femtosecond laser direct writing was used to form porous micron-sized groove on the surface of YSZ-substrate. High performance mixed-potential-type NO_2 sensor using the processed YSZ-substrate with $NiCr_2O_4$ sensing electrode was fabricated and tested.

2. Experimental

The schematic of femtosecond laser direct writing system was shown in Fig. 1. The surface of YSZ-substrate (8 wt.% Y_2O_3-doped, 2 mm × 2 mm, 0.2 mm thickness, Tosoh Corp., Japan) was processed by titanium sapphire amplified femtosecond laser (SPTF-100F-1KHPR) with 800-nm wavelength, 200-mW power, 150-fs pulse width, 1-kHz pulse recurrence frequency and 50-μm facula diameter. The focused femtosecond laser can cause the sublimation of YSZ. The YSZ-substrate was placed on the Transfer Stage which could motion along two orthogonal directions under the control

* Corresponding author. Tel.: +86 431 85168384; fax: +86 431 85167808.
** Corresponding author. Tel.: +86 431 85167808; fax: +86 431 85167808.
E-mail addresses: liangxs@jlu.edu.cn (X. Liang), lugy@jlu.edu.cn (G. Lu).

http://dx.doi.org/10.1016/j.snb.2014.02.098

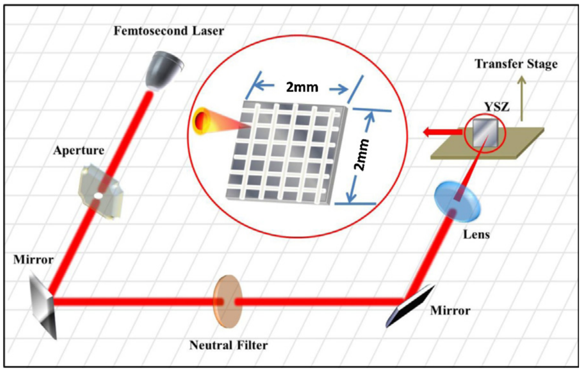

Fig. 1. Schematic of femtosecond laser direct writing system.

of PC. Two kinds of grooves array pattern with different groove spacing were formed on the surface of YSZ-substrate.

The planar NO_2 sensors were fabricated using the processed YSZ-substrate with $NiCr_2O_4$ synthesized by citric acid method [16]. The structure of the planar NO_2 sensor was showed in Fig. 2. The stripe-shaped Pt (0.5 mm × 2 mm) acted as reference electrode (RE) and $NiCr_2O_4$ covering the point-shaped Pt (0.8 mm × 2 mm) acted as sensing electrode (SE). The devices were sintered at 900 °C for 2 h.

Field-emitting Scanning Electron Microscopy (FE-SEM; JEOL, JSM-7500, Japan) was used to observe the surface of YSZ-substrate. The NO_2 sensing characteristics were measured by increasing NO_2 concentration from 5 ppm to 500 ppm (NO_2 + 21 vol.% O_2 + N_2 balanced) at the operating temperature of 800 °C. The electric potential difference between SE and RE was recorded by the digital electrometer (Digital Multimeter; Rigol Technologies, Inc., DM3054, China).

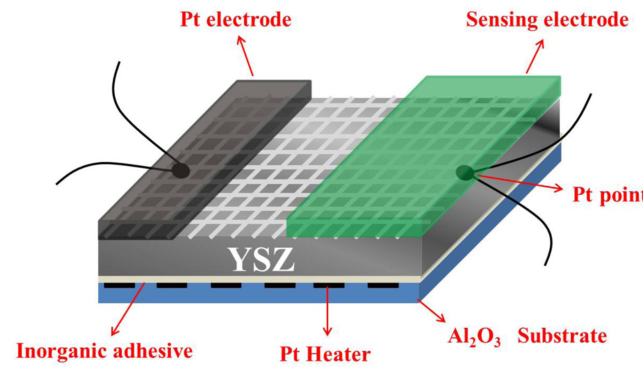

Fig. 2. Schematic of the sensor structure.

3. Results and discussion

Fig. 3a showed the SEM images of the smooth surface of unprocessed YSZ-substrate. Fig. 3b and c showed the surface of two kinds of processed YSZ-substrate with different groove spacing. Fig. 3d and e was the enlarge details of the surface. It could be seen clearly that micron-sized grooves were formed on the surface of YSZ-substrate. The groove spacing was 130 μm and 240 μm, respectively. Fig. 3f showed the rough and porous microstructure of these grooves. These porous grooves might provide larger contact area between YSZ and sensing electrode materials.

Fig. 4 exhibited the response transients to various NO_2 concentrations of the sensors using unprocessed YSZ-substrate and two kinds of processed YSZ-substrate (short for S (smooth), S (130 μm) and S (240 μm)). It could be seen that the sensors with processed YSZ-substrate increased the change of electric potential difference (ΔV) (electric potential difference (V_{NO2}) – electric potential difference (V_{air})) and the sensor S (130 μm) outputted the highest response value. The ΔV for sensor S (130 μm) to 100 ppm NO_2 was 100 mV. The response time for each sensor was about 8 s.

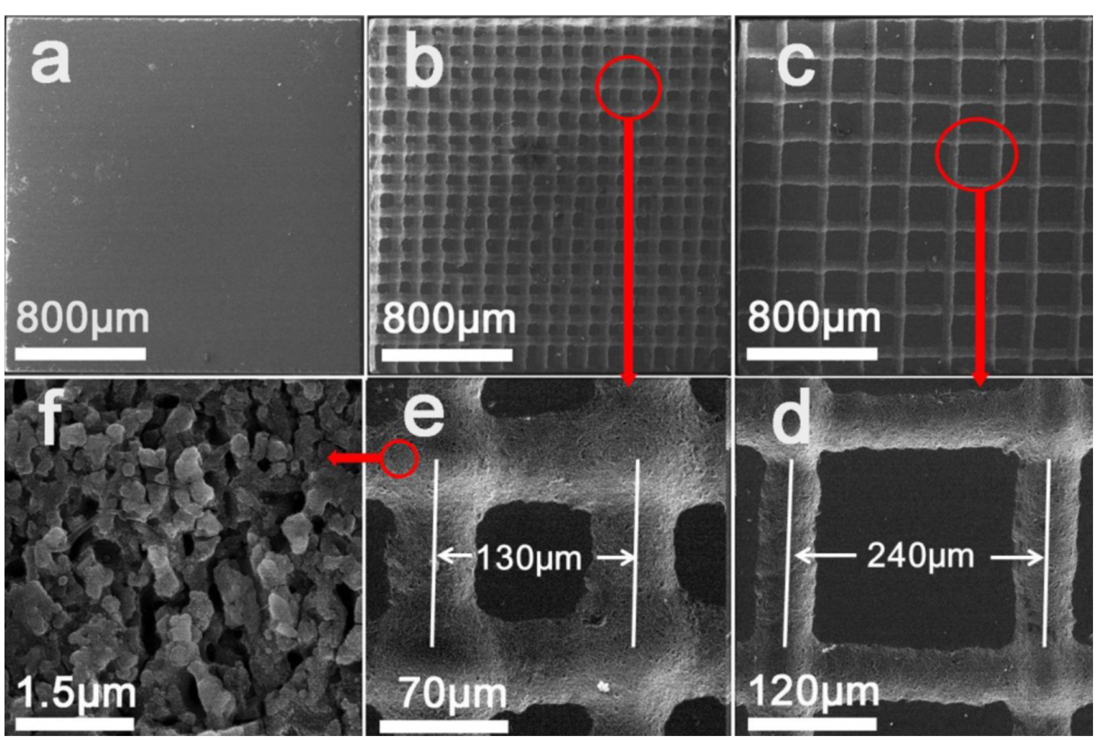

Fig. 3. SEM images of YSZ-substrate surface. (a) Unprocessed YSZ-substrate, (b) processed YSZ-substrate with 130 μm groove spacing, (c) processed YSZ-substrate with 240 μm groove spacing, (d) partially enlarged detail of (c), (e) partially enlarged detail of (b), (f) microstructure of YSZ-substrate where was irradiated by laser pulse.

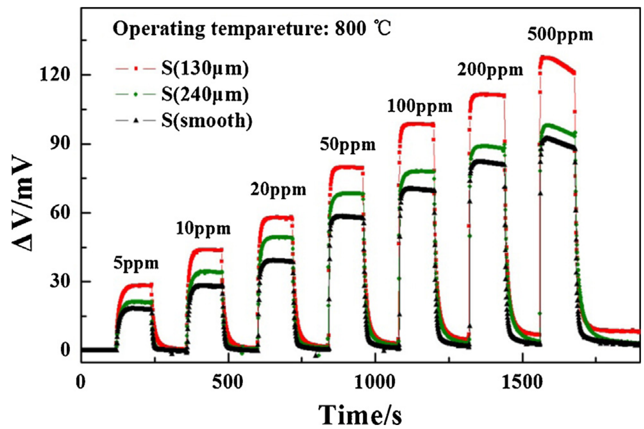

Fig. 4. Response transients of the sensors using unprocessed YSZ-substrate and processed YSZ-substrate with 130 μm and 240 μm groove spacing to various NO_2 concentrations in the range from 5 ppm to 500 ppm at 800 °C.

The sensing behavior of this kind of potentiometric sensor could be explained by mixed-potential mechanism [14–18]. The device could be described by the following electrochemical cells:

Inair : O_2, $NiCr_2O_4$/YSZ/Pt, O_2

Insamplegas : O_2+NO_2, $NiCr_2O_4$/YSZ/Pt, NO_2+O_2

In air, only the following equilibrium took place at TPB of each electrode (RE and SE):

$$1/2O_2(\text{gas}) + V_O^{\bullet\bullet} + 2e^- \rightleftharpoons O^{2-}{}_{(\text{YSZ})} \quad (1)$$

Here, $V_O^{\bullet\bullet}$ represented an oxygen vacancy in the YSZ. The electrons in the equilibrium transferred between electrodes and YSZ. Because the equilibrium took place at different rates at SE and RE, an electric potential difference (V_{air}) between SE and RE was generated.

In sample gas (NO_2+O_2), because RE is insensitive to NO_2, the potential of RE was fixed by constant O_2 concentration. On the other side, due to SE's high electrochemistry catalytic activity to NO_2, NO_2 could change the potential of SE by the following electrochemical process:

$$\text{Cathodic}: NO_2 + 2e^- \rightarrow NO + O^{2-}{}_{(\text{YSZ})} \quad (2)$$

$$\text{Anodic}: 2O^{2-}{}_{(\text{YSZ})} \rightarrow O_2 + 4e^- \quad (3)$$

When the rates of the two electrochemical reactions were equal, the potential of SE was the so-called mixed-potential. The electric potential difference between SE and RE was the V_{NO_2}.

The above electrochemistry reactions occurred at the active sites of TPB. In this case, the processed YSZ with 130 μm groove spacing had the largest surface which might enlarge the TPB and accelerate the reactions. Therefore, sensor S (130 μm) showed the largest response to NO_2.

The dependence of ΔV on the logarithm of NO_2 concentration for sensor S (130 μm) and S (smooth) was showed in Fig. 5a. The ΔV values were almost linear to the logarithm of NO_2 concentration. The slope was promoted from 35 mV/decade (for S (smooth)) to 55 mV/decade (for S (130 μm)). The continuous response-recovery transients (Fig. 5b) showed the stable and repeatable performance of sensor S (130 μm). In addition, 3 weeks long-term stability of sensor S (130 μm) was compared with sensor S (smooth) as shown in Fig. 5c. It could be seen that sensor S (130 μm) kept good response to 50 ppm NO_2 within ±2% change.

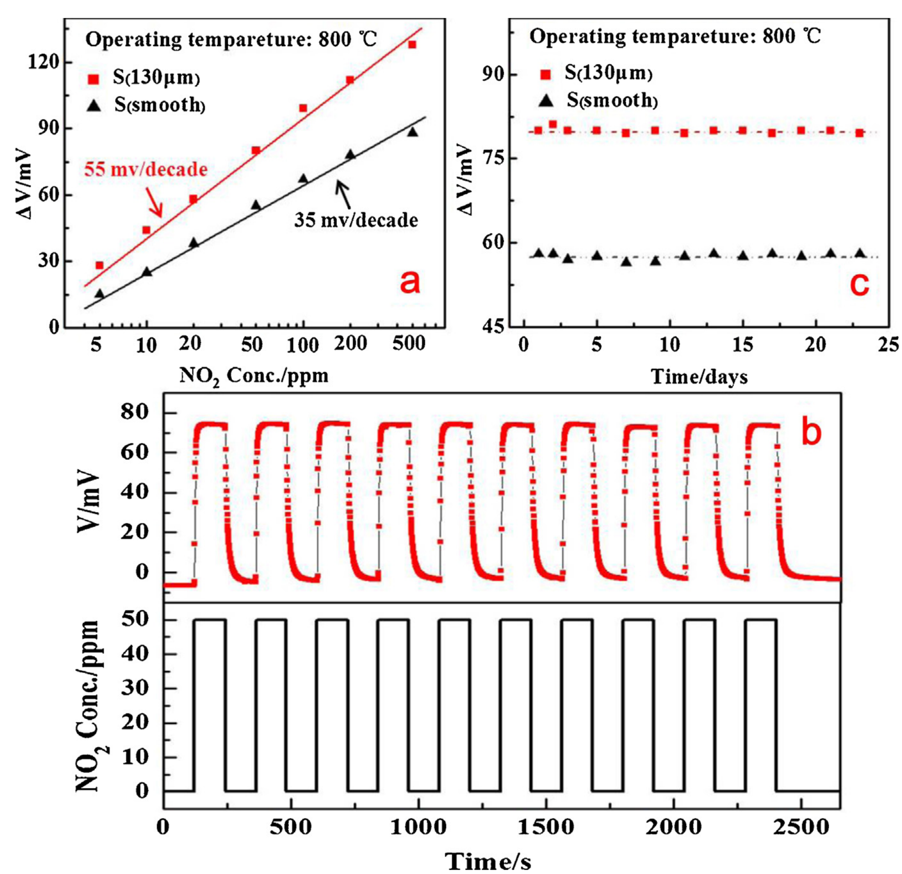

Fig. 5. (a) The dependence of the ΔV on the logarithm of NO_2 concentrations for sensor S (130 μm) and sensor S (smooth), (b) continuous response-recovery transients of sensor S (130 μm) to 50 ppm NO_2 at 800 °C, (c) time dependence of the ΔV to 50 ppm NO_2 for sensor S (130 μm) and sensor S (smooth).

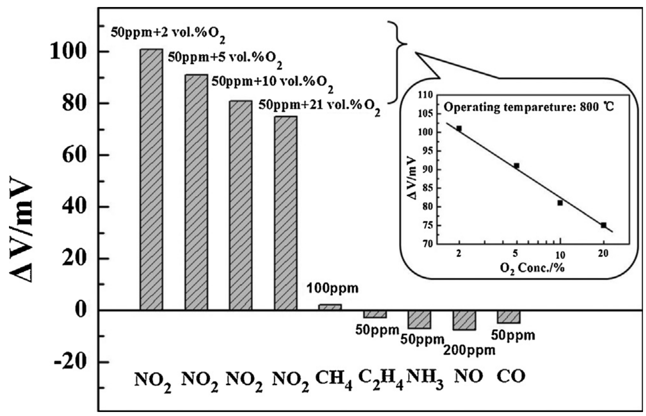

Fig. 6. Cross-sensitivities to various gases and dependence of the ΔV on the logarithm of O_2 concentrations for the sensor S (130 μm) at 800 °C.

In addition, the cross-sensitivities to various gases for the sensor S (130 μm) were exhibited in Fig. 6. It was seen that the present sensor displayed rather high selectivity to NO_2. The inset showed the dependence of the ΔV to 50 ppm NO_2 on the logarithm of O_2 concentrations for sensor S (130 μm). It was observed that the slope was linear and negative. Such a result examined the sensing mechanism involved in the mixed-potential.

4. Conclusions

In this article, femtosecond laser direct writing technology was used to process YSZ-substrate to form structured surface. The response of YSZ-based mixed-potential-type sensor to NO_2 in the range of 5–500 ppm at 800 °C was improved by this method. The better performance might be explained by the larger TPB. Moreover, the sensor with processed YSZ-substrate maintained good response-recovery transients, repeatability and cross-sensitivity to NO_2.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Nos. 61327804, 61134010, 61104203), Program for Chang Jiang Scholars and Innovative Research Team in University (No. IRT13018) and “863” High Technology Project (2013AA030902).

References

[1] S. Fischer, R. Pohle, B. Farber, R. Proch, J. Kaniuk, M. Fleischer, R. Moos, Method for detection of NOx in exhaust gases by pulsed discharge measurements using standard zirconia-based lambda sensors, Sens. Actuators B 147 (2010) 780–785.
[2] T. Hibino, Y. Kuwahara, T. Otsuka, N. Ishida, T. Oshima, NOx detection using the electrolysis of water vapor in a YSZ cell. Part II. Electrochemical oxygen pump, Solid State Ion. 107 (1998) 217–220.
[3] C. Pliangos, C. Raptis, Th. Badas, C.G. Vayena, Electrochemical promotion of NO reduction by C_3H_6 on Rh/YSZ catalyst-electrodes, Solid State Ion. 136–137 (2000) 767–773.
[4] T. Striker, V. Ramaswamy, E.N. Armstrong, P.D. Willson, E.D. Wachsman, J.A. Ruud, Effect of nanocomposite Au–YSZ electrodes on potentiometric sensor response to NOx and CO, Sens. Actuators B 181 (2013) 312–318.
[5] K.Y. Ho, M. Miyayama, H. Yanagida, NOx response properties in dc current of Nd_2CuO_4/YSZ/Pt element, J. Ceram. Soc. Jpn. 104 (1996) 995–999.
[6] H.C. Cho, S. Takase, J.H. Song, Y. Shimizu, Sensing behavior of solid-state impedancemetric NOx sensor using solid electrolyte transducer and oxide receptor, Sens. Actuators B 187 (2013) 94–98.
[7] P. Elumalai, N. Miura, Performances of planar NO_2 sensor using stabilized zirconia and NiO sensing electrode at high temperature, Solid State Ion. 31–34 (2005) 2517–2522.
[8] N.F. Szabo, P.K. Dutta, Correlation of sensing behavior of mixed potential sensors with chemical and electrochemical properties of electrodes, Solid State Ion. 171 (2004) 183–190.
[9] S. Zhuiykov, T. Nakano, A. Kunimoto, N. Yamazoe, N. Muria, Potentiometric NOx sensor based on stabilized zirconia and $NiCr_2O_4$ sensing electrode operating at high temperatures, Electrochem. Commun. 3 (2001) 97–101.
[10] E.D. Bartolomeo, N. Kaabbuathong, M.L. Grilli, E. Traversa, Planar electrochemical sensors based on tape-cast YSZ layers and oxide electrodes, Solid State Ion. 171 (2004) 173–181.
[11] W.Z. Xiong, G.M. Kale, Novel high-selectivity NO_2 sensor incorporating mixed-oxide electrode, Sens. Actuators B 114 (2006) 101–108.
[12] L.P. Martin, I.Q. Pham, R.S. Glass, Effect of Cr_2O_3 morphology on the nitric oxide response of a stabilized zirconia sensor, Sens. Actuators B 96 (2003) 53–60.
[13] P. Elumalai, J. Zosel, U. Guth, N. Miura, NO_2 sensing properties of YSZ-based sensor using NiO and Cr-doped NiO sensing electrodes at high temperature, Ionics 15 (2009) 405–411.
[14] J. Park, B.Y. Yoon, C.O. Park, W.-J. Lee, C.B. Lee, Sensing behavior and mechanism of mixed potential NOx sensors using NiO, NiO(+YSZ) and CuO oxide electrodes, Sens. Actuators B 135 (2009) 516–523.
[15] X. Liang, S. Yang, J. Li, H. Zhang, Q. Diao, W. Zhao, G. Lu, Mixed-potential-type zirconia-based NO_2 sensor with high-performance three-phase boundary, Sens. Actuators B 158 (2011) 1–8.
[16] Q. Diao, C. Yin, Y. Guan, X. Liang, S. Wang, Y. Liu, Y. Hu, H. Chen, G. Lu, The effects of sintering temperature of $MnCr_2O_4$ nanocomposite on the NO_2 sensing property for YSZ-based potentiometric sensor, Sens. Actuators B 177 (2013) 397–403.
[17] T. Ono, M. Hasei, A. Kunimoto, T. Yamamoto, A. Noda, Performance of the NO_X sensor based on mixed potential for automobiles in exhaust gases, JSAE Rev. 22 (2001) 49–55.
[18] E.L. Brosha, R. Mukundan, D.R. Brown, F.H. Garzon, J.H. Visser, Development of ceramic mixed potential sensors for automotive applications, Solid State Ion. 148 (2002) 61–69.

Biographies

Yingzhou Guan received the B.Eng. degree in Department of Electronic Sciences and Technology in 2012. He is currently studying for his M.E. Sci. degree in College of Electronic Science and Engineering, Jilin University, China.

Chunhao Li received the B.Eng. degree in Department of Electronic Sciences and Technology in 2012. He is currently studying for his M.E. Sci. degree in College of Electronic Science and Engineering, Jilin University, China.

Xiaoyang Cheng received the B.Eng. degree in Department of Electronic Science and Technology in 2013. She is currently studying for her M.E. Sci. degree in College of Electronic Science and Engineering, Jilin University, China.

Biao Wang received the doctorate degree in electronic sciences in 2008. Now he is an associate professor of Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences. His current research interests include the software and hardware development of embedded systems.

Ruize Sun received the B.Eng. degree in Department of Electronic Science and Technology in 2013. He is currently studying for her M.E. Sci. degree in College of Electronic Science and Engineering, Jilin University, China.

Xishuang Liang received the B.Eng. degree in Department of Electronic Science and Technology in 2004. He received his Doctor's degree in College of Electronic Science and Engineering at Jilin University in 2009. Now he is a lecturer of Jilin University, China. His current research is solid electrolyte gas sensor.

Jihong Zhao received the B.Eng. degree in Department of Electronic Science and Technology in 2006. She received his Doctor's degree in College of Electronic Science and Engineering at Jilin University in 2011. Now she is a lecturer of Jilin University, China. Her current research is fabrication of semiconductor optoelectronic devices.

Hong Chen received the Dr. Eng. degree from Stuttgart University in Germany. Now she is a professor of College of Communication Engineering, Jilin University, China. Her current research interests include the advanced control theory and technology.

Geyu Lu received the B.Sc. degree in electronic sciences in 1985 and the M.Sc. degree in 1988 from Jilin University in China and the Dr. Eng. degree in 1998 from Kyushu University in Japan. Now he is a professor of Jilin University, China. His current research interests include the development of chemical sensors and the application of the function materials.