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Study on Photoconductivity in Air and Vacuum of ZnO Prepared by different materials

Ravi Shankar Saxena¹

¹Department of Electronics and communication, St. Martin's Engineering College, Dhulapally, Secundarabad

Abstract: In the present work, zinc oxalate [$ZnC_2O_4 \cdot 2H_2O$] and zinc nitrate [$Zn(NO_3)_2 \cdot 6H_2O$] was used as precursor to prepare zinc oxide by thermal decomposition method. Its photoconductivity and dark-conductivity properties have been studied in air as well as in vacuum. Voltage dependence of photocurrent and dark-current has been observed at room temperature in air under UV-vis illumination. Structural study of ZnO microstructures has been analyzed by X-ray diffraction (XRD) and scanning electron microscopy (SEM). Rise and decay curve in air exhibits anomalous behavior wherein the photocurrent decreases even during steady illumination. In vacuum, the rise of photocurrent becomes slow and prolonged.

Keywords: Photoconductivity, Zinc Oxalate, Zinc Nitrate, XRD, Thermal decomposition.

I. INTRODUCTION

Photoconductivity is described as electrical conductivity resulting from photo-induced electron excitations in which light is absorbed. In semiconductors, photoconductivity arises due to photo-generation of electron hole pairs after absorption of photons which increases carrier density and conductivity of material. Photoconductivity, the increase in the electrical conductivity of certain materials when they are exposed to light of sufficient energy, serves as a tool to understand the internal processes in these materials, and it is also widely used to detect the presence of light and measure its intensity in light sensitive devices. In order for photoconductivity to be produced, light must be absorbed in the process of creating free carriers by intrinsic or extrinsic optical absorption. Zinc oxide (ZnO) is a material of particular interest because it possesses unique optical and electrical properties. It is a wide-band semiconductor (3.37 eV) and is a good candidate for many applications[1-8]. For example thin films of ZnO were reported to display good photoconductivity and high transparency in visible region and has been used as transparent electrodes for solar cells. It is also used prominently for its application as an ultraviolet (UV) light detector. Many authors have reported photoconductivity in ZnO thin films, nanorods, nanowires, nanoparticles and thick films. A number of synthesis methods have been used to synthesize ZnO such as chemical vapour deposition, sol-gel, spray pyrolysis, co-precipitation, thermal decomposition and hydrothermal methods. Thermal decomposition is a simple, low-cost and mass-scale production method [9-10].

In the present work ZnO structures synthesized by thermal decomposition of Zinc Oxalate and Zinc Nitrate have been studied for their photoconductivity properties by observing variation of photocurrent and dark-current as a function of applied voltage and time in air as well as in vacuum under ultraviolet visible (UV-vis) illumination. Structural and morphological studies also have been performed for synthesized ZnO structures. Study of photoconductivity in ZnO structures synthesized by thermal decomposition of zinc oxalate and zinc nitrate is perhaps first of its kind to the best of our knowledge.

II. EXPERIMENTAL SECTION

A. Chemicals

The Zinc Oxalate ($ZnC_2O_4 \cdot 2H_2O$) and Zinc Nitrate [$Zn(NO_3)_2 \cdot 6H_2O$] (purity: 99%) was procured from E.Merck Ltd., Mumbai. This chemical was directly used without special treatment.

B. Sample preparation

The Zinc Oxalate ($ZnC_2O_4 \cdot 2H_2O$) and Zinc Nitrate [$Zn(NO_3)_2 \cdot 6H_2O$] was used as precursor to synthesize ZnO structures. Two gram of Zinc Oxalate and Zinc Nitrate was placed in a crucible and was calcined at 500°C in a muffle furnace for three hours. ZnO structures are obtained in powder form.

C. Instrumentation

The crystal structure of ZnO nano structures was characterized by X-ray diffraction (XRD, PANalytical). SEM images were obtained by using JEOL scanning electron microscope. For photoconductivity and dark conductivity measurements, a cell was formed by spreading a thick layer of powdered sample in between Cu electrodes etched on a Cu plate (PCB). The powdered layer was pressed with transparent glass plate. 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 UV-vis photo-response was measured using aHg lamp of 300W as a photo-excitation source and the current was measured using RISH Multi 15S with adapter RISH Multi SI 232. 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. For measuring photoconductivity in vacuum, we used Tarson Rockyvac 300 vacuum pump to create vacuum in a glass chamber.

III.RESULTS AND DISCUSSIONS

A. Structural study

Figure 1a shows the XRD pattern of ZnO structures prepared by thermal decomposition of zinc oxalate at 500 °C for 3h. All the diffraction peaks can be indexed to the ZnO wurzite structure corresponding to JCPDS card No. 75-0576. No other characteristic peaks of impurities, such as Zn(OH)₂, are observed, indicating that the prepared ZnO is of high purity. The crystallite size (D) of the sample is calculated using Debye Scherrer formula:

$$D = \frac{0.9\lambda}{\beta \cos\theta}$$

where β is full width at half maximum (FWHM) in radians, λ is the X-ray wavelength and θ is the Bragg's angle.

Figure 1b shows X-ray diffraction (XRD) pattern of ZnO microstructures prepared by thermal decomposition of zinc nitrate at 500 °C for 3h. All the diffraction peaks can be indexed to ZnO wurzite structure corresponding to JCPDS card No. 36-1451. Similar results have been reported by Baskoustas et al. [11].

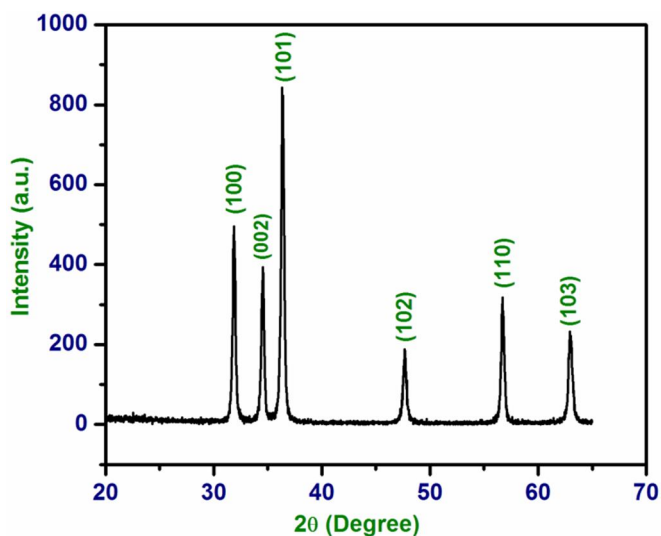


Figure 1a: X-ray diffraction (XRD) pattern of ZnO synthesized by thermal decomposition of zinc oxalate.

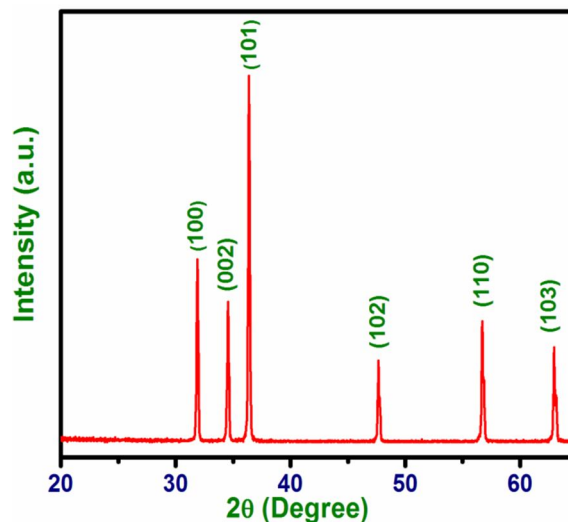


Figure 1b: X-ray diffraction (XRD) pattern of ZnO microstructures synthesized by thermal decomposition of zinc nitrate.

B. Morphology Study

Figure 2a and 2b shows the SEM images of synthesized ZnO structures prepared by zinc oxalates. It is observed that structures of zinc oxide consist of irregular cuboids form by a large number of rectangular platelets.

Figures 3a and 3b show SEM images of the synthesized ZnO particles formed by thermal decomposition of zinc nitrate at 500 °C for 3h. The aggregated morphology of six sided pyramid particles are observed. Similar morphology has been reported by N.Uekawa et al. for ZnO particles synthesized by heating zinc nitrate hexahydrate [12].

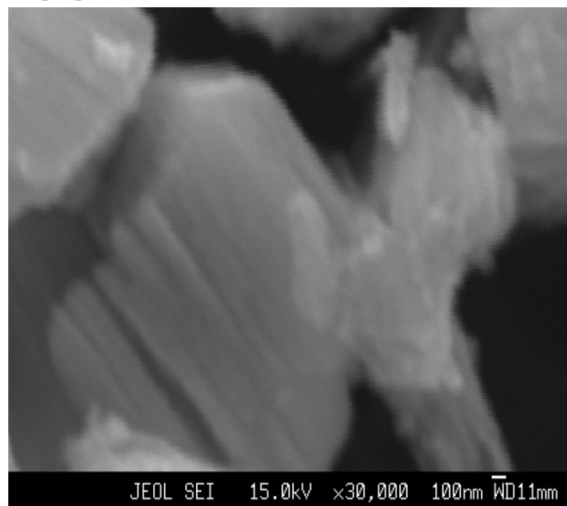
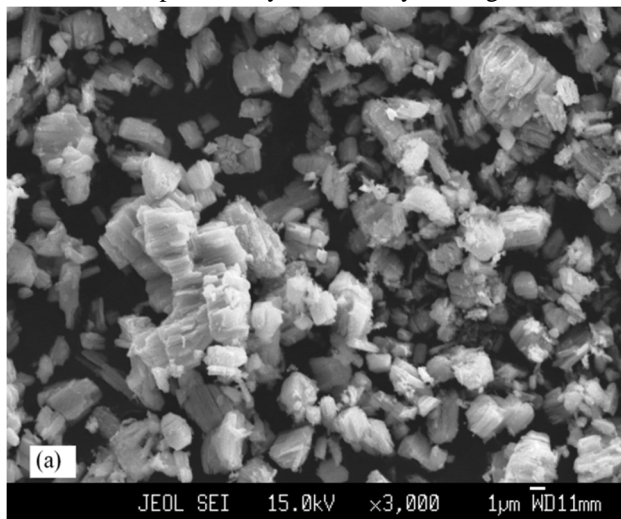


Fig. 2 SEM images (a) at low magnification and

(b) at high magnification of ZnO synthesized by thermal decomposition of zinc nitrate.

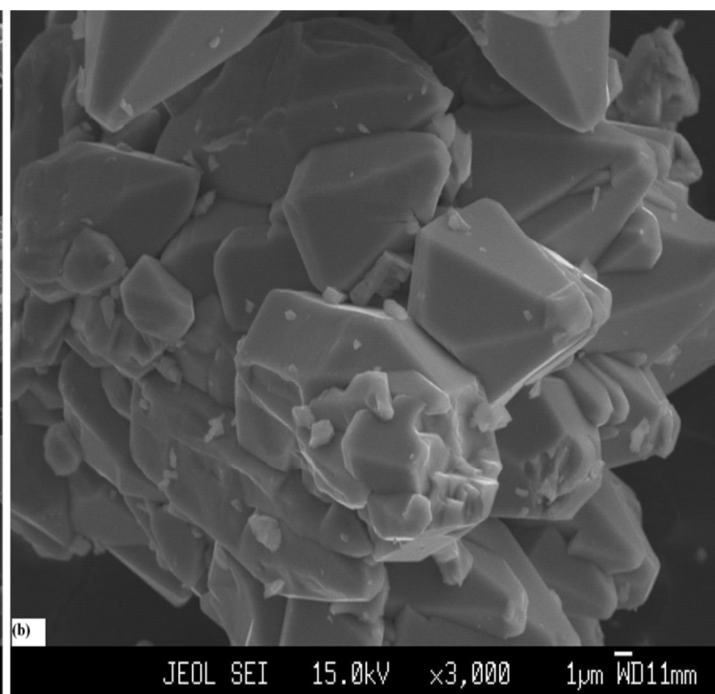
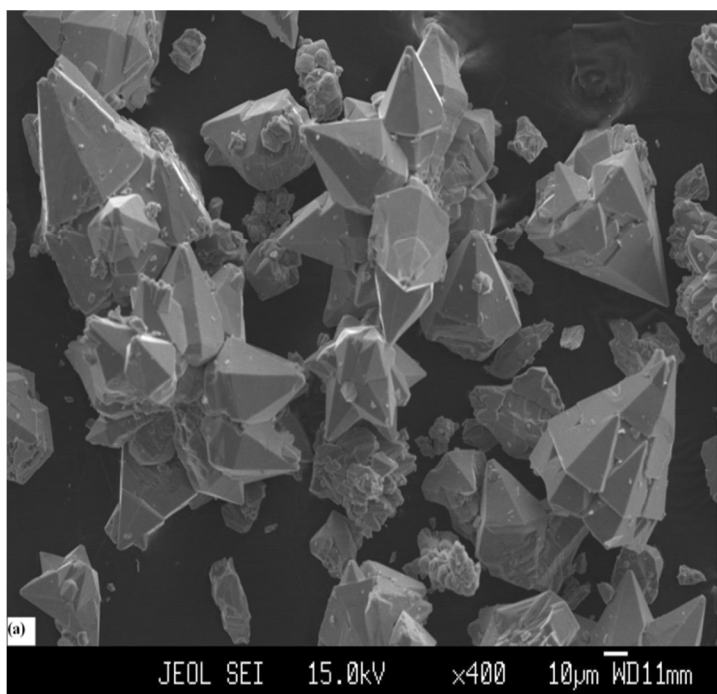


Fig. 3: SEM images (a) at low magnification and

(b) at high magnification of ZnO synthesized by thermal decomposition of zinc nitrate.

UV-visible absorption study Figure 4a shows room temperature UV-visible absorption spectrum of ZnO structures synthesized by a thermal decomposition of zinc oxalate. The ZnO particles have band edge absorption at 370 nm. Blue shifting of band edge as compared to its bulk counterpart may be attributed to dimension of ZnO [3,13].

Figure 4b shows UV-visible absorption spectrum of ZnO microstructures prepared by thermal decomposition of zinc nitrate at 500 °C for 3h which exhibits absorbance peak at 381 nm. Similar absorbance peak has been reported by Wan et al. and Singh et al.[14].

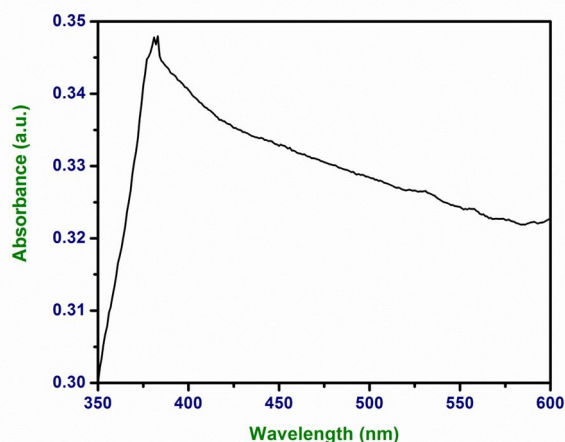


Fig. 4a: Room temperature UV visible of ZnO synthesized by zinc oxalate.

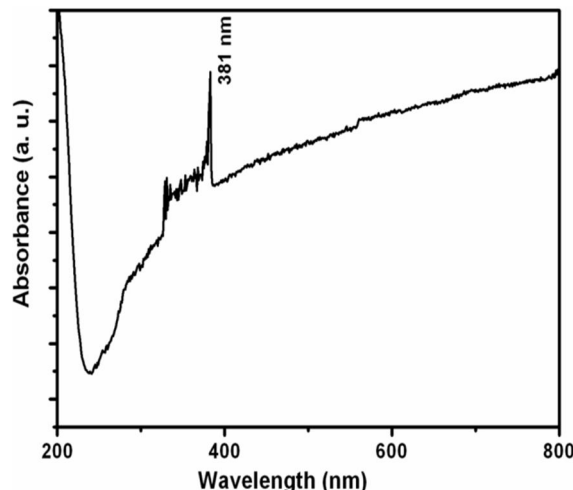
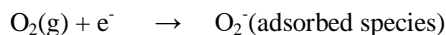


Fig. 4b: Room temperature UV visible of ZnO synthesized by zinc nitrate.

C. Rise And Decay Of Photocurrent

Figure 5a shows rise and decay curve of photocurrent under UV illumination in air with fixed photo flux and bias voltage. The cell is initially kept in dark till the dark current gets stabilized. When the light is switched on, the photocurrent initially increases very fast due to fast process of generation of electron and hole pairs as a result of absorption of photons. After attaining a peak, the photocurrent starts decreasing slowly even during illumination. This kind of anomalous behaviour may be attributed to slow process of photo induced chemisorption of oxygen molecules on the surface of ZnO nano structures [15]. Oxygen molecules get adsorbed on the surface as follows:



When the light is switched off the current decreases very fast initially which may be attributed to recombination of free electron and holes [1]. Later the current decreases slowly which may be attributed to slow process of desorption of oxygen molecules as follows:

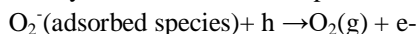
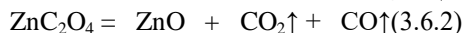
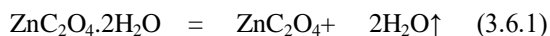


Figure 5b shows variation of photocurrent in vacuum. When the UV light is switched on an initially fast increase in photocurrent is followed by a slow increase. Eventually the photocurrent reaches to a steady state value but in more than half an hour. This comparatively slow and prolonged response in vacuum may not be attributed to desorption of oxygen molecules on the surface of ZnO structures. Instead carbon-catalyzed photolysis of ZnO nano structures resulting in slow increase of lattice oxygen as suggested by Jiming Bao et al. [15] may be responsible for such slow and prolonged rise evidenced by the participation of carbon in thermal decomposition of zinc oxalate as follows:



The process is found to be reversible by exposure to gaseous oxygen in the dark. The steady state value of photocurrent in vacuum is higher than the photocurrent in air by an order of one. This may be attributed to increased dark current in vacuum which is also higher than the dark current in air by order of one. The high dark current in vacuum may be attributed to the increased concentration of free electrons as a result of non-availability of oxygen molecules in vacuum to be adsorbed on the surface of ZnO structures by capturing free electrons. When the light is switched off, the decay of current in vacuum is fast as compared to that in air. This may be due to absence of slow process of adsorption of oxygen molecules. The slow portion of decay may be due to presence of traps [16].

The trap depth is calculated by peeling off the decay portion of the curves into the possible number of exponentials. The exponentials are given by the equation $I = I_0 \exp(-pt)^r$ according to Bube model where I_0 is the current at the time when light is switched off, I is the photocurrent at any instant of time, r is the exponent which is equal to 1 for rise and decay function and p ($\exp(-E/kT)$) which is probability of escape of an electron from trap per second discussed in the theory of Randall and Wilkins. The trap depth E for different exponentials can be calculated by following equation [1]

$$E = kT[\log_e S - \log_e \frac{\log_e(I_o/I)}{t}]$$

where E denotes trap depth, k is Boltzman constant (1.381×10^{-23} J/K), T is absolute temperature and S is the frequency factor of the order of 10^9 at room temperature. The trap depth is calculated as 0.65eV using slow portion of decay of photocurrent in vacuum.

Figure 6a shows rise and decay curve of photocurrent under UV-vis Illumination with fix photo flux and bias voltage, measured in air as well in vacuum (10^{-3} mm of Hg pressure). In air when the light was switched on, the photocurrent increased very fast due to quick generation of electron and hole pairs as a result of absorption of photons. After attaining a peak, the photocurrent started to decrease slowly even during steady illumination. This kind of anomalous behavior may be attributed to slow process of photoinduced chemisorption of oxygen molecules on the surface of ZnO microstructures. Photocurrent transients were measured by illuminating the sample under the periodic pulses of UV-vis illumination, at a fixed bias voltage of 20 V in air as well in vacuum. The photocurrent transient cycles show that the photocurrent peak in air slightly reduces in each cycle that may be attributed to increased rate of recombination as a result of anomalous behavior of photocurrent in air

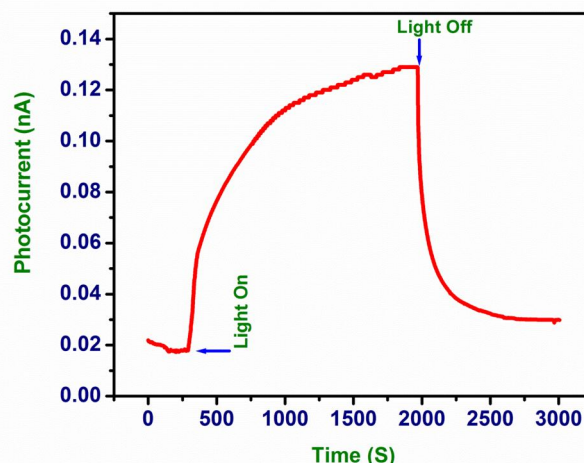
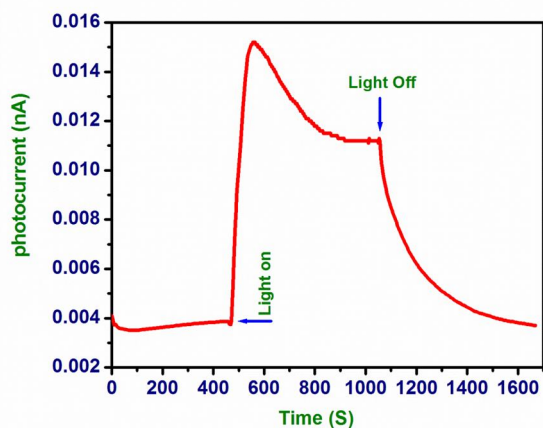


Fig. 5a: Rise and decay of ZnO structures in air prepared by zinc oxalate.

Fig. 5b: Rise and decay of ZnO structures in vacuum prepared by zinc oxalate.

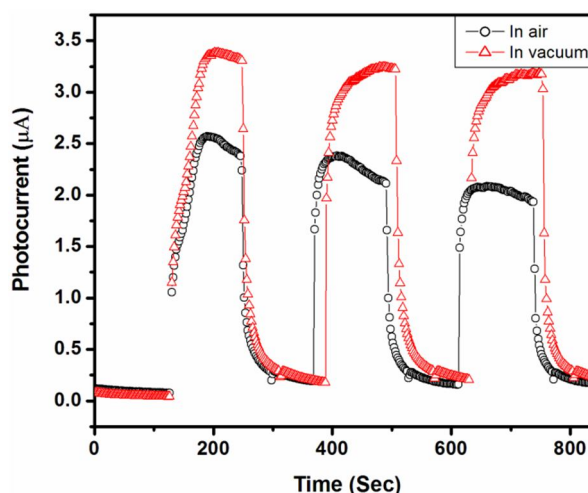
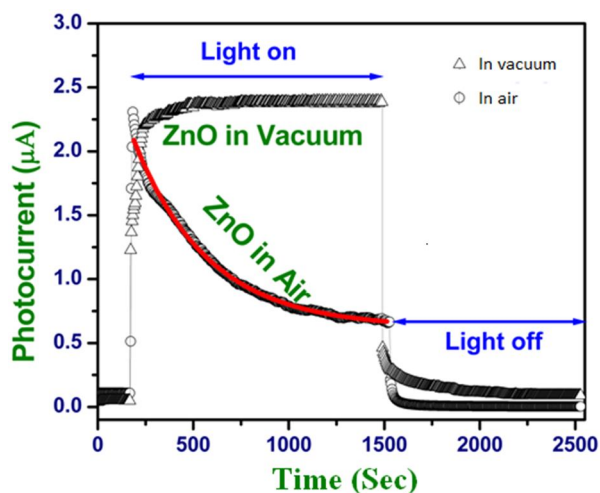


Fig. 6a: Rise and decay curves in ZnO microstructures in air and well as in vacuum.

Fig. 6b: Rise and decay under the periodic (2 min) illumination of ZnO microstructures in air as well as in vacuum.

IV. CONCLUSIONS

In the present work, ZnO structures have been synthesized by thermal decomposition of zinc oxalate ($\text{ZnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) and zinc nitrate [$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$] at 500°C for three hours. This method is inexpensive and reproducible for mass-scale synthesis of ZnO structures. X-ray diffraction (XRD) result shows that the prepared samples have hexagonal wurzite structure of ZnO. SEM images shows formation of rectangular platelets arranged in a form of irregular cuboids for ZnO prepared from zinc oxalate. For ZnO prepared from zinc nitrate SEM images shows aggregated morphology of six sided pyramid particles. From UV-vis spectroscopy it is observed that absorption edges at 381nm. The photocurrent in air exhibits anomalous behavior where in the photocurrent decreases even during steady illumination. Photocurrent in vacuum is found to rise slowly for prolonged duration. So for switching applications the ZnO prepared with zinc nitrate showing fast response as compared to zinc oxide prepared with zinc oxalate.

V. ACKNOWLEDGMENT

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