



Crossed zinc oxide nanorods for ultraviolet radiation detection

Guangyu Chai^a, Oleg Lupan^{b,c,*}, Lee Chow^b, Helge Heinrich^{b,d}

^a Apollo Technologies Inc., 205 Waymont Court, S111, Lake Mary, FL 32746, USA

^b Department of Physics, University of Central Florida, Orlando, FL 32816-2385, USA

^c Department of Microelectronics and Semiconductor Devices, Technical University of Moldova, 168 Stefan cel Mare Blvd., MD-2004 Chisinau, Republic of Moldova

^d Advanced Materials Processing and Analysis Center, and Department of Mechanical, Materials, and Aerospace Engineering, University of Central Florida, PO Box 162385, Orlando, FL 32816-2455, USA

ARTICLE INFO

Article history:

Received 9 July 2008

Received in revised form

28 December 2008

Accepted 30 December 2008

Available online 6 January 2009

PACS:

81.07.Bc

42.79.Pw, detectors optical

85.60.Gz, photodetectors

Keywords:

Crossed zinc oxide nanorods

Photosensor

Self-assembly

Ultraviolet

ABSTRACT

An ultraviolet photosensor has been successfully constructed by the in situ lift-out method in a focused ion beam system. The prototype consists of individual naturally self-assembled crossed ZnO nanorods grown by an aqueous solution process. The current–voltage (I – V) characteristics show linear behavior. The photosensor exhibits a response of ~ 15 mA/W for UV light (361 nm) under 1 V bias. Response measurements showed that such a photosensor is suitable for low levels of ultraviolet detection. The method is simple, rapid and applicable to research prototypes for further studies of crossed ZnO nanorods for nano-device applications.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Ultraviolet (UV) photosensors are devices that have a range of applications in medicine, ecology, commercial, space communications, high-temperature plasma research, chemical and biological sensing, and in military as flame and missile launching detection, etc. [1–4]. UV detectors are used to monitor and determine the Earth's ozone layer thickness. This wide area of UV sensor applications implies multiple requirements that cannot be satisfied by a single device. Solid-state UV photodetectors are more efficient and lightweight [3,4] and can be easily incorporated in different novel types of micro/nanosystems and MEMS/NEMS. These portable devices can help people to monitor their exposure to solar UV radiation, etc.

In the last few years there was an increased interest in solid-state UV sensors based on the fact that miniature detectors for

the UV range in comparison with other spectral ranges are so far not commonly used. Although now several kinds of photosensors are provided for the UV range, the development of nanosensors for these applications will enable more portable detectors.

Usually, direct wide-band-gap materials like GaN [5], ZnSe [6], and AlGaIn [7] are used as sensing material. Analog to III–V materials, ZnO also possesses high UV photosensitivity which is most important for ultraviolet photodetection. Thus, zinc oxide is also a potentially strong UV sensing material [8–11].

ZnO attracted great interest for such applications due to its large binding energy of 60 meV, wide band gap of 3.37 eV at 300 K, its capability to operate at a high temperature and in harsh environment [2]. In addition, ZnO exhibits the most abundant configurations of nanostructures.

Recently, one-dimensional zinc oxide nanorods, nanowires demonstrated potential applications as next-generation of UV sensors [9–11]. However, its photocarriers life-time is long and it has lower photosensitivity [8].

To date, only a few papers report on single zinc oxide nanorods, nanowires [8,11–13], but none addresses the UV sensitivity of self-assembled crossed ZnO nanorods grown by aqueous solution.

Recently, the physical properties of nano-structured ZnO materials, such as nanorods [12], nano-tripods [13], nano-ribbon [14]

* Corresponding author at: Department of Physics, University of Central Florida, 4000 Central Florida Blvd, Orlando, FL 32816-2385, USA. Tel.: +1 407 823 2333; fax: +1 407 823 5112.

E-mail addresses: guangyuchai@yahoo.com (G. Chai), lupan@physics.ucf.edu, lupanoleg@yahoo.com (O. Lupan).

and nano-tetrapods [15–17] have been studied. In particular, nano-tetrapods have demonstrated their potential applications [15–17] in gas sensing, and UV sensing. It should be noted that there are two main advantages of these types of nano-structures: (a) these are multi-terminal devices, so potentially a bias can be applied, (b) because of the junctions between the different terminals, new functionality can be envisioned. For example in a recent report, the importance of the junction has been demonstrated for ZnO tetrapods [18].

In this work, we report a self-assembled ZnO nanocross based UV photosensor. The present study shows a simple and cost-effective method to fabricate a crossed ZnO nanorods device, possibly leading to a next generation of photosensors for a wide range of applications.

2. Experimental details

The crossed ZnO nanorods in this study were synthesized in a hydrothermal reactor with an aqueous solution deposition technique. As a starting materials, zinc sulfate $Zn(SO_4) \cdot 7H_2O$ and ammonia solution NH_4OH (29.6%) were used. All chemicals were analytical reagents and without further purification. The procedures of the preparation were as follows: the complex solution was placed in a reactor, and then glass or Si substrates were introduced. The reagents were stirred vigorously to obtain a transparent solution. This technique has been reported in details in our previous work [19]. The only difference is that we employed a different preparation route of the substrates. The glass substrates were treated in H_2SO_4/H_2O (3:1 volume) at $75^\circ C$ for 40 min and in $H_2O/NH_4OH/H_2O_2$ (5:1:1 volume) of $75^\circ C$ for 45 min and another step of deionized (DI) water (H_2O): hydrochloric acid (HCl): hydrogen peroxide (H_2O_2) 5:1:1 ratio to increase the hydrophilicity of the glass surface. The substrates were stored in deionized water for later use. The final products were washed in deionized water and dried at $150^\circ C$ for 3 min. Then ZnO nanorods were annealed at $650^\circ C$ for 20 s in air.

The crystalline quality and orientations of as-prepared ZnO nanorods were analyzed by an X-ray diffraction (XRD) and the morphology of the products was studied by scanning electron microscopy (SEM). Transmission electron microscopy (TEM) confirmed that the nanorods are crystalline. For the device fabrication we used an in situ lift-out technique in a focused ion beam (FIB/SEM) instrument. Current–voltage (I – V) characteristics were measured using a semiconductor parameter analyzer with an input impedance of $2.00 \times 10^8 \Omega$. The UV sensitivity was measured using a two-terminal ZnO nanorod device. The UV source used in the photosensitivity responses and current–voltage (I – V) characteristics measurements consists of an LED with a peak wavelength of 361 nm. The peak power output of the LED is 0.7 mW at 20 mA. The readings were taken after a UV light was turned on.

3. Results and discussion

3.1. Characterization

Fig. 1 shows the typical growth result of self-assembly for crossed ZnO nanorods in the SEM micrograph. A close view of the ZnO nanorods illustrates a hexagonal cross-section of these nano-structures.

Further structural characterization was carried out using a 300 kV high-resolution transmission electron microscope (FEI-Tecnai F30). A high resolution TEM image at the edge of a single leg of single-crystalline crossed ZnO nanorods is shown in Fig. 2. The spacing of 0.26 nm between adjacent lattice planes corresponds to (002) lattice planes and confirms the growth along the predomi-

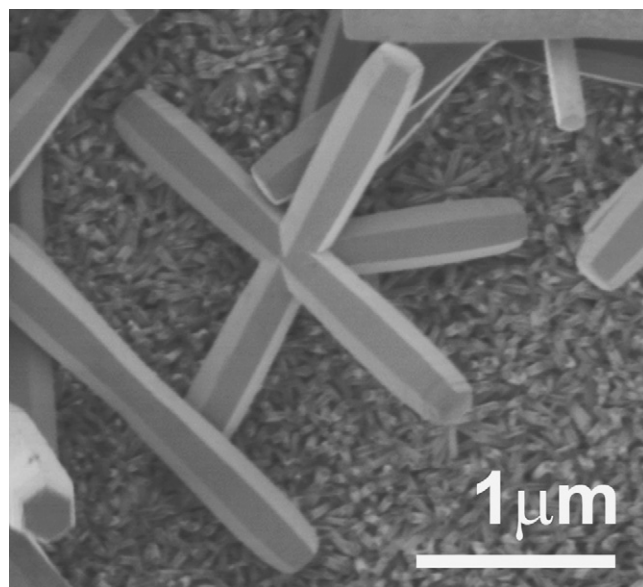


Fig. 1. SEM image of the self-assembly crossed ZnO nanorods.

nant [001] direction of ZnO. No dislocations or stacking faults were found. The single-crystalline nature and hexagonal configuration of the crossed nanowires were confirmed using selected area electron diffraction (SAED). Electron diffraction patterns obtained from different parts of the nanorod indicate the same pattern without tilting of the nanorod, which demonstrates single-crystallinity across the whole nanorod. From these results lattice constants $a = 3.24 \text{ \AA}$ and $c = 5.20 \text{ \AA}$ was calculated which are within limits of the experimental error in agreement with XRD data presented in details in our previous works [11–13,19].

The chemical composition of the as grown ZnO nanorods was determined by energy dispersive X-ray (EDX) spectrometry for the cross-nanorod material synthesized in large quantity which fully covers the substrates. It can be seen in Fig. 1. Only Zn and O, and no other elements are detected. It is concluded that the obtained ZnO

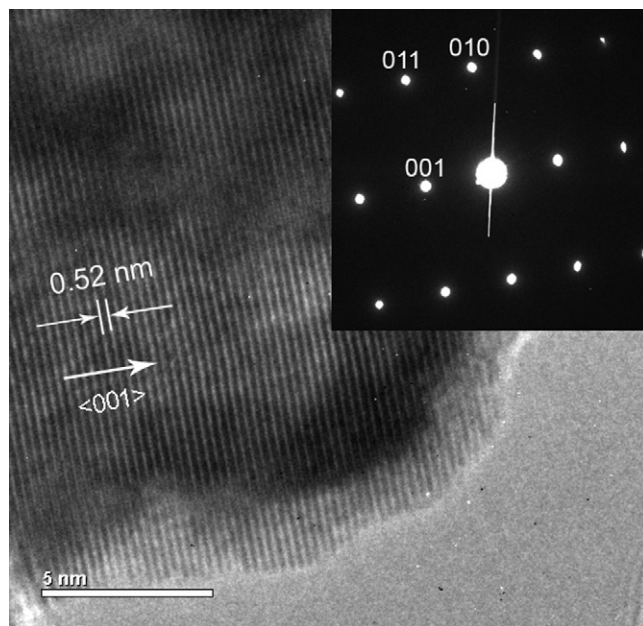


Fig. 2. TEM image of the edge of an as-synthesized ZnO nanorod and a typical SAED pattern of a single nanorod (inset). The long axis of the nanorod is parallel to the [001] direction.

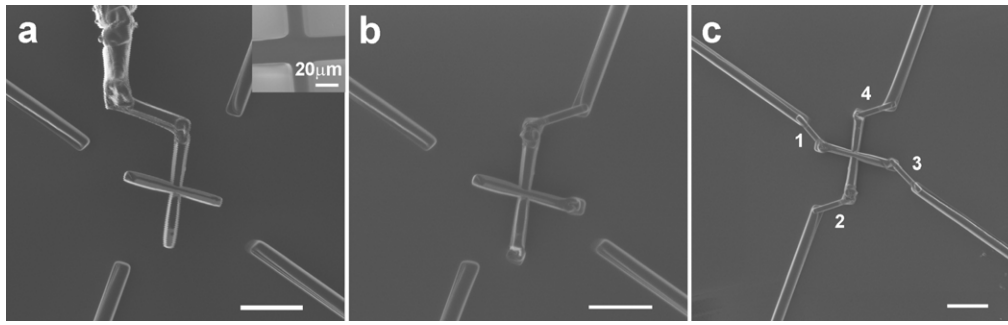


Fig. 3. Secondary electron images showing the steps of the in situ lift-out fabrication procedure in the FIB system. (a) The tungsten needle with an intermediate nanorod and is attached to a single cross ZnO nanorods selected for sensor fabrication; inset is the nanosensor substrate template (glass with Cr/Au contacts as contact electrodes); (b) the crossed ZnO nanorods is placed on the substrate and connected to the external electrodes; (c) the single crossed ZnO nanorods after welding to the four electrode/external connections as final nanosensor. The scale bar is $3\ \mu\text{m}$.

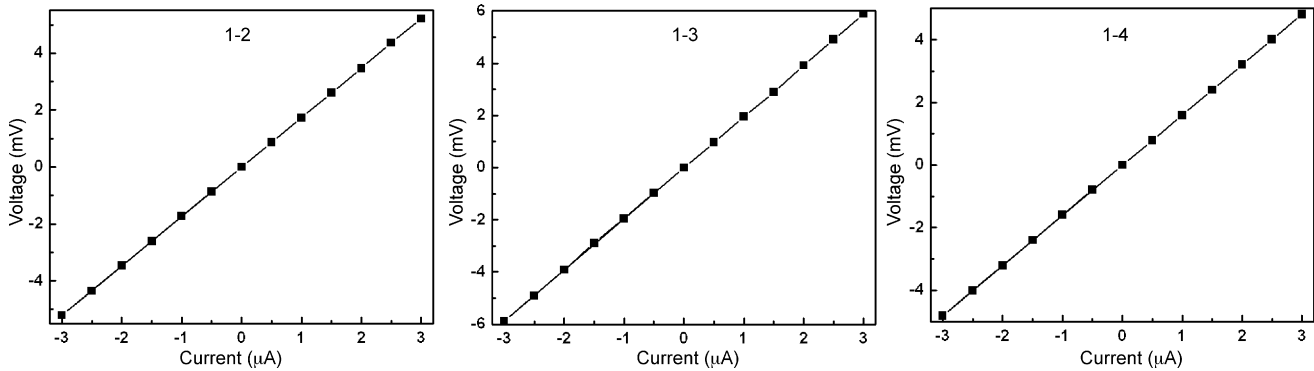


Fig. 4. I - V characteristics of the crossed ZnO nanorods photodetector.

nanocrosses are in a 0.55:0.45 stoichiometry of zinc and oxygen and are composed of Zn and O only.

3.2. Nanofabrication of a photodetector by the in situ lift-out technique

The in situ lift-out procedure is described here for photosensor fabrication. A focused ion beam system FEI-200TEM was used to contact single crossed ZnO nanorods.

Fig. 3a shows a single nanorod cross attached to an intermediate ZnO nanorod on the tungsten needle tip in the FIB system. In order to realize the easy attachment the nanorod is deposited and micro/nanomanipulated onto a SiO_2/Si substrate already processed to have respective distribution of pre-patterned external electrodes (inset Fig. 3a).

In Fig. 3b, the single crossed ZnO nanorods is shown as it is placed on the substrate and attached to one of external electrodes. All four

contacts in each end of the crossed ZnO nanorods are connected using the gallium beam to deposit the Pt strip (Fig. 3c).

3.3. UV sensing properties

We measured the current–voltage (I - V) curves of the crossed ZnO nanorods with contacts realized by the in situ lift-out method. Fig. 4 illustrates the characteristics of a four-terminal crossed ZnO nanorod photodetector in ambient air. The I - V measurements were performed by changing the bias voltages from $+5\ \text{mV}$ to $-5\ \text{mV}$ and vice versa for different connections (from 1 to 4 according to Fig. 3). The voltage increment and delay time were set to $0.25\ \text{mV}$ and $2\ \text{s}$.

The room temperature sensitivity of the crossed ZnO nanorods based-sensor to UV radiation is shown in Fig. 5.

We observed photoresponse at a smaller fraction of UV light from sunlight. In order to understand the device sensing mech-

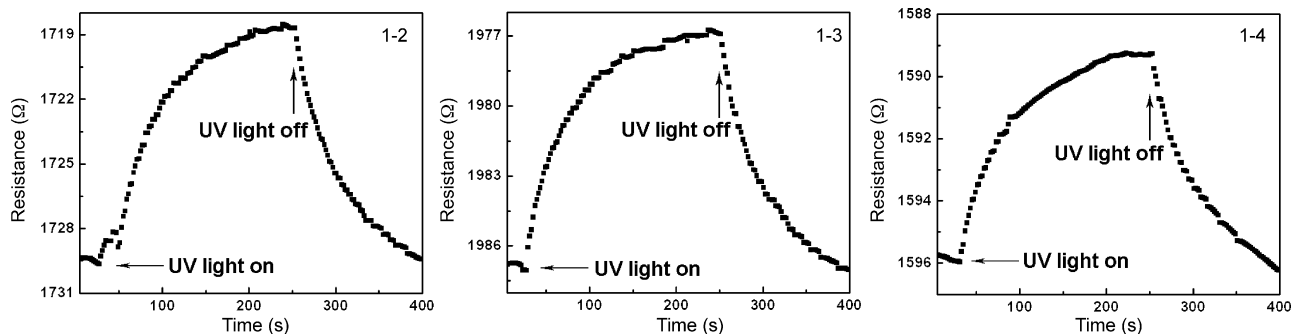


Fig. 5. The resistance change of the crossed ZnO nanorod-based UV photosensor fabricated from a single crossed ZnO nanorods by the in situ lift-out technique in the FIB system. Notations of external connections are from 1 to 4 according to Fig. 3.

anism we considered that oxygen chemisorption on ZnO surface plays an important role in control the photosensitivity [9,20]. When the crossed nanorods sensor is placed in the dark, oxygen molecules adsorb on the surface extracting free electron from ZnO



This creates a depletion layer with low conductivity near the cross ZnO nanorods surface. When the photosensor is exposed to UV light it starts to generate electron–hole pairs. Holes will recombine with e^- from adsorbed oxygen ions through surface recombination releasing oxygen atoms from the surface:



The remaining electrons in the conduction band will contribute to an increase in the photoconductivity of the crossed ZnO nanorods. By using thinner crossed ZnO nanowires, the UV sensitivity may be improved and single photon detectors could be fabricated. The receiving UV is proportional to the surface area and the UV effect is inverse proportional to the volume (excited electron density). Thus, thinner wire means more sensitivity.

4. Conclusion

In summary, the first single crossed ZnO nanorod–UV photosensor is demonstrated. An in situ lift-out technique has been employed to fabricate this photosensor based on a self-assembled crossed nanorods. The photoresponse of the photosensors suggest that they can be considered as candidates for optoelectronic devices and may be used for UV switches and position sensors.

The prototype device provides a simple method for nanowires synthesis and demonstrates the possibility of constructing nanoscale photodetectors for nano-optics applications.

4.1. Future work

The research will explore the possibility of widening the band gap by doping with Mg in order to cover UV-A (315–400 nm), UV-B (280–315 nm) and UV-C (100–280 nm) regions of the ultraviolet spectrum.

Acknowledgements

Dr. L. Chow acknowledges partial financial support from Apollo Technologies Inc. and Florida High Tech Corridor Research Program. The research described in this publication was made possible in part by Award No. MTFP-1014B Follow-on (for young researchers) of the Moldavian Research and Development Association (MRDA) and the U.S. Civilian Research and Development Foundation (CRDF).

References

- [1] E. Monroy, F. Omnes, F. Calle, Wide-bandgap semiconductor ultraviolet photodetectors, *Semicond. Sci. Technol.* 18 (2003) R33–R51.
- [2] L. Luo, Y.F. Zhang, S.S. Mao, L.W. Lin, Fabrication and characterization of ZnO nanowires based UV photodiodes, *Sens. Actuators A* 127 (2006) 201–206.
- [3] J.P. Cheng, Y.J. Zhang, R.Y. Guo, ZnO microtube ultraviolet detectors, *J. Cryst. Growth* 310 (2008) 57–61.
- [4] F. Masuoka, K. Ooba, H. Sasaki, H. Endo, S. Chiba, K. Maeda, H. Yoneyama, I. Niikura, Y. Kashiwaba, Applicability of ZnO single crystals for ultraviolet sensors, *Phys. Status Solidi (c)* 3 (2006) 1238–1241.
- [5] A. Osinsky, S. Gangopadhyay, R. Gaska, B. Williams, M.A. Khan, D. Kuksenkov, H. Temkin, Low noise p–pi–n GaN ultraviolet photodetectors, *Appl. Phys. Lett.* 71 (1997) 2334–2336.
- [6] C.A. Smith, H.W.H. Lee, V.J. Leppert, S.H. Risbud, Ultraviolet–blue emission and electron–hole states in ZnSe quantum dots, *Appl. Phys. Lett.* 75 (1999) 1688–1690.

- [7] E. Monroy, F. Calle, E. Munoz, F. Omnes, B. Beaumont, P. Gibart, Visible-blindness in photoconductive and photovoltaic AlGaIn ultraviolet detectors, *J. Electron. Mater.* 28 (1999) 240–245.
- [8] J.H. He, Y.H. Lin, M.E. McConney, V.V. Tsukruk, Z.L. Wang, G. Bao, Enhancing UV photoconductivity of ZnO nanobelt by polyacrylonitrile functionalization, *J. Appl. Phys.* 102 (2007) 084303.
- [9] H. Kind, H. Yan, B. Messer, M. Law, P. Yang, Nanowire ultraviolet photodetectors and optical switches, *Adv. Mater.* 14 (2002) 158–160.
- [10] C. Soci, A. Zhang, B. Xiang, S.A. Dayeh, D.P.R. Aplin, J. Park, X.Y. Bao, Y.H. Lo, D. Wang, ZnO nanowire UV photodetectors with high internal gain, *Nano Lett.* 7 (2007) 1003–1009.
- [11] O. Lupan, L. Chow, G. Chai, L. Chernyak, O. Lopatiuk, H. Heinrich, Focused-ion-beam fabrication of ZnO nanorod-based UV photodetector using the in-situ lift-out technique, *Phys. Status Solidi (a): Appl. Mater.* 205 (11) (2008) 2673–2678.
- [12] O. Lupan, G. Chai, L. Chow, Novel hydrogen gas sensor based on single ZnO nanorod, *Microelectron. Eng.* 85 (2008) 2220–2225.
- [13] O. Lupan, G. Chai, L. Chow, Fabrication of ZnO nanorod-based hydrogen gas nanosensor, *Microelectron. J.* 38 (2007) 1211–1216.
- [14] P. Gao, Z.L. Wang, Self-assembled nanowire–nanoribbon junction arrays of ZnO, *J. Phys. Chem. B* 106 (49) (2002) 12653–12658.
- [15] C. Xiangfeng, J. Dongli, A.B. Djuricic, Y.H. Leung, Gas-sensing properties of thick film based on ZnO nano-tetrapods, *Chem. Phys. Lett.* 401 (2008) 426.
- [16] T. Gao, T.H. Wang, Synthesis and properties of multipod-shaped ZnO nanorods for gas-sensor applications, *Appl. Phys. A: Mater. Sci. Process.* 80 (2005) 1451.
- [17] K.H. Zheng, Y.C. Zhao, K. Deng, Z. Liu, L.F. Sun, Z.X. Zhang, L. Song, H.F. Yang, C.Z. Gu, S.S. Xie, Effectively enhanced oxygen sensitivity of individual ZnO tetrapod sensor by water preadsorption, *Appl. Phys. Lett.* 92 (2008) 213116.
- [18] J. Huh, G.-T. Kim, J.S. Lee, S. Kim, A direct measurement of the local resistances in a ZnO tetrapod by means of impedance spectroscopy: the role of the junction in the overall resistance, *Appl. Phys. Lett.* 93 (2008) 042111.
- [19] O. Lupan, L. Chow, G. Chai, B. Roldan, A. Naitabdi, A. Schulte, H. Heinrich, Nanofabrication and characterization of ZnO nanorod arrays and branched microdots by aqueous solution route and rapid thermal processing, *Mater. Sci. Eng. B* 145 (2007) 57–66.
- [20] Y. Takahashi, M. Kanamori, A. Kondoh, H. Minoura, Y. Ohya, Photoconductivity of ultrathin zinc-oxide films, *Jpn. J. Appl. Phys.* 33 (1994) 6611–6615.

Biographies

Guangyu Chai is the Research Director at Apollo Technologies Inc., Orlando, FL, USA. He received his BS in physics in 1999 from the Peking University, Beijing, China. He received PhD in Condensed Matter Physics from University of Central Florida, Orlando, FL, USA in 2004. Research interest: ZnO nanorod sensors; individual carbon nanotube devices, focused ion beam fabrication of nanodevices.

Oleg Lupan received his M.S. in microelectronics and semiconductor devices from the Technical University of Moldova (TUM) in 1993. He received his Ph.D. in solid-state electronics, microelectronics and nanoelectronics from the Institute of Applied Physics, Academy of Sciences of Republic of Moldova in 2005. He is a visiting professor and researcher at the Department of Physics, University of Central Florida, USA. In 2008 he was promoted to associate professor in solid-state electronics, microelectronics and nanoelectronics at the Department of Microelectronics and Semiconductor Devices of the Technical University of Moldova (TUM). His current research interests range over semiconductors oxides nano-architectures and thin films for gas, chemical sensors and solar cells; development of nanotechnologies with self-assembly and hydrothermal synthesis; design and investigation of novel nanodevices.

Lee Chow is the associate chair and professor of the Department of Physics, University of Central Florida, Orlando. He received his B.S. in physics in 1972 from the National Central University, Taiwan. He received Ph.D. in Physics from Clark University, Worcester, MA, USA in 1981. In 1981–1982 was postdoc in physics at the University of North Carolina, Chapel Hill, NC. He joined University of Central Florida in 1983 as an assistant professor, and was promoted to associate professor in 1988, and to professor in 1998. Areas of expertise: chemical bath deposition, nanofabrications of carbon nanotubes and metal oxides architectures, diffusion in semiconductors, high T_c thin film, hyperfine interactions, high pressure physics, thin films.

Helge Heinrich is assistant Professor of the Department of Physics University of Central Florida, Orlando. He received his physics M.S. in 1990 from University of Braunschweig, Germany. He received Ph.D. in physics in 1994 from Swiss Federal Institute of Technology, ETH Zürich, Switzerland. From 1996 to 2003, he worked at ETH Zürich as a research associate and lecturer applying mainly electron microscopy in materials science and physics. Since the end of 2003, Dr. Heinrich has been an assistant professor since 2003 at the University of Central Florida in Orlando in the Advanced Materials Processing and Analysis Center (AMPAC) and in the Physics department. Areas of expertise: the microstructural characterization of materials; interfaces and chemical reactions in thin-film solar cells, nanodevices and nanosensors.