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Effect of orientation and configuration of ZnO nanorods on electrical conductivity prepared through hydrothermal method on suspended substrate

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Abstract: Hexagonal oriented and dumbbell shaped ZnO nanorods were prepared through hydrothermal method on gold coated glass substrate suspended in growth solution at various precursors concentrations. Tower and dumbbell shaped ZnO nanorods were observed on the substrates. The morphology, crystalline structure, and electrical conductivity of the synthesized ZnO nanorods were observed through Field emission scanning electron microscopy (FESEM), X-rays diffraction (XRD) and four point probe. Each sample consists of ZnO nanorods having various direction of orientation. The FESEM, XRD and Four point probe studies reveals that the orientation and configuration of ZnO nanorods has a significant effect on the electrical conductivity. ZnO nanorods with well hexagonal shape and orientation has the better electrical conductivity (10688 seimens/meter, 7022.2 seimens/meter and 8238 seimens/meter) then the dispersed and congested nanorods.

Keyword: ZnO; Hexagonal; nanorods; dumbbell; orientation; electrical conductivity.

1. Introduction

One dimensional (1D) nanostructures are useful materials to study the dependence of thermal, mechanical and electrical transport properties on size reduction [1]. The fabrication of novel nanostructures for different morphologies has gained more attention in recent years because of their significant potential applications. The controlled on the synthesis of complexed nanostructures is a challenging task in nanotechnology because these nanostructures can be applied in data storage, photonics field emitters, pollution trace detection and sensing [2]. ZnO nanostructures can be found in variety of shapes such as nanoneedles [3], nanotubes [4], nanowalls [5], nanonails, nanobridges, tube, tower and flower like structures. ZnO crystal has a noncentral symmetric wurtzite structure and are composed of closed packed O^{2-} and Zn^{2+} layers piled alternatively along c-axis, producing positively charged Zn-terminated (0001) polar surfaces and negatively charged O-terminated (000-1) polar surfaces. Besides of these two polar surfaces there are some other more fast growing directions of (01-10) and (2-1-10) facilitate anisotropic growth of ZnO with various one dimensional structures including c-axis oriented nanowires [6, 7].

Dumbbell shaped ZnO nanorods has recently received some attention due to its excellent in sensing and optical properties. It has been synthesized by wet chemical solution and hydrothermal methods. Wang et. al. [8] prepared dumbbell shaped ZnO crystallites on cotton fabrics to investigate the UV blocking properties. Li-Yun Yang et. al. [9] prepared dumbbell shaped ZnO polycrystalline through microwave heating for the investigation of photocatalytic activity. Weiliang Feng et. al. [10] prepared the dumbbell shaped ZnO nanostructures through a simple solvothermal method by using zinc acetate and dimethylacetamide (DMAc) as precursors. They observed a change in nanostructure from quasi-spherical ZnO nanoparticles to dumbbell shape when the contents of DMAc were decreased from 80% to 60%. N Rajkumar et. al. [11] proposed a model for the dumbbell shaped ZnO nanostructures shows that in the formation of dumbbell shape ZnO nanorods the hexagonal ZnO nanorods tend to have sharp edged (cone shape) top view due to insufficient ions for further growth. After the completion of reaction the sharp edges of the two hexagonally grown nanorods attract each other to form dumbbell shape nanostructures. V Baranwal et al. [12] synthesized dumbbell ZnO microstructures with hexagonal shape with variable length and diameter through starch assisted hydrothermal method.

Doping is the basic method for controlling band gap, ferromagnetism and electrical conductivity [13] of ZnO nanorods. Various

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metals such as Ga [14], Co [15], Cu [16], and Al [17] has been studied by various groups for the enhancing of electrical properties. Doping is an expensive and time consuming process for the enhancement of properties of semiconductors. In this research an alternating way is found to enhance the electrical conductivity of ZnO nanorods.

2. Experimental setup

ZnO dumbbell and hexagonal shaped nanorods were prepared through a simple hydrothermal method on gold coated substrate suspended in the growth solution. An equimolar solution of zinc nitrate hexahydrate Zn(NO3)26H2O and hexamethylenetetramine C6H12N4 of various concentrations (5 mM to 9 mM) was prepared in 50 ml deionized (DI) water stirred through magnetic bar stirrer overnight. The gold coated substrate is overlapped in a tin sheet with an exposed coated face downward in solution. The precursor's solutions with suspended Au coated substrate were kept in a pre-heated oven at 90°C for 6 hours.

After deposition the samples were rinsed with DI water for 1 minute and kept to dry in ambient condition. The schematic diagram of experimental setup is shown in Fig. 1.

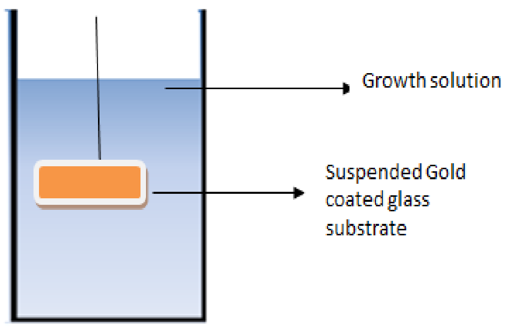

Fig. 1 Schematic of experimental setup.

The morphological and structural evolution of deposited were investigated by field emission scanning electronic microscope (FESEM) and X-ray diffraction (XRD), whereas the electrical conductivity of the prepared nano-structures were investigated using four point probe.

3. Results and Discussions

The morphology of the deposited ZnO was investigated by FESEM techniques. Fig. 2 presents microscopy images of the prepared ZnO nanorods through hydrothermal method from various precursors concentrations (5mM-9mM). The figure consists of hexagonal ZnO nanorods Fig. 2(a) , (b) and (c) which are nearly similar in shape, size and grow along c-axis on the substrate and (d) and (e) are dispersed and dumbbells. These images indicate that the nanorods consist of hexagonally shaped ZnO nanorods and the tips taper off in a stepwise fashion. Interestingly ZnO nanorods with such shape have shown a better gas sensing ability and field emission characteristics as compared to the plate tip shape ZnO nanorods [18]. Most of the nanorods are oriented and properly spaced, these gives them a greater surface area for immobilization in immonosensing / biosensing applications. Furthermore the products of Fig. 2 (a) and (c) suggest that the resultant product shows that the hexagonal rod structure has narrow size distribution though the rod formation is incomplete. The dumbbell shaped ZnO nanorods Fig. 2 (d) are grown on the substrate and then self organized into the dumbbell shape structures. Some of the dumbbell shapes consists of several nanorods and can be formed by self assembly of ZnO nanorods as shown in Fig. 2 (e).

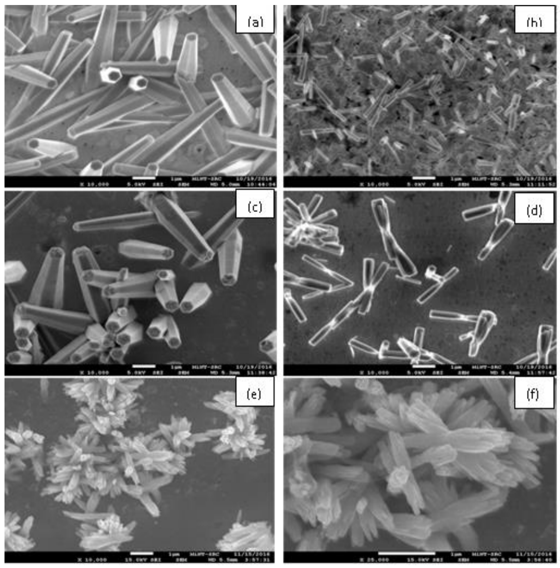

Fig. 2 Surface morphology of ZnO nanorods at 10000 magnification (a) 5 mM (b) 6 mM (c) 7 mM (d) 8mM (e) 9 mM (f) 9 mM 25,000 magnification.

Fig. 2 (b) and (d) indicates a lower density of nanorods due to the sticking of two nanorods from the tail and form a single dumbbell shape nanorods. Fig. 2 (e) consists of a group of nanorods (agglomerated nanorods) and produce nanoflower shapes. Fig. 2 (f) shows the high magnification image of these nanoflowers. The growth mechanism shows a close agreement with De et al. [19] which shows that the ZnO nanorods results from initial heterogeneous nucleation on substrate followed by homogeneous growth of ZnO nanorods around these nuclei.

Fig. 3 shows the XRD pattern of ZnO nanorods grown by hydrothermal method on gold coated glass substrate in range of 20-80°. The XRD pattern shows that all the diffraction peaks can be indexed as hexagonal wurtzite ZnO crystal structure. There are no other diffraction peaks found, indicates the highly pure phase of ZnO. The stronger and narrow peaks exhibit a high crystallanity of the nanostructures.

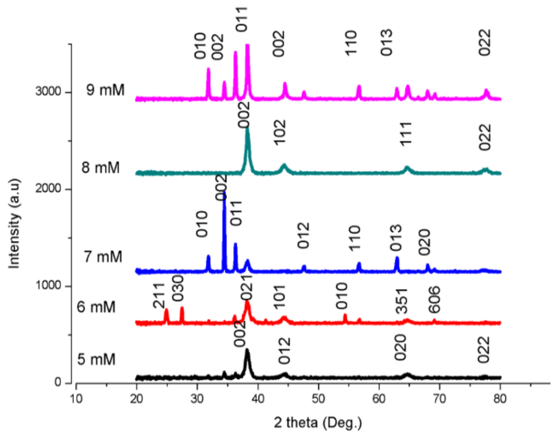

Fig. 3 X-ray diffraction patterns of ZnO nanorods formed Cr-Au coated glass substrate.

As can be seen in Fig. 3, at concentration of 5 mM, 7 mM and 8 mM, the peak (002) is much stronger than the other peaks, revealing that ZnO nanorods are preferably aligned and growth in c-axis polar direction. It also indicates that ZnO nanorods favour to grow in (002) orientation because of the lowest free energy per unit area of the (002) in ZnO nanocrystals. A weak (002) peak in 9 mM show poor orientation of synthesized ZnO nanorods.

The electrical conductivity of as grown ZnO nanorods is shown in the Table 1. It can be seen from the table that at 5 mM, 7mM and 8 mM has the highest conductivity of 10688 S/m, 7022.2 S/m and 8238.6 S/m respectively, due to its broad (002) peak shows a good orientation. The low conductivity at 9 mM is due to its poorest orientation and which is shown by its lowest broadening (002) peak in XRD data. Another reason of increasing electrical conductivity may be because of the fact that electronic conductivity of ZnO nanorods is enhanced when exposed to light with certain wavelength [20]. In given results the oriented nanorods has more exposed surface to light and as a result has a better electrical conductivity.

Table 1: Electrical conductivity of ZnO nanorods at various precursors' concentrations.

S/No	Concentration (mM)	Conductivity (Siemens/meter)
1	5.0	10688.0
2	6.0	1907.4
3	7.0	7022.2
4	8.0	8238.6
5	9.0	4694.0

This indicates that it is not only the quantum confinement effect that enhances the electrical conductivity of ZnO nanorods, the configuration and orientation of ZnO nanorods also has a significant effect on the electrical conductivity.

4. Conclusion

ZnO nanorods of two different morphologies and various orientations were successfully synthesized on gold coated glass substrate suspended in growth solution having different concentrations at the same deposition time and temperature. Hexagonal and dumbbell shaped nanorods were observed has different configuration at different precursor concentrations. The oriented hexagonal shaped ZnO nanorods shows better electrical conductivity, than dumbbell and dispersed nanorods.

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