Ultraviolet photodetector fabricated from atomic-layer-deposited ZnO films

C. X. Shan, J. Y. Zhang, B. Yao, D. Z. Shen, X. W. Fan et al.

Ultraviolet photodetector fabricated from atomic-layer-deposited ZnO films

C. X. Shan,[a)] J. Y. Zhang, B. Yao, D. Z. Shen, and X. W. Fan
Laboratory of Excited State Processes, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033, China

K. L. Choy
School of Mechanical, Materials, and Manufacturing Engineering, Nottingham University, University Park, Nottingham NG7 2RD, United Kingdom

(Received 8 December 2008; accepted 17 February 2009; published 29 May 2009)

Zinc oxide (ZnO) films have been prepared on glass substrate in layer-by-layer mode using an atomic-layer deposition (ALD) technique, and a metal-semiconductor-metal structured photodetector has been fabricated on the ZnO films employing interdigital Au as metal contacts. The photodetector shows a cutoff wavelength at around 390 nm and has an obvious responsivity in the whole UVA spectral range. Because the response of the ZnO photodetector covers the whole UV solar irradiation that can reach the earth, the photodetector promises to be useful in monitoring UV solar irradiation to protect people from harm caused by the solar irradiation. Furthermore, the capability of preparing large-area uniform ZnO films of ALD makes it favorable for possible mass production of this kind of photodetector. © *2009 American Vacuum Society.*
[DOI: 10.1116/1.3098502]

I. INTRODUCTION

Ultraviolet (UV) light can cause skin cancer; hence, it is necessary to monitor the UV solar irradiation to avoid any possible harm to humans. It is known that only UVA with wavelength ranging from 320 to 400 nm of the soalr irradiation can pass through the atmosphere and reach the earth's surface. Therefore, it is of great significance and importance to develop UV photodetector with response area lying in the UVA region. Zinc oxide (ZnO) has a direct and large bandgap of 3.37 eV at room temperature, which lies squarely in the UVA region. Therefore, ZnO has been regarded as one of the strongest candidates for UV photodetectors considering its low price and biocompatible character.[1–5] The ZnO films for photodetector applications have been prepared by metal-organic chemical vapor deposition,[6] magnetron sputtering,[7] pulsed laser deposition,[8] etc. Atomic-layer deposition (ALD) is one of the variations of chemical vapor deposition, and it employs a self-limiting layer-by-layer growth mode, which ensures large-area smooth layers with atomically precise control over thickness can be obtained.[9–11] Although some reports on ALD growth of ZnO films have been demonstrated,[12–15] no reports on photodetectors fabricated from ZnO films grown by ALD are available to the best of our knowledge.

In this article, ZnO films have been prepared using an ALD technique, and a metal-semiconductor-metal (MSM) structured UV photodetector has been fabricated from these films. The photodetector shows significant response to UV light shorter than 400 nm with a peak responsivity at about 370 nm, which covers the whole UVA region. This indicates that the photodetectors fabricated from ZnO may be used in UV irradiation monitoring.

[a)]Electronic mail: phycxshan@yahoo.com.cn

II. EXPERIMENT

The growth of the ZnO films was carried out in a Cambridge Nanotech ALD system employing glass as substrates. The precursors used were diethylzinc (DEZn) and water, the vapor of which was carried into the growth chamber by high-purity nitrogen. During deposition, the surface of the substrate was initially exposed to a dose of water vapor until it became saturated with up to one monolayer (1 ML) of coverage. Any excess unreacted vapor was then evacuated. Then, a DEZn dose was brought into the chamber by the carrier gas, and it reacts with the water precursor adsorbed on the substrate surface to form Zn–O bonds. The excess DEZn vapor was also pumped away. The exposure time for both DEZn and water were fixed at 10 and 15 ms, respectively, and the exhaust time after each precursor dose was kept at 3 s. The above-mentioned growth cycles were repeated thousands of times for each growth. The thickness of the ZnO films was characterized using a JY DeltaPsi ellipsometer. The structural properties were studied using a Rigaku D/max-RA x-ray diffractometer (XRD) with Cu $K\alpha$ line ($\lambda = 0.154$ nm) as the irradiation source. A JY630 micro-Raman spectrometer was used to measure the photoluminescence (PL) spectrum of the ZnO films, and the 325 nm line of a He–Cd laser was employed as the excitation source. Both optical transmission and absorption spectra were recorded in a Shimadzu UV-3101PC scanning spectrophotometer.

The photodetectors were fabricated by depositing Au film onto the ZnO films; then conventional UV lithography and wet-etching methods were employed to configure the Au film into interdigital electrodes. In this way, a MSM structured photodetector was prepared. The dark current was obtained by measuring the current-voltage (I-V) characteristics of the photodetector in a Hall measurement system (LakeShore 7707) under van der Pauw configuration at room tempera-

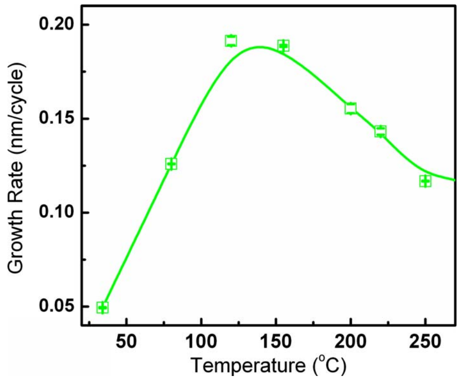

FIG. 1. (Color online) Dependence of growth rate of ZnO films on substrate temperature.

ture. A standard lock-in amplifier technique was employed to measure the photoresponse properties of the photodetector, where a 150 W xenon lamp was used as the illumination source.

III. RESULTS AND DISCUSSION

The dependence of the growth rate on substrate temperature is shown in Fig. 1, in which the scattered symbols are experimental data, while the solid line is used to outline the variation trend. The growth rate increases from 0.05 to 0.19 nm/cycle when the temperature is increased from 30 to 120 °C. Then, the growth rate remains almost constant from 120 to 155 °C. As the substrate temperature increases further, the growth rate decreases. It is noted that the growth rate saturates at about 0.19 nm/cycle from 120 to 155 °C. Considering that the bond length of Zn–O bonds is 0.190 ± 0.01 nm,[16] one can conclude that self-limiting layer-by-layer growth has been adopted in this temperature range; thus, the growth rate is about 1 ML/cycle. From the variation trend, one can determine that the temperature "window" for self-limiting layer-by-layer growth is between 120 and 155 °C. The above-mentioned substrate temperature-dependent growth rate can be understood in terms of the growth mode of the ALD technique. At relative low growth temperature (30–120 °C), the thermally activated chemisorption of the precursors onto the substrate is poor; thus, radicals absorbed on the substrate surface are so few that they do not completely cover the substrate. As a result, the average growth rate is less than 1 ML/cycle. At moderate temperature (120–155 °C), both species can fully cover the substrate surface, and the excess species are removed by the exhaust system. Consequently, self-limiting layer-by-layer growth is realized. However, when the substrate temperature increases further, the adsorbed radicals will re-evaporate, and the growth rate decreases.[17]

Because the temperature window for self-limiting growth lies in the 120–155 °C range, the ZnO films for photodetector fabrication in this study were grown at 150 °C, and the thickness determined by ellipsometry is about 450 nm. Hall measurements indicate that the ZnO films show n-type conduction, with an electron concentration of 2.3×10^{19} cm^{-3} and an electron mobility of 23 cm^2 V^{-1} S^{-1}. Shown in Fig. 2 is a typical XRD pattern of the ZnO films. The XRD pattern shows three peaks at 32.1°, 34.7°, and 56.8°, which correspond to the diffraction from (100), (002), and (110) facets of hexagonal wurtzite ZnO, respectively.[18] The XRD pattern indicates clearly that the ZnO films are crystallized in wurtzite structure. The PL spectrum of the ZnO films shows an intense near-band-edge emission at 380 nm and a broad deep-level-related emission at about 500 nm.

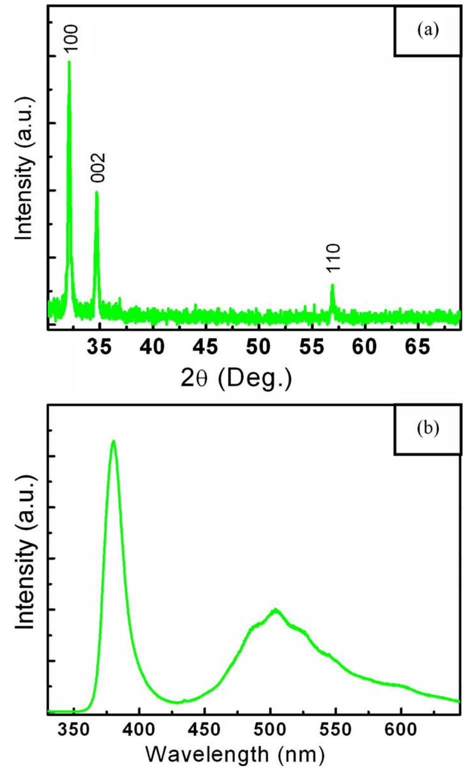

FIG. 2. (Color online) Typical XRD pattern (a) and room-temperature PL spectrum (b) of the ZnO films grown at 150 °C.

The absorption and transmission spectra of the ZnO films are shown in Fig. 3. In the absorption spectrum, an abrupt absorption edge at around 380 nm can be observed, and the film shows a strong absorption in the spectrum range shorter

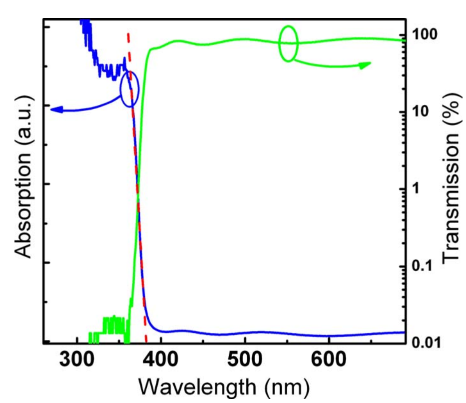

FIG. 3. (Color online) Room-temperature absorption and transmission spectra of the ZnO film, in which the dashed line is a guide to the eyes.

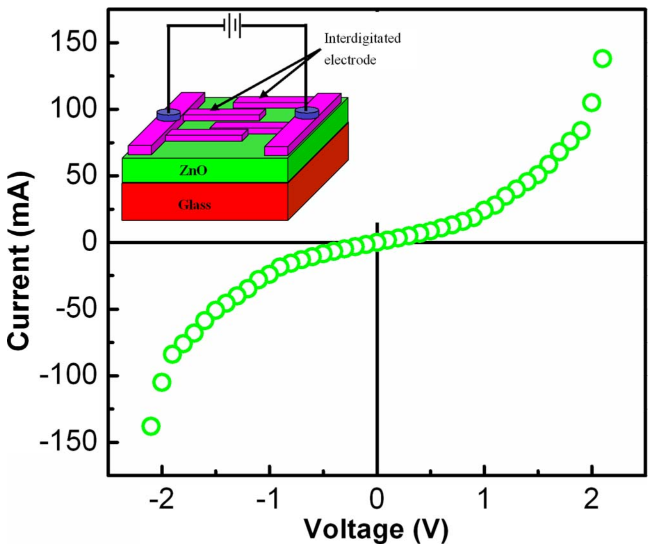

FIG. 4. (Color online) *I-V* curve of the photodetector fabricated from the ZnO films in dark; the inset shows the schematic diagram of the photodetector.

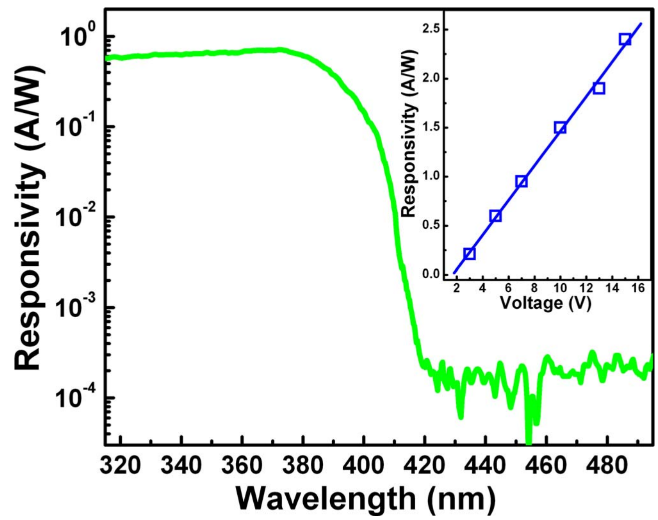

FIG. 5. (Color online) Photoresponse of the photodetector at 5 V bias; the inset shows the dependence of the responsivity of the photodetector at 370 nm on bias applied.

than 380 nm, while it is almost transparent in the visible range. The average transmission in the visible region of the ZnO films is greater than 80%. The above facts reveal that the ZnO films are promising in realizing photodetectors with a high UV/vis rejection ratio.[19]

The schematic of the photodetector fabricated from the ALD ZnO films is shown in the inset of Fig. 4, in which interdigital Au electrodes are deposited onto the ZnO films using photolithography and wet-etching method. The length and width of the Au fingers are 500 and 5 μm, respectively, and the spacing between the fingers is 10 μm. The *I-V* curve of the photodetector measured under dark conditions is shown in Fig. 4. An obvious rectifying effect can be observed from the curve, which indicates that Schottky behaviors have been obtained at the metal-semiconductor contact formed at the Au/ZnO interface. The dark current is about 100 mA at 2 V bias. It is speculated that the relatively large dark current is resulted from the very low resistivity of the ZnO films used (1.2×10^{-2} Ω cm).

The response spectrum of the photodetector at 5 V bias is shown in Fig. 5. The photodetector shows an obvious broad response to the UV spectrum shorter than 400 nm, and the cutoff response wavelength is located at around 390 nm. The spectrum has a maximum responsivity of 0.7 A/W at around 370 nm. We note that by increasing the bias applied, the maximum responsivity of the photodetector increases almost linearly in the range from 3 to 15 V. The UV/vis rejection ratio, which is closely related with the signal-to-noise ratio of the photodetector, is nearly four orders of magnitude for the photodetector, which is among the largest corresponding value reported in ZnO MSM structured photodetectors.[7,20]

IV. CONCLUSIONS

An UV photodetector has been fabricated on ZnO films prepared in layer-by-layer mode in an ALD technique, and the photodetector shows a wide spectral response span that almost covers the whole UVA spectrum region. The maximum responsivity of the photodetector is about 0.7 A/W at around 370 nm at 5 V bias, and the rejection ratio is nearly four orders of magnitude. The results reported in this article suggest that the ZnO photodetector can be potentially used to monitor UV solar irradiation. Additionally, the technique used in this study, ALD, excels in preparing large-area uniform thin films, which is favorable for possible mass production of this kind of ZnO-based photodetector considering that both ZnO material and glass substrate employed in this study are inexpensive and abundant.

ACKNOWLEDGMENTS

This work is supported by the Key Project of the NNSFC (50532050), the "973" Program (2006CB604906 and 2008CB317105), The Knowledge Innovative Program of CAS (KJCX3.SYW.W01), and the NNSFC (10674133, 10774132, and 60776011).

[1]D. C. Oh, T. Suzuki, T. Hanada, T. Yao, H. Makino, and H. J. Ko, J. Vac. Sci. Technol. B **24**, 1595 (2006).
[2]T. K. Lin, S. J. Chang, Y. K. Su, B. R. Huang, M. Fujita, and Y. Horikoshi, J. Cryst. Growth **281**, 513 (2005).
[3]N. W. Emanetoglu, J. Zhu, Y. Chen, J. Zhong, Y. M. Chen, and Y. C. Lu, Appl. Phys. Lett. **85**, 3702 (2004).
[4]I. Takeuchi, W. Yang, K. S. Chang, M. A. Aronova, T. Venkatesan, R. D. Vispute, and L. A. Bendersky, J. Appl. Phys. **94**, 7336 (2003).
[5]S. S. Hullavarad, S. Dhar, B. Barughese, I. Takeuchi, T. Venkatesan, and R. D. Vispute, J. Vac. Sci. Technol. A **23**, 982 (2005).
[6]D. Park and K. Yong, J. Vac. Sci. Technol. B **26**, 1933 (2008).
[7]Z. Bi, J. Zhang, X. Bian, D. Wang, X. Zhang, W. Zhang, and X. Hou, J. Electron. Mater. **37**, 760 (2008).
[8]W. Yang, R. D. Vispute, S. Choopun, R. P. Sharma, T. Venkatesan, and H. Shen, Appl. Phys. Lett. **78**, 2787 (2001).
[9]H. Kim, J. Vac. Sci. Technol. B **21**, 2231 (2003).
[10]M. Leskela and M. Ritala, Angew. Chem., Int. Ed. **42**, 5548 (2003).
[11]B. S. Lim, A. Rahtu, and R. G. Gordon, Nature Mater. **2**, 749 (2003).
[12]S. Y. Pung, K. L. Choy, X. H. Hou, and C. X. Shan, Nanotechnology **19**, 435609 (2008).

[13]K. Saito, Y. Yamamoto, A. Matsuda, S. Izumi, T. Uchino, K. Ishida, and K. Takahashi, Phys. Status Solidi B **229**, 925 (2002).
[14]S. Jeon, S. Bang, S. Lee, S. Kwon, W. Jeong, H. Jeon, H. J. Chang, and H. H. Park, J. Electrochem. Soc. **155**, H738 (2008).
[15]D. M. King, X. H. Liang, C. S. Carney, L. F. Kakim, P. Li, and A. W. Weimer, Adv. Funct. Mater. **18**, 607 (2008).
[16]C. Yang, Y. Yu, and L. C. Li, Chin. J. Chem. Phys. **19**, 137 (2006).
[17]M. A. Rueter and J. M. Vohs, Surf. Sci. **262**, 42 (1992).
[18]JCPDS card No. 80-0075 (unpublished).
[19]M. Razeghi and A. Rogalski, J. Appl. Phys. **79**, 7433 (1996).
[20]D. Y. Jiang, J. Y. Zhang, Y. M. Lu, K. W. Liu, D. X. Zhao, Z. Z. Zhang, D. Z. Shen, and X. W. Fan, Solid-State Electron. **52**, 679 (2008).