

Synthesis of Nanofibrous ZnO by Magnetron Sputtering and its Integration in Dye-Sensitized Solar Cells

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Abstract — This work demonstrates a cost-effective synthesis of nanofibrous ZnO layers by a magnetron sputtering. We present the results of layer characterization by scanning electron microscopy, X-ray diffraction, energy dispersive X-ray spectrometry, Raman spectroscopy, and photoluminescence which are indicative of good structural properties of the layers. The nanofibrous ZnO layers proves good structural properties offering a new nanomaterial for dye-sensitized solar cells (DSCs) application. Their successful integration in DSC for solar energy conversion is demonstrated by impedance spectroscopy, and photo-current-voltage (*J-V*) studies. OCIS codes: (160.0160) Materials; (160.4236) Nanomaterials; (360.6050) Solar Energy

Index Terms — magnetron sputtering, nanofirous, SEM, solar cells, ZnO.

I. INTRODUCTION

ZnO-based nanostructures have attracted the attention of many research groups due to their unique properties and potential applications in nanodevices [1].

Among numerous nanostructures, nanofibrous layers are of great interest due to their large specific surface area which facilitates the adsorption/desorption processes [2-3].

Dye-sensitized solar cells (DSCs) as a new generation of solar cells have attracted great attention of scientists because they are characterized by promising efficiency and environmental protection [4]. However, for extensive applications of DSCs it should be found an inexpensive transparent material for electron transportation to allow efficient charge collection [5]. Thus, ZnO is a metal oxides with wide-band gap which became of great interest for DSC applications [3-6].

Typically, the nanomaterials based on ZnO can be fabricated by various growth techniques, including electrodeposition [3], hydrothermal synthesis [7], vapor-liquid-solid (VLS), vapor-solid (VS) [1] processes, metal-organic chemical vapor deposition (MOCVD) [1], chemical vapor deposition [1], etc. The magnetron sputtering technique has been widely used to synthesize ZnO materials [1]. However, there are no reports on fabrication of ZnO nanofibrous layers by magnetron sputtering and applications in DSCs.

II. EXPERIMENTAL

ZnO nanofibrous layer was synthesized by the magnetron sputtering method[1]. Glass covered with tin oxide films was used as substrate. Substrate cleaning was performed in mixed solution of chromium (7g K₂Cr₂O₇ -10ml H₂O - 100ml H₂SO₄) at 22°C, then it was rinsed with abundant distilled water (18.2 MΩ·cm) flow. Afterwards it was mounted on a working electrode for direct current (DC) magnetron sputtering in a classical set-up. A disc of pure zinc (99.99 %) was used as metal target. A constant vacuum pressure of 5×10^{-3} Torr was regulated by the argon working gas pressure. The direct current DC was 0.15 A and temperature was 210°C. The obtained nanofibrous ZnO layers on tin oxide/glass substrate were annealed at 480 °C for 45 min in an O₂ atmosphere. The sample characterization was performed as described in previous publications [3,6].

III. REZULTS AND DISCUSSIONS

The SEM images of the nanofibrous ZnO material are presented in Figure 1. The surface of the ZnO nanofiber-based layers is fairly uniform. The short nanofibers are interconnected and form a continuous very porous membrane. One can see that the average diameter is of about 100 nm (Figure 1). According to the results of XRD study (not shown) all observed Bragg reflections are in accordance with the Wurtzite *P6₃mc* space group and hexagonal crystal system. The crystal lattice constants *a* and *c* were determined as *a* = 0.325 nm and *c* = 0.520 nm.

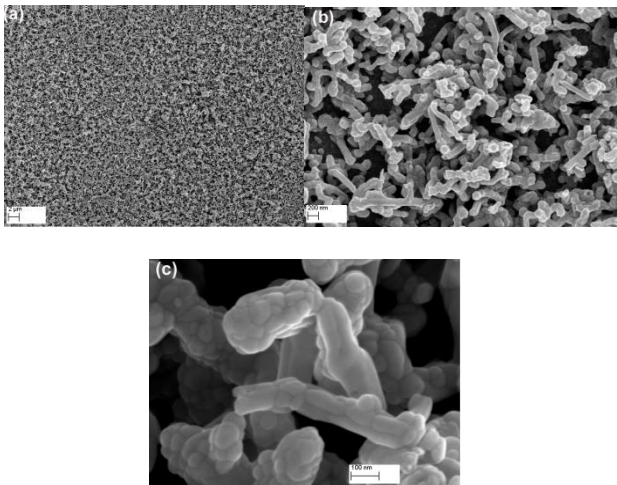


Fig. 1. (a,b,c) SEM top views of ZnO nanofibrous layers grown by magnetron sputtering. (b) and (c) are zoom-in views of (a).

The Raman investigation of the ZnO nanofibrous layer proves the high quality wurtzite crystal structure. Raman scattering peaks have been detected at 100 cm^{-1} , 332 cm^{-1} , 438 cm^{-1} , 582 cm^{-1} , and 644 cm^{-1} , which corresponds to low-frequency E_{2L} , $E_{2H} - E_{2L}$, high frequency E_{2H} , $E_{1L} - LO$, E_1 , $E_2 - TA + LO$ modes, respectively.

Room temperature photoluminescence band with the maximum at 379 nm was evidenced, which overlaps with its phonon replica. We studied the photocurrent-voltage (J - V) characteristics for DSCs based on ZnO nanofibrous layers deposited on tin oxide film/glass substrate. It should be noted that the behavior exhibited by the cells is typical of that inherent to DSC cells. The DSC characteristics were explored under 1 Sun AM 1.5 simulated sunlight. The performances for ZnO nanofibrous solar cells are: a power conversion efficiency of $\sim 1.7\%$, an open circuit voltage (V_{oc}) of 0.49 V, a Fill Factor (FF) of 40.2% and a short circuit photocurrent density (J_{sc}) of 8.45 mA/cm^2 . It is of importance to mention that current density J_{sc} is quite high, which makes such nanomaterial very promising for future DSC applications.

IV. CONCLUSION

Nanofibrous ZnO layers were successfully synthesized on tin oxide/glass substrates using magnetron sputtering technique and were used after sensitization as a photoelectrode of a DSC. The fabricated device yielded to a maximum conversion efficiency of $\sim 1.7\%$.

We found that J_{sc} is quite high ($J_{sc(\text{exp})} = 8.45\text{ mA.cm}^{-2}$),

which is the highest reported value for a such fibrous photoelectrode. The nanomorphology and high crystallinity reduce the charge recombination between photo-excited electrons and oxidized dye and electrolytes, which are processes responsible for increasing the $J_{sc(\text{exp})}$.

Note that that the efficiency depended on the layer thickness, which is currently under investigation

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REFERENCES

- [1] I. M. Tiginyanu, O. Lupan, V. V. Ursaki, L. Chow, M. Enachi, "Nanostructures of Metal Oxides" in *Comprehensive Semiconductor Science & Technology*, Chapter 105, pp. 396-479 (Elsevier 2011).
- [2] S. Li, X. Zhang, X. Jiao, H. Lin, "One-step large-scale synthesis of porous ZnO nanofibers and their application in dye-sensitized solar cells," *Materials Letters* **65**, 2975-2978 (2011).
- [3] O. Lupan, V.M. Guérin, I.M. Tiginyanu, V.V. Ursaki, L. Chow, H. Heinrich, T. Pauporté, "Well-aligned arrays of vertically oriented ZnO nanowires electrodeposited on ITO-coated glass and their integration in dye sensitized solar cells," *Journal of Photochemistry and Photobiology A: Chemistry* **211**, 65-73 (2010).
- [4] B. O'Regan, M. Grätzel, "A low-cost, high-efficiency solar-cell based on dye sensitized colloidal TiO_2 films," *Nature* **353**, 737-740 (1991).
- [5] K.Okada, H. Matsui, T. Kawashima, T. Ezure, N. Tanabe, "100mm_100 mm large-sized dye sensitized solar cells," *Journal of Photochemistry and Photobiology A: Chemistry* **164**, 193-198 (2004).
- [6] V. M. Guérin, C. Magne, T. Pauporté, T. Le Bahers, J. Rathousky, "Electrodeposited Nanoporous versus Nanoparticulate ZnO Films of Similar Roughness for Dye-Sensitized Solar Cell Applications," *ACS Appl. Mater. Interfaces* **2**, 3677-3685 (2010).
- [7] L. Chow, O. Lupan, G. Chai, "Self-assembly of densely packed and aligned bilayer ZnO nanorod arrays," *Applied Physics Letters* **94**, 163105 (2009).