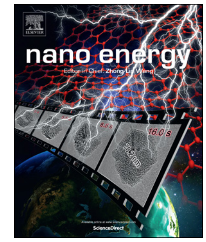
Nano Energy (2014) **9**, 101–111

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/nanoenergy



RAPID COMMUNICATION

High temperature processed ZnO nanorods using flexible and transparent mica substrates for dye-sensitized solar cells and piezoelectric nanogenerators

Do Yeob Kim[a,1], **Sangmin Lee**[b,1], **Zong-Hong Lin**[c], **Kyoung Hwan Choi**[d], **Seok Gwang Doo**[d], **Hyuk Chang**[d], **Jae-Young Leem**[e], **Zhong Lin Wang**[c], **Sung-O Kim**[a,*]

[a]*Holcombe Department of Electrical and Computer Engineering, Center for Optical Materials Science and Engineering Technologies (COMSET), Clemson University, Clemson, SC 29634, USA*
[b]*School of Mechanical Engineering, Chung-Ang University, Seoul 156-756, Republic of Korea*
[c]*School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30332, USA*
[d]*Energy Lab, Material Center, Samsung Advanced Institute of Technology, Yongin 446-712, Republic of Korea*
[e]*Department of Nano Systems Engineering, Center for Nano Manufacturing, Inje University, Gimhae 621-749, Republic of Korea*

Received 25 May 2014; received in revised form 28 June 2014; accepted 8 July 2014
Available online 17 July 2014

KEYWORDS
Zinc oxide;
Nanorod;
Thermal annealing;
Dye-sensitized solar cell;
Piezoelectric nanogenerator

Abstract
The authors report the synthesis of ZnO nanorods on flexible and transparent mica substrates. The coupled use of polyethylenimine and ammonium hydroxide provided a direct method for growing vertically well-aligned ZnO nanorods with a high aspect ratio. Using mica as a substrate material enabled thermal annealing processes, which improved the structural and optical properties of ZnO nanorods with uniform surface coverage and excellent adhesion, increased transmittance of indium tin oxide (ITO)/mica (52%), and decreased sheet resistance of ITO/mica (80%). We have fabricated ZnO nanorod-based dye-sensitized solar cells (DSSCs) and piezoelectric nanogenerators (NGs) and investigated their annealing effects on the device performances. Specifically, the thermal treatment at 500 °C for 30 min increased the energy conversion efficiencies of DSSCs by 53%. Furthermore, we observed a three-fold increase in the NG's output voltage and output current density through this thermal annealing process. As

*Corresponding author. Tel.: +1 864 656 3651; fax: +1 864 656 5910.
E-mail address: sok@clemson.edu (S.-O. Kim).
[1]These authors contributed equally to this work.

http://dx.doi.org/10.1016/j.nanoen.2014.07.004
2211-2855/

shown below, mica, which can function under extremes of temperature, is useful as a substrate for flexible and transparent electronics.

Introduction

The development of optically transparent electronic devices fabricated on mechanically flexible substrates has been the subject of much recent research, in that it represents the next generation electronics technology because of its great potential and functionality to significantly enhance many industries from a commercial perspective. Substantial research has been conducted on developing and analyzing transparent and/or flexible devices, such as thin-film transistors, light emitting diodes, solar cells, supercapacitors, and batteries [1-5]. Metal foil, polyethylene terephthalate (PET), polyethylene naphthalate (PEN), and cellulose nanopaper have commonly been used as flexible and transparent substrate materials [6-10]. However, these substrate materials have some limitations. For example, dye-sensitized solar cells (DSSCs) using opaque metal foil as a substrate material must be illuminated from the back-side of the cell and there are large losses of incident light through the counter electrode and electrolyte before the light reaches the dye attached onto the photoanode. This reverse illumination decreases the energy conversion efficiency by 20% compared to the front-side illumination [11,12]. Another consideration is the typical use of thermal annealing processes, which are essential for improving the overall device performance in a variety of applications. Indium tin oxide (ITO) is widely used as transparent conductive oxide, and the transparency and conductivity of ITO can be improved by a thermal annealing process in excess of 300 °C [13-15]. A post-growth annealing process has also been useful for improving the crystal quality of active layers in devices [16-19]. PET, PEN, and cellulose nanopaper are highly flexible and transparent materials but their processing temperatures, 78 °C for PET, 120 °C for PEN, and 200 °C for cellulose nanopaper, prevent their use above these temperatures. The transference of active layers to PET, PEN, or cellulose nanopaper substrates after the annealing process at high temperature is another viable alternative for improving the crystal quality of active layers, though this process is somewhat more complex to undertake [20,21]. Consequently, determining novel substrate materials with high flexibility, transparency, and thermal stability is a critical necessity for developing flexible and transparent applications.

Muscovite mica sheets are chemically inert, highly transparent, flexible, light-weight, perfectly insulating, and are also stable when exposed to moisture, light, and high temperatures. In addition, they cleave perfectly into very thin pliable sheets whose two principal axes are almost parallel to the cleavage plane, thus providing a sufficiently large sheet of uniform thickness [22]. These outstanding characteristics of mica satisfy the requirements of the substrate material for flexible and transparent applications.

In this work, we will first elucidate the development of our high temperature processed ZnO nanorods on flexible and transparent mica substrates using a hydrothermal method depending on the several growth conditions, including growth temperatures and concentrations of polyethylenimine (PEI) and ammonium hydroxide. Under elaborately managed growth conditions, vertically well-aligned ZnO nanorods with a high aspect ratio were successfully grown on mica substrates. We have fabricated flexible and transparent ZnO nanorod-based DSSCs and piezoelectric nanogenerators (NGs), and investigated the effects of both the growth time and the annealing process on DSSCs and NGs.

The use of mica substrates enabled annealing processes at higher temperatures, which consequently improved the structural and optical properties of ZnO nanorods as well as the transmittance and sheet resistance of ITO/mica substrates. We expect that this approach will provide a breakthrough for overcoming the limited process temperature on plastic substrates for flexible and transparent electronics.

Experimental section

Growth of ZnO nanorods on mica substrates

The mica used as substrates in this research was high quality muscovite mica (Ted Pella Inc.) and the mica sheets were cleaved to ensure high transparency. The cleaved mica substrates were cleaned ultrasonically in acetone for 10 min and then rinsed with deionized (DI) water. ZnO seed layers were deposited on mica substrates using a sol-gel spin-coating method. Specifically, the sol-gel solution was prepared by dissolving 0.005 M zinc acetate dehydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$, 99%, Sigma-Aldrich) in ethanol. After spin-coating, the ZnO seed layers were heated at 350 °C for 20 min in order to evaporate the solvent and remove the organic residue. The spin-coating and pre-heating processes were repeated four times. In order to crystallize, the ZnO seed layers were over-heated in an air atmosphere at 500 °C for 30 min.

ZnO nanorods were grown on the ZnO seed layers *via* a hydrothermal process. The samples were transferred into a Teflon jar that contained an aqueous solution of 0.05 M zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$, 99%, Sigma-Aldrich), 0.05 M hexamethylenetetramine ($C_6H_{12}N_4$, 99.5%, Sigma-Aldrich), 0.005 – 0.015 M PEI (end-capped, molecular weight 800 g/mol LS, Sigma-Aldrich), and 0.1 – 0.4 M ammonium hydroxide (NH_4OH, 28 – 30%, Sigma-Aldrich). To investigate the effect of temperature on the nanorod growth, the growth temperature was varied from 75 to 95 °C. After a