Chemical Physics Letters 610–611 (2014) 39–44

Contents lists available at ScienceDirect

Chemical Physics Letters

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

Role of zinc oxide nanomorphology on Schottky diode properties

Somnath Middya [a], Animesh Layek [a], Arka Dey [a], Joydeep Datta [a], Mrinmay Das [a], Chandan Banerjee [b], Partha Pratim Ray [a,*]

[a] *Department of Physics, Jadavpur University, Kolkata 700 032, India*
[b] *CEGESS, Indian Institute of Engineering Science and Technology, Shibpur, Howrah 711103, West Bengal, India*

A R T I C L E I N F O

Article history:
Received 4 May 2014
In final form 1 July 2014
Available online 8 July 2014

A B S T R A C T

Here, we present the solvothermal synthesis of surfactant guided rod and sphere like zinc-oxide (ZnO) nanoparticles and their application in ITO/ZnO/Al based Schottky diode. Morphology dependent device parameters like ideality factor, barrier potential and series resistance have been analyzed on the basis of charge transport phenomena. The effect of ZnO nanomorphology on device performance has been explained on the basis of multi generation-recombination via interface traps. Carrier mobility, carrier concentration and density of states near Fermi level were also evaluated to see the morphological effect on device property. Finally device performance has been correlated with ZnO morphology.

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1. Introduction

Semiconducting ZnO with wide band gap is a distinguish and unique material and its nanostructures have attracted great attention due to its peculiar properties like high electron mobility, high thermal conductivity and good transparency. The exciton binding energy (60 meV) [1] and optical transparency [2] of ZnO is very high. Based on all these fascinating properties, ZnO has been chosen as a suitable material for the fabrication of semiconductor devices [3,4]. It was applied efficiently in metal-semiconductor Schottky diodes [5], light emitting diodes [6,7], optical sensors [8] and solar cells [9]. The large excitonic binding energy of ZnO leads to extreme stability of excitons at high temperature [10] and enables the devices to function at low threshold voltage. Another important property of ZnO nanoparticle is the morphology dependent electron mobility. Nanomaterial with a suitable band gap for a particular device application can be prepared by changing their morphology. Absorption depends on the effective surface area of the material, which effectively modifies the direct band gap. According to Burstein–Moss effect, the absorption edge of semiconducting nanoparticles is pushed to higher energies as a result of all states close to conduction band being populated. This can be influenced by changing the morphological growth and doping concentration [11]. The n-type semiconductor material with higher band gap is suitable for the formation of Schottky barrier at higher temperature.

As a classical semiconductor, ZnO with higher band gap is compatible with metal-semiconductor Schottky diode. Many metals have been reported for the fabrication of ZnO based Schottky barrier diodes, such as Ag [7,12], Au [13], Pd [14] and Pt [15,16]. For all these metal-semiconductor Schottky diodes, barrier height remains in the range of 0.6–0.8 eV and ideality factor remains around 1.5 [12–16].

There had been a tremendous effort to synthesize ZnO nanoparticles of different morphology. Flower-shaped, prism-shaped, rod-shaped, snowflakes-shaped ZnO nanoparticles had been reported by Zhang et al. [17]. Gao et al. reported the synthesis of flower shaped ZnO by thermolysis technique [18]. Yang et al. presented the synthesis of flower-shaped, disk-shaped and dumbbell-shaped ZnO structures by using capping molecules like citric acid and polyvinyl alcohol [19]. But the morphological impact of inorganic nano-semiconducting material on metal-semiconductor junction physics has so far been unexplored.

In this approach, we have demonstrated the solvothermal synthesis of sphere-like and rod-like ZnO nanoparticles by using CTAB [cetyl-trimethyl-ammoniumbromide] and PVP [poly (vinyl-pyrrolidone)] as capping reagent respectively. Synthesized nanomaterials have been studied by characterizing their structural, optoelectronic and electrical properties. The variation of morphology dependent absorption of the ZnO nano-semiconducting materials has been analyzed. The Schottky diodes having structure ITO/ZnO/Al (given in graphical abstract) were fabricated with

* Corresponding author.
E-mail addresses: partha@phys.jdvu.ac.in, parthapray@yahoo.com (P.P. Ray).

http://dx.doi.org/10.1016/j.cplett.2014.07.003
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synthesized nanoparticles. The rectifying nature in *I–V* characteristics were in agreement with Schottky diode characteristic. The significant change in diode behavior as well as ideality factor and barrier potential was investigated aptly with the variation of the morphology of ZnO nanoparticles. We have also analyzed the *I–V* characteristics on the basis of standard theory to get better insight of the charge transport mechanisms within the device.

2. Experimental

2.1. Synthesis of ZnO nanoparticles of different morphology

In a typical synthesis of surfactant-coated ZnO nanoparticles, 0.05 g of 1 mM anhydrous Zinc acetate was dissolved in 20 ml of ethanol by vigorous stirring at about 50 °C temperature. Then it was diluted to net volume of 200 ml followed by cooling to room temperature. The solution was then divided into two aliquot volumes – each of which was taken into separate flasks. The specific surfactant CTAB [cetyl-trimethyl-ammoniumbromide] and PVP [poly(vinyl-pyrrolidone)] was added into the above pre-marked solution under vigorous stirring. Ethanol based 15 ml of 0.02 M NaOH solution was added drop-wise to each of the mixture within few minutes under stirring condition. A white precipitate (ppt) was obtained in each solution, which was stable at ambient conditions. Thereafter each solution was transferred to a Teflon-lined stainless steel autoclave and heated at 160 °C for 48 h. After cooling down to room temperature, ppts were washed with distilled water and ethanol repeatedly and sequentially to extract ZnO by centrifuge technique. Finally the white ZnO nanopowder was collected by heating at about 120 °C and grinding in a mortar.

2.2. Fabrication of ITO/ZnO/Al based Schottky diode

Prior to Schottky diode fabrication, the ITO coated glass substrates were cleaned with soap solution, acetone, ethanol and distilled water by ultrasonication technique sequentially. The dispersed solutions of ZnO nanoparticle of different morphology in chloroform medium (at appropriate weight ratio) were prepared under sonication. After obtaining the desired solution, they were spin coated (at a spinning speed of 1200 rpm for 2 min) on pre-cleaned ITO coated substrate followed by annealing at 100 °C for 30 min under vacuum. The thicknesses of films were measured (~400 nm) with the help of surface profiler. Aluminum was deposited on these thin films to prepare the metal-semiconductor interface by thermal evaporation technique, maintaining the effective diode area as 7.065×10^{-2} cm^2 with shadow mask. The device architecture is illustrated in Graphical abstract.

3. Characterizations

3.1. Material characterization

In analytical measurements, XRD pattern of the ZnO nanoparticles was recorded with the help of Bruker D8 X-Ray Diffractometer with CuK$_\alpha$ (λ = 1.5418 Å) radiation. The microscopic images of the ZnO nanomaterials were taken by Hitachi S-4800 scanning electron microscope (SEM). Fourier transform infrared spectra of ZnO were recorded with the help of FTIR-8400S Spectrophotometer of Shimadzu. Optical absorption spectra were studied by Shimadzu make 2401PC spectrophotometer. The optical band gap of sphere and rod like ZnO nanoparticles were estimated with the help of Tauc's plots from UV–vis absorption spectrum.

3.2. Device characterization

The current–voltage (*I–V*) characteristics of metal (Al) – semiconductor (ZnO nanoparticles of different morphology) Schottky barrier diodes were characterized by Keithley 2400 Source Meter interfaced with computer. From rectifying *I–V* characteristic curves, the diode parameters like ideality factor, potential barrier height and series resistance were evaluated. Also the charge transport mechanism has been analyzed on the basis of standard semiconductor theory.

4. Results and discussions

Figure 1a and b represent the SEM images of the synthesized materials. These images exhibit that the particles are sphere-like and rod-like in shape with size in nanoscale. The architectural growths of the nanomaterials were highly controlled by the capping reagents CTAB and PVP.

Figure 2 represents the respective X-Ray diffraction spectra for different morphology of the synthesized materials. The JCPDS Card No: 36-1451 approves the powder XRD spectra of materials with no phase impurity [17]. The average particle size was estimated as 77 nm and 46 nm of the sphere and rod like nanoparticles respectively with the help of the Scherrer's peak broadening equation (Eq. (1)) [20]:

$$D = \frac{0.9\lambda}{B\cos\theta} \tag{1}$$

where D is the crystallite size (nm), λ is the wavelength of the monochromatic X-Ray beam (λ = 0.15418 nm for CuK$_\alpha$ radiation), B is the full width at half-maximum for the diffraction peak under consideration and θ is the Bragg's angle.

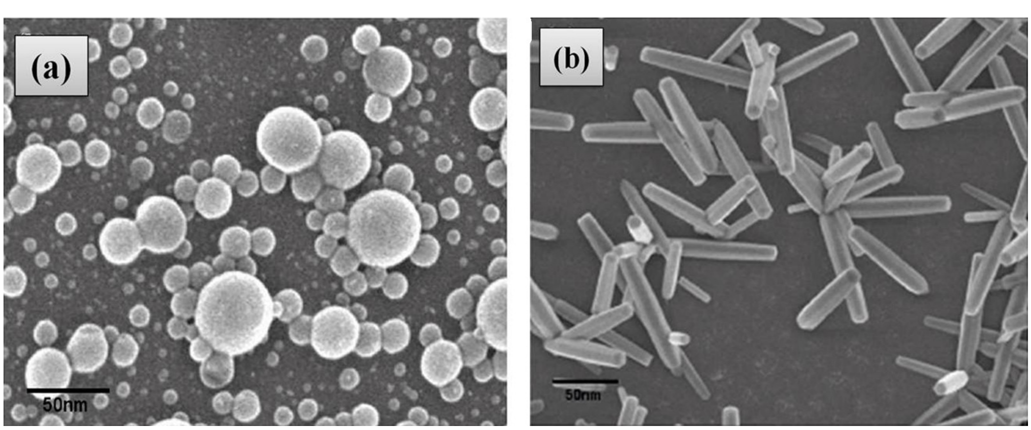

Figure 1. Scanning electron microscopy image of (a) ZnO sphere, and (b) ZnO rod.

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