GCEP Report

New Pathways Towards High Performance Transparent Conductive Oxides

Investigators

Xiaolin Zheng, Associate Professor, Mechanical Engineering
Hyun Soo Han, Postdoc Researcher, Mechanical Engineering

Abstract

Our proposed research is to develop the nanostructured three-dimensional (3D) transparent conductive oxides (TCOs) and to evaluate their electrical and optical property. 3D-TCO consist of the tin doped indium oxide ($Sn:In_2O_3$, ITO) nanowire arrays can increase not only the carrier mobility due to the single crystalline nature but also the optical path length due to randomly diffused light. This ITO nanowire arrays can be grown on arbitrary substrates such as stainless steel mesh, glass and carbon fibers, therefore we can fabricate various types of TCO substrate using the ITO nanowire. This research, which covers the topics of renewable energy and advanced materials and catalysts, represents a groundbreaking approach promising widespread application.

Background

TCOs are key materials for high performance optoelectronic devices such as flat-panel displays, light-emitting diodes and solar energy conversion devices. TCOs have been made from many semiconductors, including impurity-doped In_2O_3, SnO_2 and ZnO as well as multicomponent oxides consisting of combinations of In_2O_3, SnO_2 and ZnO, including some ternary compounds existing in their systems. Frequently, for an ideal TCO, a compromise between its electrical conductivity and optical transmittance has to be made. In this regard, a nanostructured three-dimensional (3D) TCO electrode, such as TCO nanowire arrays, can be an effective way to manage the light absorption by tuning light reflection and scattering, while maintaining high electrical conductivity along the nanowires. In addition, nanowire arrays provide large surface to volume ratios that can be beneficial for high surface area electrode applications. Earlier time of this project, we successfully grown ZnO nanowires and test their electrical conductivity that needs to be significantly. Since then, we have focused on tin-dope indium oxide (Sn: In_2O_3, ITO) nanowires since ITO has excellent electrical conductivity (resistivity: ~10^{-5} Ω cm).[1]

Results thus far

a. Successful preparation of solution growth conditions of ZnO wire arrays with high density and large diameter

We have successfully optimized the solution growth conditions to grow high density ZnO nanowire arrays on glass substrates. The ZnO nanowires are about 100 nm in diameter and 1.5 micron in length (Fig. 1, top) and they are grown uniformly over a centimeter scale area. In addition, on top of the ZnO nanowires, we have coated ZnO shell conformally (Fig. 1, bottom). For TCO applications, we will further grow ZnO with micron size diameter or larger and the all the space between ZnO wires will be fully filled with ZnO by sol-flame method.

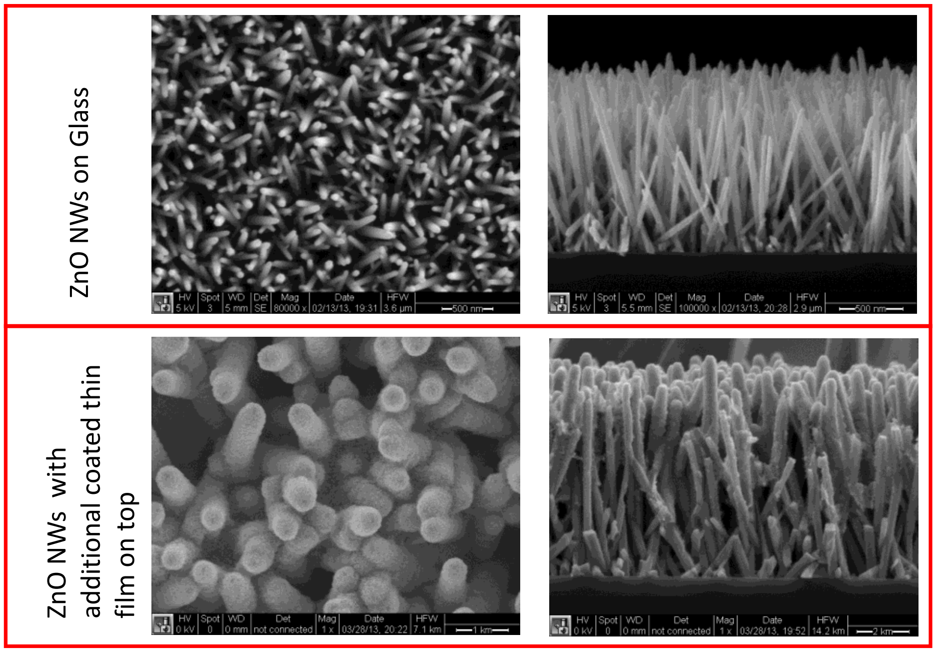
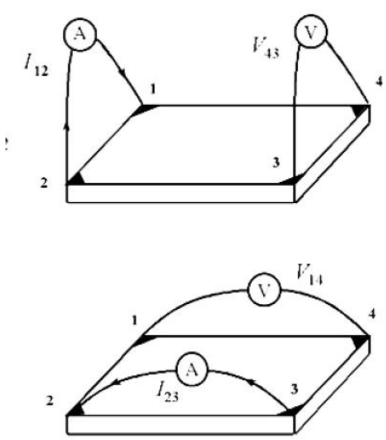


Figure 1. Scanning electron microscope images of (top) ZnO nanowire arrays grown on glass substrates; (bottom) ZnO nanowire arrays that are further coated with ZnO shells by the sol-flame method.

b. Identification of the method to measure the sheet resistance of various ZnO thin film

We have identified the well-established van der Pauw Method to measure the sheet resistance of various ZnO thin films that we prepare. The benefit of this method is that it can accurately measure the sheet resistance of the properties of thin films and remove the impact of contact resistance. The details of implementing this method is illustrated in Fig. 2.



Eight measurements:

$$R_{21,34} = V_{34}/I_{21},\ R_{12,43} = V_{43}/I_{12},$$

$$R_{32,41} = V_{41}/I_{32},\ R_{23,14} = V_{14}/I_{23},$$

$$R_{43,12} = V_{12}/I_{43},\ R_{34,21} = V_{21}/I_{34},$$

$$R_{14,23} = V_{23}/I_{14},\ R_{41,32} = V_{32}/I_{41}.$$

Van der pauw equation:

$$\exp(-\pi R_A/R_S) + \exp(-\pi R_B/R_S) = 1$$

where: Rs = sheet

$$R_A = (R_{21,34} + R_{12,43} + R_{43,12} + R_{34,21})/4 \text{ and}$$

$$R_B = (R_{32,41} + R_{23,14} + R_{14,23} + R_{41,32})/4$$

Figure 2. Schematics and details of the Van der paum measurement that will be used to determine the sheet resistance of ZnO based TOC films.

c. Successful preparation of ITO nanowire arrays with high density

We have successfully synthesized highly conductive single crystalline ITO nanowire arrays on ITO/Glass substrate using a vapor transport method (Fig. 3). Specially, a mixture of indium (99.99%) and tin (99.99%) metal powders (In:Sn = 10:3, atomic ratio) were loaded into a quartz boat and placed in the center of a quartz tube. Those powers are evaporated and oxidized by the carrier gas O_2 and the ITO vapor condenses as nanowires on a substrate placed further downstream. The as-grown ITO nanowires are single crystal with about 100 nm in diameter (Fig. 3b-e) and their length can be controlled by growth time. They can be grown uniformly on diverse substrates, such as ITO/Glass substrates, stainless steel mesh, glass fibers and carbon fibers (Fig. 4).

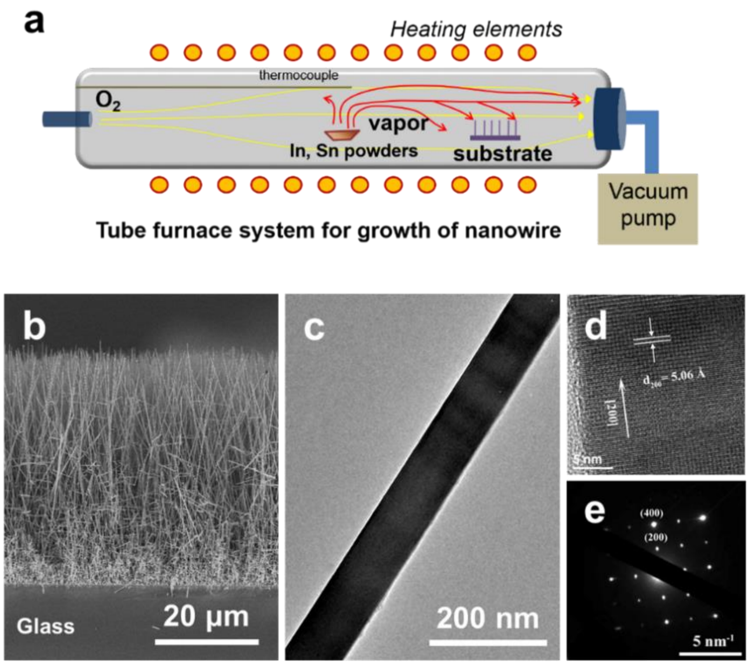


Figure 3. a) Schematic illustration of vapor transport method for synthesis of ITO nanowire arrays. b) Scanning electron microscopy image of ITO nanowire arrays grown on the ITO/Glass substrate. c) Transmission electron microscopy image, d) High-resolution transmission electron microscopy image and e) selected-area electron diffraction (SAED) pattern of single ITO nanowire.

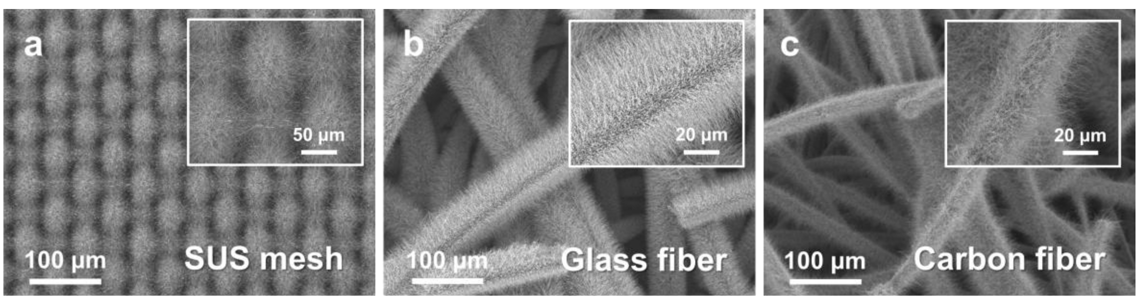


Figure 4. Scanning electron microscopy images of ITO nanowire arrays grown on a) stainless steel meshes, b) glass fibers and c) carbon fibers.

Conclusions

In this investigation, we prepared high density and uniform ZnO and highly conductive ITO nanowires. We have identified the method to measure the sheet resistance of those films. As a next step, we will need to characterize the electrical and optical properties of ITO nanowires and extend the growth and characterization to branched ITO nanowires.

Publications and Patents

1 "Sol-Flame Synthesis of Cobalt-doped TiO_2 Nanowires with Enhanced Electrocatalytic Activity for Oxygen Evolution Reaction", L. L. Cai, I. S. Cho, M. Logar, A. Mehta, C. H. Lee, P. M. Rao, Y. Z. Feng, F. Prinz and **X. L. Zheng**, ***Phys. Chem. Chem. Phys.***, DOI:10.1039/C4CP01748J (2014).

2 "Morphological control of heterostructured nanowires synthesized by sol-flame method ", R. L. Luo, I. S. Cho, Y. Z. Feng, L. L. Cai, P. M. Rao and **X. L. Zheng, *Nanoscale Research Letters,*** 8:347, DOI:10.1186/1556-276X-8-347 (2013).

3 "Codoping TiO_2 Nanowires with (W, C) for Enhancing Photoelectrochemical Performance", I. S. Cho, C. H. Lee, Y. Z. Feng, M. Logar, P. M. Rao, L. L. Cai, D. R. Kim, R. Sinclair and **X. L. Zheng, *Nature Communications,*** *Vol.* 4, Article number: 1723, DOI: 10.1038/ncomms2729 (2013).

References

1. T. Minami, Transparent conducting oxide semiconductors for transparent electrodes, *Semicond. Sci. Technol.*, 2005, 20, S35.
2. Q. Wan et al., High-Performance Transparent Conducting Oxide Nanowires, *Nano Lett*., 2006, 6, 2909.

Contacts

Xiaolin Zheng: xlzheng@stanford.edu
Hyun Soo Han: erichan1@stanford.edu