GCEP Report

New Pathways Towards High Performance Transparent Conductive Oxides

Investigators
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Abstract

Our proposed research will study how employment of a composite microwire array and nanoparticle film structure and application of rapid high temperature flame doping method (the Sol-flame Method) can enhance the electrical conductivity of solution-processed transparent conductive oxides (TCOs). The long-range results can expand the material choice for TCOs and substantially reduce global green-house gas emissions through their increased use in solar panels at decreased deposition costs. This research, which covers the topics of renewable energy and advanced materials and catalysts, represents a groundbreaking approach promising widespread application.

Background

Crystalline TCOs, in comparison to amorphous TCOs and non-oxides, are still the most attractive candidates for TC applications due to their excellent stability and low cost. Significant efforts have been devoted to improve solution processed crystalline TCOs with the aim of competing sputtering and PVD methods over the past two decades, [1] but these efforts have been focused on the optimization of individual step of the solution deposition process under the constrain of all steps under low temperature. Fundamentally, low temperature leads to low conductivity. The step-out idea of our proposed research is to apply rapid high temperature flame treatments into existing solution methods. The high temperature annealing is kept brief enough to protect the temperature sensitive substrates and yet long enough to render TCOs with properties only available at high temperature, such as epitaxial growth and high dopant concentrations.

Electrical conductivity (σ, unit S cm^{-1}) of a TCO film is determined by $\sigma = Ne\mu$ (1), where N is the carrier concentration (# cm^{-3}), e is the carrier charge (C), and μ is the mobility ($cm^2\ V^{-1}\ s^{-1}$). Mobility (μ) describes how easy carriers move through materials and mobility decreases when carriers are scattered by impurity, defects and grain boundaries. Since the solution processed TCO films have much smaller grains than those of gas phase deposited TCO films, the former has decreased mobility. Dopants generated by the gas phase deposition methods have large diffusivity and high energy, and dopants are easier to be incorporated into the host lattice. In contrast, the low temperature nature of solution method gives dopants very low energy and diffusivity, severely hindering the dopant incorporation. Hence the pathway to enhance the electrical conductivity of solution processed TCOs is to increase both grain size and dopant concentration by incorporating rapid high temperature treatments.

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.

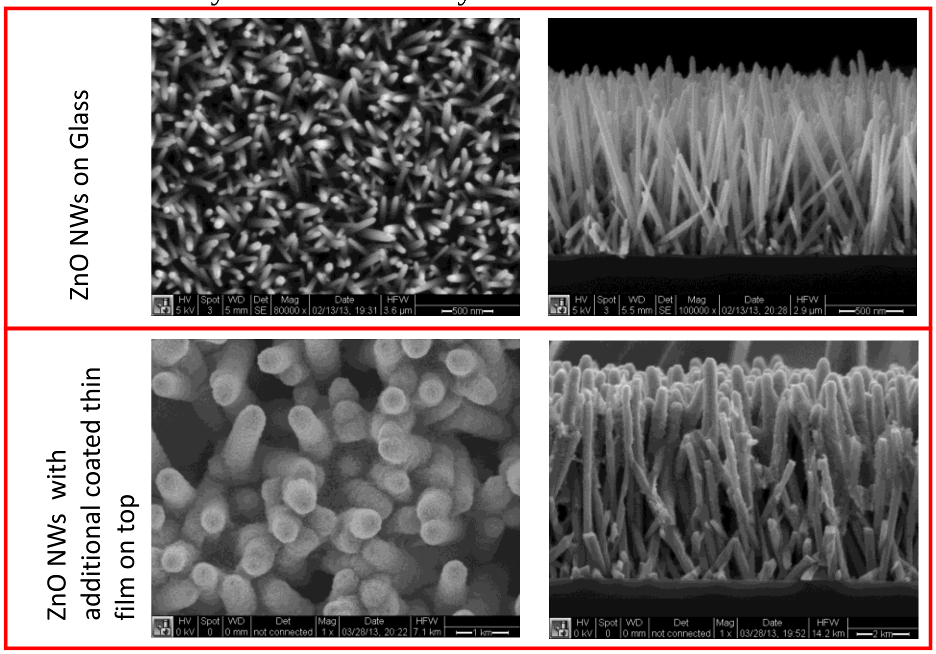
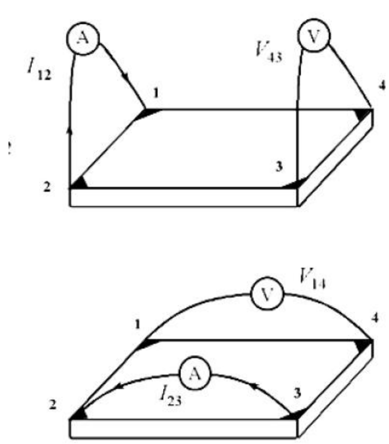


Figure 1. Scanning electron microscope images of (top) ZnO nanowire arrays grown on glass substrates; (bottom) ZnO nanowire arrays that are further coated with ZnO shells by the sol-flame method.

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.

Conclusions

In this investigation, we prepared high density and uniform ZnO nanowires and ZnO nanowires further coated with ZnO shell films as the base materials for TCO. We have identified the method to measure the sheet resistance of those films. As a next step, we will grow ZnO microwires and use them as the epitaxial substrates for the ZnO film. Finally, we will test the effect of flame doping on ZnO film on its electrical conductivity.

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 Pasquarelli, R. M., Ginley, D. S. & O'Hayre, R. Solution processing of transparent conductors: from flask to film. *Chemical Society Reviews* **40**, 5406-5441, doi:10.1039/c1cs15065k.

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