DOI 10.5162/IMCS2012/P2.0.16

Solar Driven Zinc Oxide Based Heterojunctions for Gas Sensing Applications

Alaa Eldin Gad[1], Martin Hoffmann[1], Tessa Leuning[1], Joan Daniel Prades[2], Francisco Hernandez-Ramirez[2, 3], Hao Shen [1], Sanjay Mathur,[1]*
[1]Institute of Inorganic Chemistry, University of Cologne, D-50939 Cologne, Germany
[2] Department of Electronics, University of Barcelona, E-08028 Barcelona, Spain
[3]Department of Advanced Materials for Energy Applications, Catalonia Institute for Energy Research (IREC), E-08930 Barcelona, Spain
** Correspondence: sanjay.mathur@uni-koeln.de*

Abstract:

Zinc oxide-based heterojunctions are promising material systems for optoelectronic devices to overcome the challenges of growing stable p-type ZnO. In this work, CdS@n-ZnO/ p-Si nanowires heterojunctions were fabricated through a combination of wet-chemical etching (Si NWs) and atomic layer deposition (ZnO) techniques followed by chemical bath deposition (CdS). The electrical properties of the obtained heterojunctions were evaluated by analysing current-voltage (I–V) and capacitance-voltage (C–V) characteristics. The (I-V) characteristics in dark conditions at room temperature exhibited diode characteristics, while solar light illumination shifts the I-V characteristics to a photovoltaic effect. The sensing properties, tested under solar simulated light, toward oxidizing gases, showed a good and reproducible sensing response toward oxygen gas at room temperature. These heterojunction-based devices are potential candidates for the development of a new generation of solar driven gas sensors.

Key words: Zinc oxide, ALD, heterojunction, silicon nanowires, and gas sensor.

Introduction

Zinc oxide (ZnO) has been extensively studied as an n-type semiconductor with large exciton binding energy (60 meV), and large band-gap energy (3.37 eV). [1] It also represents an attractive material combination for gas sensing applications because of the high mobility of conduction electrons, good thermal stability, and low cost. [2] Silicon nanowires exhibit considerable photo-harvesting ability [3] and their conductive behavior can be modulated by appropriate doping [4], which makes it a promising material for constructing various types of heterojunctions with other semiconductors. The use of p-n heterojunctions based on Si NWs and ZnO have been recently reported for optoelectronic applications such as photodiodes, photocatalysts, high-sensitivity photo-detectors [5,6], as alternatives to overcome the difficulty in the reproducible growth of high quality, stable, and controllable p-type ZnO. [7] Such radial heterojunctions have superior properties attributed tohigh surface/volume ratio, superior optical properties (such as optimal light absorption, low reflection of the sun illumination spectrum), and efficient free carrier collection, as compared to their conventional planar p-n junctions. [8] Most of the previous efforts have been devoted to investigate the electrical as well as the optical properties of n-ZnO/p-SiNWs heterojunction in applications that require higher specific surface and efficient charge carrier separation processes such as solar cells and gas sensors. [9-11]. Herein, we report the fabrication of a functional heterojunction system; namely CdS@n-ZnO/p-Si NWs as a gas sensor in which the needed energy for signal generation as well as surface activation is harvested solely from solar light. The open circuit voltage (V_{oc}) produced by the n-ZnO/p-Si NWs under solar illumination serves as the sensor signal and changes its value with respect to interactions between the n-ZnO and surrounding gas species. The CdS nanoparticles (NPs) on n-ZnO surface harvest the solar light as well as activate the analyte gas interaction with n-ZnO surface. Hereby, the photosensitization of wide band gap metal oxides (MO_x) with small band-gap semiconductors (such as CdS) [12] extend the photo-response of MO_x into the visible-light region.

DOI 10.5162/IMCS2012/P2.0.16

Experimental Details

Si NWs were synthesized by a metal-assisted wet chemical etching method of bulk silicon wafer p-Si (100), following a previously reported procedure [13]. The ZnO film was deposited on the Si NWs directly after etching the native silicon oxide layer by atomic layer deposition (ALD) using Beneq TFS 200 ALD system. Two liquid precursors namely; diethylzinc (DEZn) and deionized water as the oxygen source were sequentially used. The pulse durations of water and DEZn were 200 ms for each precursor. The purge and pumping periods were 1 s using N_2 as the purge gas. The substrate temperature was maintained at 200 °C during the deposition. The desired n-ZnO film thickness was achieved after 300 ALD cycles. Afterwards, the sample was annealed in ambient air at 500 °C (1 h) for achieving better crystallinity.

CdS NPs were deposited on the surface of the ZnO via a chemical bath deposition (CBD) method. [14] $CdSO_4$ and thiourea were used as CdS precursors and the CBD was done at 60 °C for 15 mins. The phase composition of the samples was characterized on a STOE-STADI MP X-Ray diffractometer using CuKα (1.5406 Å) radiation. The micro- and nanostructures of the samples were examined using field-emission scanning electron microscopy (FE-SEM, FEI Nova NanoSEM 430). Electrical measurements were performed using a Keithley 2400 Source Meter Unit (SMU). The (C-V) measurement (Keithley 4200-SCS, 1 MHz) was performed in reverse bias condition.

The sensor device was fabricated by using a conductive glass ($F:SnO_2$) as a transparent top contact on the n-ZnO shell whereas p-Si was contacted with silver paste. The different components were mechanically contacted by using metal clamps to form the prototype device. For the gas sensing tests, the device was placed in a customized test chamber with gas inlet and quartz window. The device was illuminated by a solar simulator (Newport 96000 Oriel 150 W, AM 1.5) with an output intensity of 100 mW/cm^2. The gas flow (≥ 99.999% purity) was controlled by mass flow controllers.

Results and Discussion

Figure 1 shows a schematic representation of CdS@n-ZnO/p-SiNWs gas sensing device, the fabrication details are given in experimental section. The etched Si NWs arrays architecture strongly depended on the used silicon wafer orientation (p-Si (100)). XRD patterns of the wet-etched Si NWs showed a preferential orientation along [100] direction.

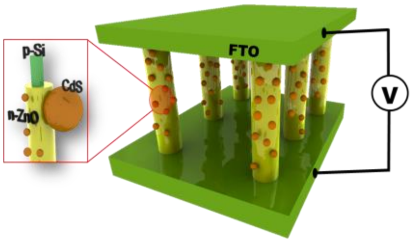

Fig. 1. Schematic representation of CdS@n-ZnO/p-SiNWs gas sensor device.

An n-type ZnO shell was coated on the p-Si NWs by using ALD technique. As shown in figure 2, the XRD pattern of CdS@n-ZnO/p-SiNWs showed the predominant growth of Si NWs along the (100) direction flanked by distinctive minor peaks in the 2θ range ~ 30°-40° ascribable to the wurzite phase of ZnO shell. The intensity of ZnO peaks indicated a good crystallinity, enhanced by a post-annealing treatment at 500°C.

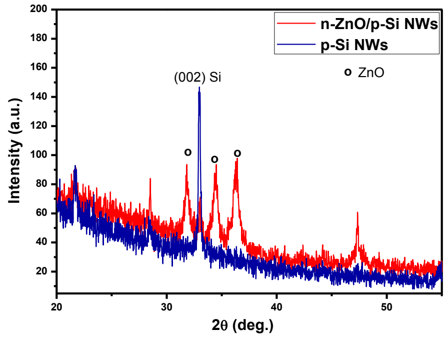

Fig. 2. XRD pattern of CdS@ZnO/p-SiNWs heterostructure and as grown p-SiNWs.

SEM images of Si NWs, (figure 3 a, b) showed vertically aligned p-Si NWs arrays with a length of 24 μm. The SEM image of n-ZnO/p-Si NWs sample confirmed the conformal ALD of ZnO of 60 nm thickness on the Si NWs. Figure 3c shows the n-ZnO/p-SiNWs sample decorated with CdS. The uniform distribution of CdS NPs on the n-ZnO surface is eivident in the cross-sectional SEM image shown in figure 3d.

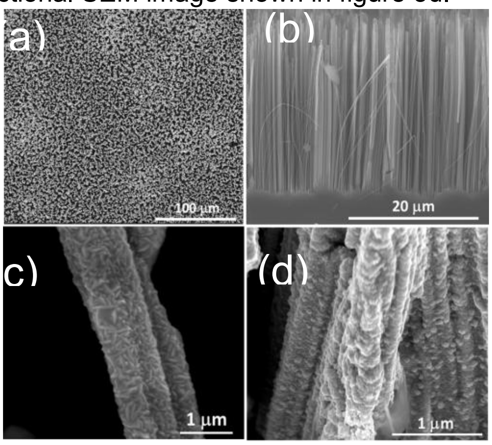

Fig. 3. (a, b) in plane and cross-sectional SEM images of p-SiNWs. Tilted SEM images of n-ZnO/p-SiNWs (c) and CdS@ZnO/p-SiNWs(d).

DOI 10.5162/IMCS2012/P2.0.16

The (I–V) curve (figure 4) of the CdS@n-ZnO//p-SiNWs under dark conditions and at room temperature showed a typical rectifying behavior. Under solar illumination the I-V characteristics showed a photovoltaic effect of the device with an open circuit voltage (V_{oc}) of 90 mV under solar illumination (inset Fig. 4).

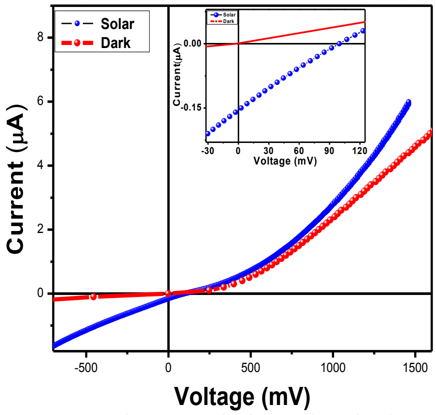

Fig. 4. I-V characteristics of CdS@n-ZnO/p-Si NWs heterojunction in dark and under solar illumination.

Figure 5 shows the capacitance-voltage (C-V) measurements of the device. $1/C^2$ vs. voltage plot displayed a linear behavior confirming the formation of a heterojunction diode at the n-ZnO/p-SiNWs interface. The carrier concentration in n-ZnO, as calculated from the slope of $1/C^2$ vs. voltage curve, was found to be 1.5 x 10^{18} m^{-3}.. The value of carrier concentration (N_D) of n-ZnO deposited by ALD is lower than that of ZnO film deposited by DC-sputter technique as reported in our previous report [15], this can be attributed to the better crystallinity as well as lower defects in the ALD deposited ZnO films.

Gas sensing measurements were performed under solar light illumination at room temperature with zero bias current, whereby the change of the open circuit voltage (V_{oc}) was monitored in oxygen and nitrogen atmospheres.

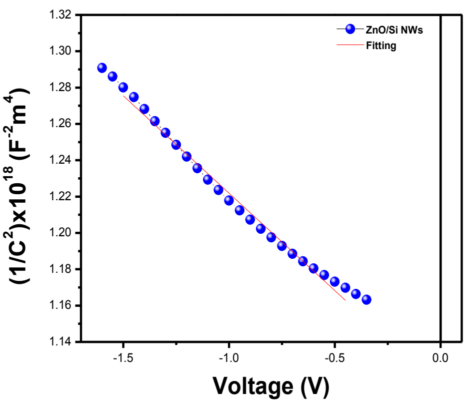

Fig. 5. C-V measurement. Mott Schottky plots ($1/C^2$ vs. V) of CdS@n-ZnO/p-Si NWs acquired at 1 MHz in the reverse bias region.

Figure 6 shows the change in V_{oc} signals of the device under solar illumination condition upon exposure to oxygen and nitrogen pulses. The V_{oc} sensing signal depended on the gas composition and it decreased under oxygen and increased in the nitrogen atmosphere.

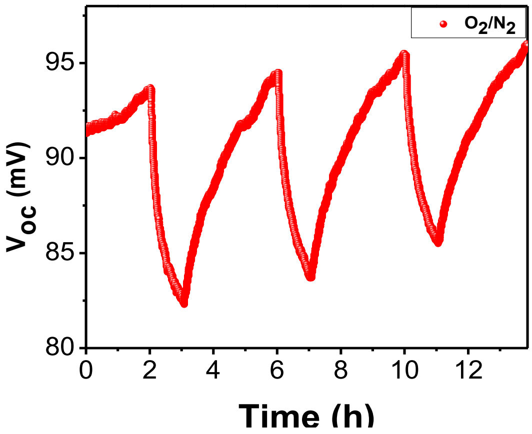

Fig. 6. ON/OFF (oxygen/ nitrogen) curves of CdS@n-ZnO/p-SiNWs sensor recorded under solar illumination with no applied current (I = 0 A) and at room temperature.

The observed reduction of charge carriers, which resulted in the decrease of the open circuit voltage (V_{oc}), is apparently due to the surface reaction of the n-ZnO surface with oxygen to form charged oxygen species (figure 7) that deplete the conduction channel resulting in a net decrease in the donor density (N_D) of ZnO.

The presence of CdS is indispensable in the sensing system not only to harvest the solar light but also to activate the analyte gas-metal oxide interaction as the results obtained without the incorporation of CdS quantum dots did not show the observed solar diode effect

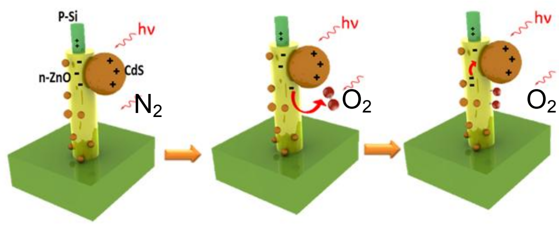

Fig. 7. Charge carrier distribution of CdS@n-ZnO/p-SiNWs in N_2 and O_2 atmospheres under solar illumination.

Conclusions

Heterojunction gas sensors based on CdS@n-ZnO/p-SiNWs systemwere fabricated through a combination of wet-etching and ALD techniques. The device showed rectification behavior in dark and a photovoltaic response under solar illumination. The donor density of n-ZnO deposited by ALD is less than that of n-

ZnO films deposited by DC sputter technique indicating the advantage of ALD technique to deposited crystalline thin film with lower defects in addition to the conformal coating of one-dimensional nanostructures with high aspect ratio. The device showed promising sensing properties at room temperature by using only solar light to drive the sensor without any external power sources. The radial heterostructures based on ZnO-containing p-n junctions provide a novel platform for developing a new generation of solar driven gas sensors, which can be envisaged to function as self-sustained power and sensing units.

Acknowledgements

The University of Cologne is gratefully acknowledged for financially supporting this work. A. E. Gad acknowledges the financial support given by the German-Egyptian long term scholarship (GERLS). D. Prades and F. Hernandez-Ramirez thank DAAD for the support.

References

[1] S. J. Pearton, D. P. Norton, K. Ip, Y. W. Heo, and T. Steiner, Recent advances in processing of ZnO, *J. Vac. Sci. Technol. B* 22, 932-948 (2004); DOI: 10.1116/1.1714985

[2] J. Xua,c, J. Hanb, Y. Zhanga, Y. Sunc, B. Xiec, Studies on alcohol sensing mechanism of ZnO based gas sensors, *Sensors and Actuators B* 132, 334–339 (2008); Doi:10.1016/j.snb.2008.01.062

[3] E.C. Garnett, P. Yang, Silicon Nanowire Radial p−n Junction Solar Cells, *J. Am. Chem. Soc.*, 130, 9224–9225 (2008); DOI: 10.1021/ja8032907

[4] Y. Cui, X. Duan, J. Hu, C.M. Lieber, Doping and Electrical Transport in Silicon Nanowires, *J. Phys. Chem. B*, 104 5213–5216 (2000); DOI: 10.1021/jp0009305

[5] M. Devika, N. K. Reddy, A. Pevzner , and F.Patolsky, Heteroepitaxial Si/ZnO Hierarchical Nanostructures for Future Optoelectronic Devices, *Chem. Phys. Chem.* 11, 809-814 (2010); DOI: 10.1002/cphc.201000021

[6] K. Sun, Y. Jing, N. Park, C. Li, Y. Bando, and D. Wang, Solution Synthesis of Large-Scale, High-Sensitivity ZnO/Si Hierarchical Nanoheterostructure Photodetectors, *J. AM. CHEM. SOC.* 132, 15465- 15467 (2010); DOI: 10.1021/ja1038424

[7] J. H. Choi, S. N. Das, K. J. Moon, J. P. Kar and J. M. Myoung, Fabrication and characterization of p-Si nanowires/ZnO film heterojunction diode, *Solid State Electron.* 54, 1582- 1585 (2010); DOI:10.1016/j.sse.2010.07.015

[8] B. M. Kayes and H. A. Atwater, N. S. Lewis, Comparison of the device physics principles of planar and radial p-n junction nanorod solar cells, *J. Appl. Phys.* 97, 114302-114311 (2005); DOI: 10.1063/1.1901835

[9] H. D. Um, S. A. Moiz, K.T. Park, J.Y. Jung, S. W. Jee, C. H. Ahn, D. C. Kim, H. K. Cho, D. W. Kim, and J. H. Lee, Highly selective spectral response with enhanced responsivity of n-ZnO/p-Si radial heterojunction nanowire photodiodes, *Appl. Phys. Lett.* 98, 033102-03 (2011); DOI: 10.1063/1.3543845

[10] Y. M. Chang, S. R. Jian, H. Y. Lee, C. M. Lin and J. Y. Juang, Enhanced visible photoluminescence from ultrathin ZnO films grown on Si-nanowires by atomic layer deposition, *Nanotechnology* 21, 385705-12(2010); DOI: 10.1088/0957-4484/21/38/385705

[11] H. Zhou, G. Fang, L. Yuan, C. Wang, X. Yang, H. Huang, C. Zhou, and X. Zhao, Deep ultraviolet and near infrared photodiode based on n-ZnO/p-silicon nanowire heterojunction fabricated at low temperature, *Appl. Phys. Lett.* 94, 013503 (2009); DOI: 10.1063/1.3064161

[12] J. Zhai, D. Wang, L. Peng, Y. Lin, X. Li, T. Xie, Visible-light-induced photoelectric gas sensing to formaldehyde based on CdS nanoparticles/ZnO heterostructures, *Sensors and Actuators B* 147, 234–240 (2010); DOI:10.1016/j.snb.2010.03.003

[13] V. A. Sivakov, G. Brönstrup, B. Pecz, A. Berger, G. Z. Radnoczi, M. Krause, and S. H. Christiansen, Realization of Vertical and Zigzag Single Crystalline Silicon Nanowire Architectures, *J. Phys. Chem. C*, 114, 3798–3803 (2010); DOI: 10.1021/jp909946x

[14] Y. Tak, S. J. Hong, J. S. Lee, and K. Yong, solution Based Synthesis of a CdS Nanoparticle/ZnO Nanowire Heterostructure Array, Cryst. Growth Des., 9, 2627–2632 (2009); DOI:10.1021/cg801076b

[15] A. E. Gad, M. Hoffmann, H. Shen, S. Mathur, Fabrication and Characterization of a Novel Nanostructured Solar Diode Sensor, *the 36th International Conference & Exposition on Advanced Ceramics & Composites (ICACC)*, January 22-27, 2012, Daytona Beach, Florida, USA.