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Photoconductivity and Dark-Conductivity of ZnO Nanoparticles under UV Illumination by Solid State Reaction Method

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Abstract: In the present work, ZnO nanoparticles (NPs) have been prepared by solid state reaction method using zinc acetate dihydrate. The XRD patterns show broadened peaks, which confirm the nanocrystalline nature of ZnO. The crystallite size of as synthesized sample of most intense peak is found to be approximately 16 nm. In the photoconductivity study, voltage dependence of darkcurrent and photocurrent under UV illumination has been investigated. The dependence of darkcurrent (I_{dc}) and photocurrent (I_{pc}) with applied voltage is found to be super linear ($r > 1$) at low as well as high voltage. Super linear variation of photo and dark current with voltage may be due to injection of additional charge carriers form electrodes. The rise and decay time transient photoconductivity response measurement help to study the photoconductivity dynamics of ZnO NPs.
Keywords: Photoconductivity, XRD, ZnO.

1. Introduction

Recently, there have been extensive studies on optical properties of semiconductor nanocrystals due to their size and shape-dependent optical responses [1–3]. In particular, high quality, II-VI semiconductor nano-crystal samples have been prepared and their luminescence properties have been studied both experimentally and theoretically [4–8] In addition, II-VI compound semiconductor nanocrystals are unique host materials for doping of optically active impurities, and semiconductor nanocrystals doped with luminescence centers exhibit efficient luminescence even at room temperature[9-10]. Different techniques have been developed to synthesize II-VI semiconductor nanocrystals doped with luminescence centers, such as transition-metal ions [9–12]. rare earth ions [13-14] and donor-acceptor pairs [15].

ZnO is an environmentally friendly material and is one of the suitable candidates for practical use as a nano-device material. The novel properties of nano scale zinc oxide particles have found applications in a variety of applications such as luminescence [1–3], varistors [4- 5], solar cells [6], gas sensors [7- 8] etc. Previously, ZnO nanoparticles have been prepared by techniques including the sol–gel method [7–9], precipitation method [10-11], thermal decomposition method [12-13], hydrothermal method [14-15], and spray pyrolysis method [16] etc. However, all of these approaches undergo calcinations or sintering. Moreover, most of them involve complex apparatus, or processing, and in many cases they involve toxic reagents or additives. The relatively high temperature, complexity and toxicity of these techniques restrict their wide spread application. Therefore, the efforts of seeking nontoxic, simple, low-cost and high-yield synthesis methods for preparing nanometer materials are being keenly pursued. Recently, Ye et al. [17] explored an effective approach to synthesize nanocrystals of oxides, sulfides, oxalates, and carbonates, etc. based on a one-step solid-state reaction. This method is fairly simple and can be carried out in air ambient at room temperature.

2. Experimental Procedure

2.1 Sample preparation The chemical regents zinc acetate dehydrate [Zn $(CH_3COOH)_2$. $2H_2O$] and, sodium hydroxide (NaOH) used in this work were of analytical grade procured from E.Merck ltd. Mumbai, India. These chemicals were used directly without special treatment. In a typical synthesis, [Zn $(CH_3COO)_2$.$2H_2O$] (2.195 gm, 0.01 mol) was ground for 5 minutes and then mixed with NaOH (0.800gm, 0.02 mol,) and ground for 30 minutes. The product was washed several times with double distilled water to remove the impurity. The final product was filtered and dried into solid powder at 100 ^{0}C for one hour in air.

2.2 Instrumentation The crystal structure of ZnO nanoparticles were characterized by X-ray diffraction (XRD), Philips Analytical X-Ray B.V. (PW3710 based) Cu K radiation. The photo and dark conductivities of ZnO NPs have been measured using thick film of powder without any binder. In photoconductivity and dark conductivity measurements, a cell was formed by putting a thick layer of powdered samples in between two Cu electrodes etched on a Cu plate (PCB), having a spacing of 1 mm. The powdered layer was pressed with a transparent glass plate. This glass plate has a slit for providing illumination area of 0.25 cm^2. In this cell type device, the direction of illumination is normal to field across the electrodes. The cell was mounted in a dark chamber with a slit where from the light is allowed

to fall over the cell. The photo−response was measured using 300−W mercury lamp and visible photo response was measured using a commercial bulb of 200 W as a photo excitation source. A stabilized dc field (50 V/cm to 500 V/cm) was applied across the cell to which a dc nano-ammeter, NM−122 (Scientific Equipment, Roorkee) for the measurement of current and RISH Multi 15S with adapter RISH Multi SI 232 were connected in series. The light intensity over the cell surface was changed by varying the distance between slit and light source. Before measuring photoconductivity of the sample, the cell is first kept in dark till it attains equilibrium.

3. Results and Discussion

3.1 Structural Study Fig. 1 shows X-ray diffraction pattern of ZnO nanoparticles. It shows a hexagonal wurtizite structure and the lattice constant values (a=3.25A^0, b=5.2A^0) obtained from the XRD pattern of zinc oxide powders were in good agreement with the reported values (JCPDS Card No 36-1451). The size of ZnO nanoparticles corresponding to most intense peak is found to be 16 nm approximately calculated using Scherer formula

$$D = \frac{0.89\lambda}{\beta \cos\theta}, \tag{3.1}$$

where λ is the wave length (Cu Kα), β is the full width half maximum (FWHM) in radians and θ is the diffraction angle.

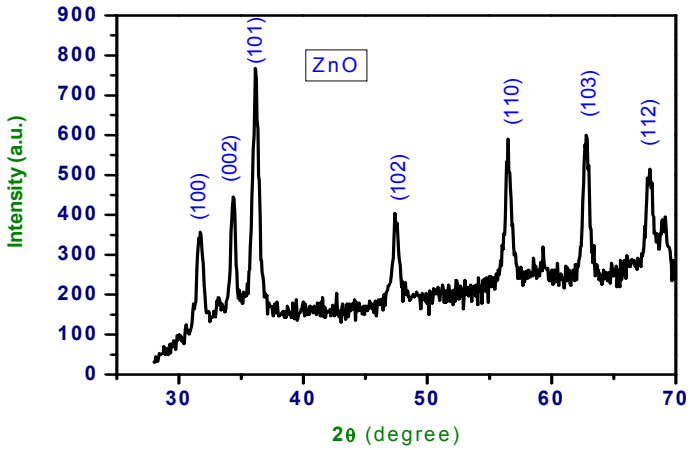

Figure 1: X-ray Diffraction (XRD) Pattern of ZnO Nanoparticles Prepared by Solid State Reaction Method

3.2 Voltage dependence of dark current and photocurrent: Figure 2(a) and 2(b) show the voltage dependence of dark current and photo current respectively. The *ln (I)* vs *ln (V)* curves are straight line having different slope according to power law, $I \alpha V^r$ where I is photocurrent (I_{pc}) or dark current(I_{dc}) ,V is the dc biasing voltage and r is the slope of different straight line segments.

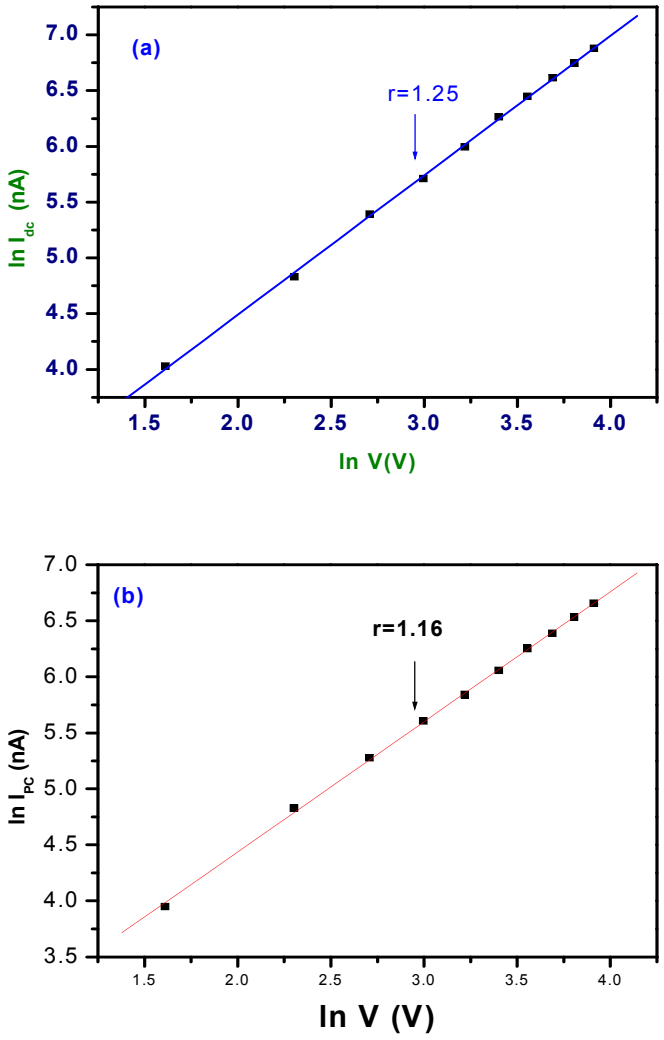

Figure 2: (a) Variation of darkcurrent on ln-ln scale and (b) Variation of photocurrent on ln-ln scale of ZnO NPs synthesized by solid state reaction method

The dark current (I_{dc}) as well as photo current (I_{pc}) of ZnO NPs vary super-linearly (r>1), which may be attributed to injection of additional charge carriers from one of the electrodes [19-20].

3.3 Rise and decay of photocurrent Figure 3 shows rise and decay of photocurrent under UV illumination. The darkcurrent is first stabilized. When the light is switched on, the photocurrent increase very fast initially, then it grows slowly and finally gets stabilized. The fast increase in photo current may be attributed to generation of electron-hole pairs as a result of absorption of photon. When the light is switched off, the photocurrent decreases initially very fast and then exponentially. The fast decay may be attributed to direct electron-hole recombinations. The slow rise and decay may be attributed to a large amount of recombination centers and presence of traps states and defects states within the band gap [19-20]. Adsorption/desorption of oxygen and water molecules on the surface of ZnO NP's may also be responsible for slow rise and decay of photocurrent.

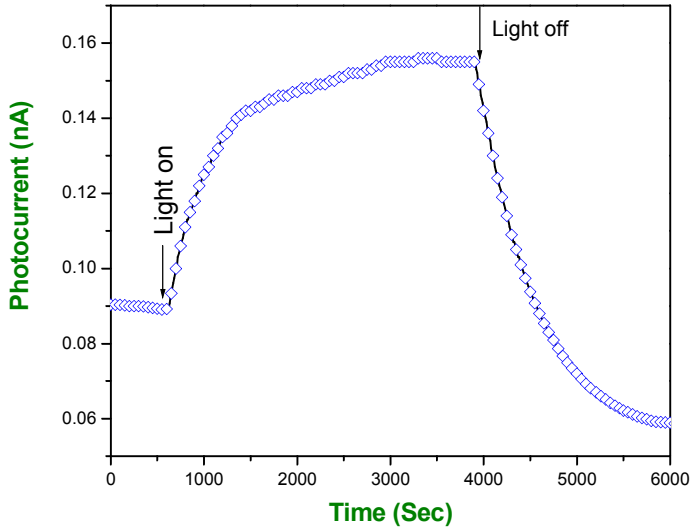

Figure 3: Rise and decay of photocurrent for ZnO NPs prepared by solid state reaction method

4. Conclusions

In the present work, we have studied photoconductivity characteristics of ZnO nanoparticles. ZnO nanoparticles with particle size of approximately 16 nm and of hexagonal wurtizite structure were synthesized by a solid state reaction method. The photocurrent and dark current varies super linearly

with voltage. The fast rise and decay in photocurrent is due to generation and recombination of electron-hole pairs respectively.

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