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Growth of zinc oxide nanowires by equimolar solution technique on conducting substrates used for optical applications

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Zinc oxide nanorods were successfully fabricated on various substrates coated with metal oxide such as platinum and gold by aqueous solution method. The current research shows the influence of conducting substrates on surface morphology and its use for optical properties zinc oxide nanostructures. Samples were analyzed by energy dispersive (EDX), X-ray Diffraction (XRD), Field Emission Scanning Electron Microscopy (FE-SEM) and UV-Visible spectroscopy (UV-vis). The fabricated zinc oxide nanorods exhibit excellent crystalline quality and hexagonal wurzite structure. The Zinc oxide nano-walls and nanorods have crystalline size from 30 to 35 nm. FE-SEM images shows that nanowires and nano-walls grown on metal oxide coated substrates have good hexagonal structure. The zinc oxide nanorods fabricated on Pt coated thin film were highly dense as compared to other substrates coated with metal oxide. The Pt lattice parameter is nearby to Zinc oxide as compared to gold. The value of optical band gap energy (Eg) of zinc oxide nanorods grown on metal oxide was approximated to 3.35 eV that have the nearest value to bulk 3.37 eV. This confirms that Zinc oxide nanorods synthesized by aqueous solution technique have characteristics similar to other conventional techniques either bulk size or thin film nanorods.

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Keywords: Lattice parameters, Technique, bulk, Aqueous solution, Oxides, Crystal structure, Transmission electron microscopy

1. Introduction

Nano-structured of semiconducting metal oxide (SMO) used in many technological field as they have novel physical and chemical characteristics. Electron transfer process in SMO materials normally depends on surface states that are directly related to impact ratio (surface to volume ratio) [1].

Zinc oxide at room temperature has wide ban- gap 3.37 eV. Its exciton binding energy is 60meV. Hence ZnO is known as promising material for different applications in optics, electronics and sensors [2]. It has been revealed from the current research that surface morphology acting a vital role in the use of zinc oxide in particular area [3]. ZnO is wurtzite in structure that has lack of charge symmetry. ZnO wurtzite structure used as mechanical transducers, nano-

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generators and detector. Zn^{2+} and O^{2-} are set in layer by layer arrangement with the c-axis in a hexagonal structure.

Different morphologies of nanostructures such as flower, rods wires can be obtained by chemical solution technique [4]. To fabricate nano-materials on large scale chemical solution method has applied because it is fast, simple, economical and works at low temperature [5]. Moreover, electron mobility of ZnO is greater, higher electron life-time, and higher intrinsic impurities. Due to these characteristics electrical resistance of ZnO decreased and enhances the electron transfer ability. Moreover, ZnO shows different defects [6]. Catalytic interaction in gas sensing process increases due to oxygen vacancies [7, 8]. Metal oxide semiconductor gas detectors are designed on the change of electrical conductivity due to flow of test gas. For higher sensitivity and selectivity metal oxide gas detectors are use. Particularly, doping layer increased the gas detection characteristics. Gas sensing enhanced due to morphology and energy band structure of the SMO. Surface to volume ratio and centers for gas reactions in the SMO also increases [9-12]. It is verified from the literature that sensitivity and conductivity of zinc oxide nanostructures can be enhanced by doping with noble metals. Such kind of doping plays a critical role in increasing chemical interactions in the gas detection process. Metal coating can increase the oxygen adsorption capability of the sensor.

In the current research, we explored the influence of thin metal coated substrate on zinc oxide nanorods by chemical growth technique. We have selected metals gold (Au) and platinum (Pt) for coating on glass substrate. Since gold and platinum metals are often used in electronic instruments. The fabrication procedure and surface morphology of zinc oxide nanorods are suggested. It has been investigated that the kind of metal coating layer acting a vital part in the shape, dimension, morphology and optical properties zinc oxide nanorods. Growth of ZnO nanowires on conducting substrates (metal coated) used in solar cells, detectors, and ultra-violet optical sensors and in optical coatings etc. Coating layer also enhance the gas detection capability could be credited to the improved precise surface area. The configuration of hetero-junctions/homo-junctions areas and interaction between nanostructures and gas can be estimated by electrochemical description and band-alignment procedure. Additionally, the improved structures for sensing show stable performance after a month [13]. Hence, recommended an exceptional stability and repeatability. Briefly, such a well-designed sensor shows potential to increased sensitivity and selectivity for gas detection with long term stability and repeatability.

2. Materials and Method

Zinc oxide nanostructures like nano-walls synthesized on metal coated thin film on glass substrate by chemical solution technique (hydrothermal process). Hydrothermal technique was proposed by Vayssieres first time [14]. Previously this technique depends upon the heating temperature of the aqueous solution in which we immersed inverted the glass substrates. The chemicals utilized in this research work were bought from Sigma Aldrich U.K with no further purification and used as received. Prepared an equimolar 100 ml solution with 0.05 M concentration by dissolving 0.74 g zinc nitrate hexahydrate [Zn (NO3)2.6H2O] and hexamethylenetetramine [C6H12N4] 0.35 g in an aqueous solution. Aqueous solution was prepared in deionized water with 18 MΩ. Magnetically stirred the aqueous solution for 1 h and 20 min. for completely dissolves all the chemicals. Substrates used for the growth of nanostructures or nano-walls were cleaned ultrasonically ethanol and acetone followed by distilled water for 20 minutes. Substrates cleaned in this way were dried in an air atmosphere. Glass substrates were coated by gold (Au) and platinum (Pt) metals. For coating sputter coater EMITECH K-550 used for 4 minutes with a pressure 10^{-1}mbar, DC voltage 12 vdc, AC voltage 12 vac and deposition current 20mA. Metal-coated silicon substrate placed inverted in a sealed glass disk. Subsequently substrates were put in an electric oven at 95^{o}C for 12 h and change the solution for every 3 h. Hence, to remove residual salts and impurities the samples were washed with deionized water and dried in air atmosphere. Synthesis of nanostructures depends on the growth time in the nutrient solution. Density of the nanowires and nanowals closely related with the concentration of reagents solution [14, 15]. Subsequently, the morphology and chemical combination of the as grown

nanowalls were determined by field emission scanning electron microscopy (FESEM, JEOL-6340F) at different magnifications. The orientation and crystal pattern of the zinc oxide nanowalls was determined with X-ray diffraction (XRD machine Bruker-D8 Advance). Rradiation source CuKα (40 kV, 40 mA, wavelength λ = 0.15406 nm). Optical transmittances were determined with UV/VIS/NIR spectro-meter (LAMBDA-900).

3. Results and Discussion

EDX spectra of the zinc oxide nanowalls show the elemental combination of Zn, Au and oxygen spectrum processing: Peaks possibly omitted: 0.264, 3.706 keV with processing option: All elements analyzed (Normalised). Number of iterations = 4. Graph shows pattern of EDX of zinc oxide nanowalls grown on platinum coated substrate. Crystallographic parameters obtained from the XRD pattern of zinc oxide naorods and nanowalls on gold coated substrate The thicknesses of ZnO nanowalls deposited on silicon coated substrates were calculated by a SOPRA GES-5E spectroscopic ellipsometry (SE) technique. The surface analysis of all the deposited samples were observed with field emission scanning electron microscope (FESEM) and wide-angle XRD analysis were recorded with a Bruker D-8 Advance powder X-ray diffracto-meter. Use Ni filtered Cu-Kα radiation and generator settings at 40 mA, 40 kV (λ=1.5406 Å). The incident beam was monochromatic. Scan axis was Gonio type. Start position 2θ= 2.0000 and end position 2θ=79.9590 with pre-set time. Temperature maintained during the experiment was 25°C. Reference code for x-ray diffraction = 01-089-0510. Crystal system was hexagonal with space group: P63mc, space group number: 186. The lattice parameters are: a (Å): 3.2488 = b (Å): 3.2488 and c (Å): 5.2054. Alpha (°): 90.0000, Beta (°): 90.0000 and Gamma (°): 120.0000. The deposited gold layer was much thin after 4 coatings.

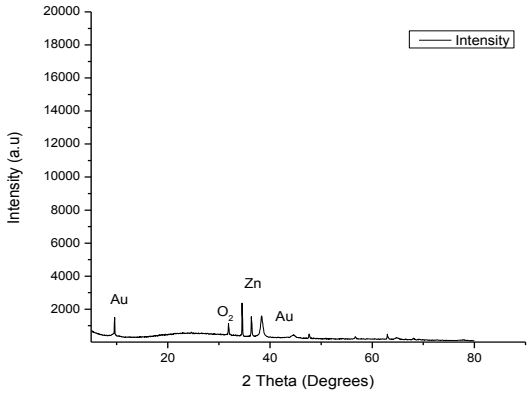


Fig. 1. (a) XRD analysis of gold coated silicon substrate.

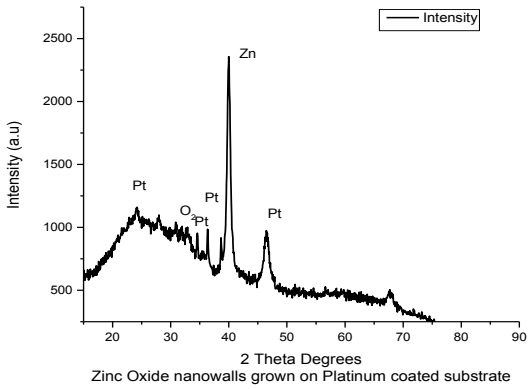


Fig. 1. (b) XRD analysis of Pt-coated silicon substrate.

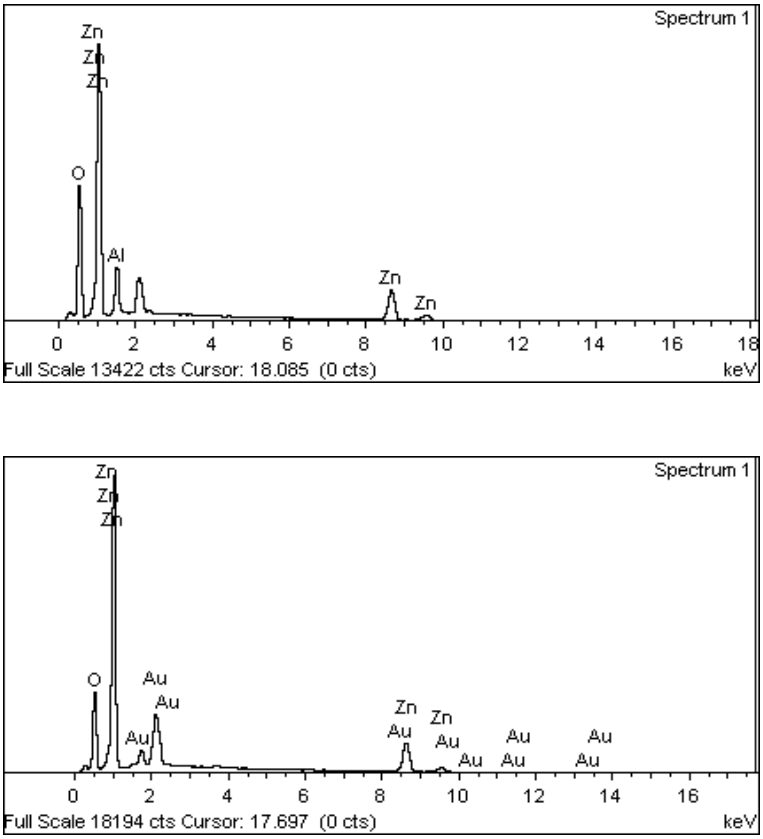


Fig. 2. EDX analysis of gold and Pt coated silicon substrate.

SEM images are taken at different magnifications such as 11000, 4300, 9500 and 15000 respectively. We have used format JEOL/EO, instrument JSM-6340F, accelerating voltage10.00KV signal SE, WD 10 and in standard display mode.

SEM images of zinc oxide nanorods taken at different magnifications. The fig.3 shows images at various magnifications 5000, 6000, 22000 and 8500 with standard mode.

Figure 2 shows SEM images of ZnO nanostructures synthesized on various conducting substrates at 90 °C. Different types ZnO nanostructures synthesized on various conducting substrates like hexagonal, oval shape and flower like with particular features and arrangement. Nano-structures synthesized on metal-coated silicon substrates such as Au, and Pt. Metal coated substrates acts as catalyst for the synthesis of ZnO nanostructures. Morphology of multiple ZnO nanostructures depends on the lattice variations between metals (Au, and Pt) and ZnO. Figure-2 (a) surface analysis of ZnO nanowires synthesized on gold coated silicon substrates. Furthermore combine morphologies of ZnO nanostructures such as flower like and oval-shaped on conducting substrates are in particular direction.

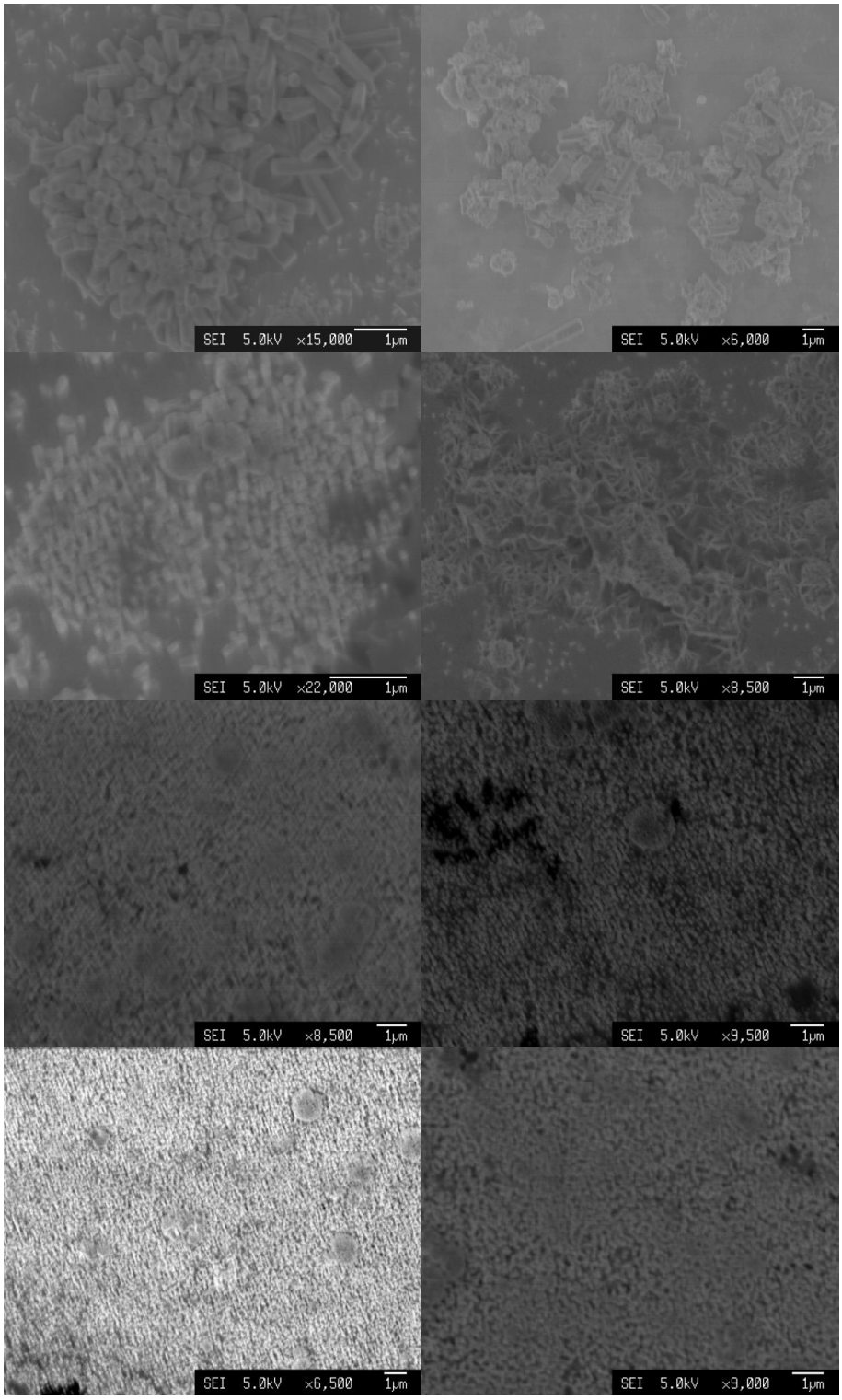


Fig. 3. (a): SEM images of gold coated silicon substrate.

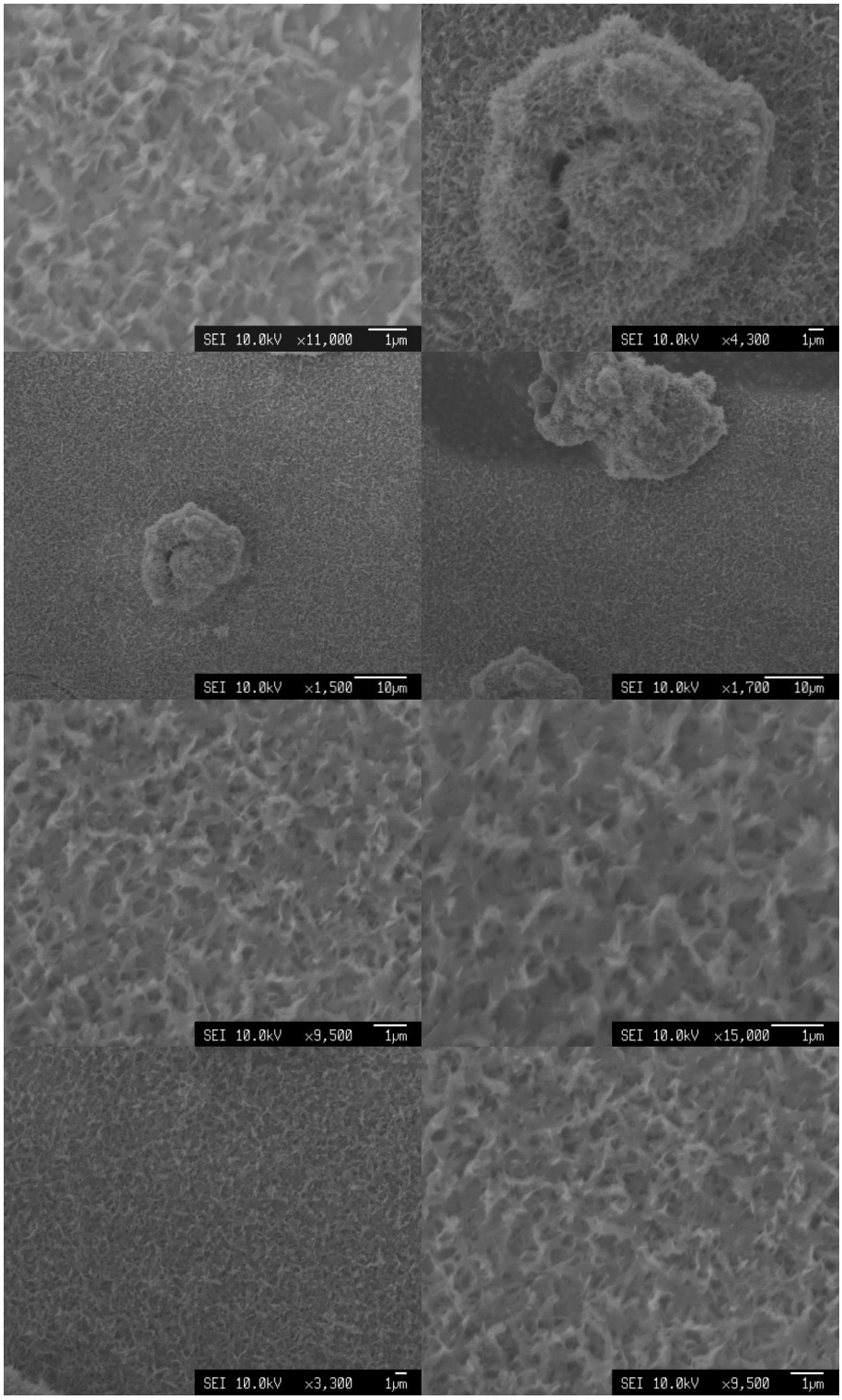
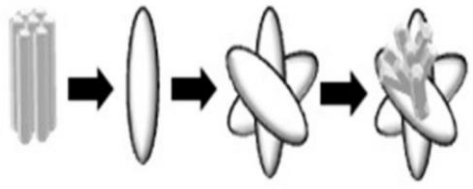


Fig. 3. (b). SEM pattern of zinc oxide nanowalls on platinum coating glass substrate.

Oval shaped morphology created due to coalescence between tinny hexagonal nanostructures. Flower shaped nanowires synthesized on the upper part of oval structures. Flower like structures are created due to proffered secondary growth on zinc oxide not because of metal substrate.

Hexagonal wires are shown in figure-4 (c), oval shaped nanostructure and nanowires arrays simultaneously exist on Pt substrate. At greater magnification zinc oxide nanowires array

directly grow on metal substrate as shown in figure 2(d). Such structures are particularly synthesized on substrate or zinc oxide seed layer. Yamada et al. has stated [16], the existence of such kind of nanowires arrangement is due to lattice inequality that lies in zinc oxide and Pt substrate. The lattice difference between zinc oxide and Pt is ~1.4%. Due to this mismatch nanowire array structure to be created. Such nanowire array not seen by zinc oxide structures synthesized on Au coated substrate. SEM images shows that not all the zinc oxide nanowire array section create secondary growth region. Secondary growth regions are shown by flower like structures. Such creation is due to selectively synthesis on nanowire site [17].



(i) *(ii)* *(iii)* *(iv)*

Fig. 4. Flower shaped structures of zinc oxide: (i) bundle form of hexagonal nanowires (ii) oval-like coalescence, (iii) oval shaped branch structure and (d) flower shaped nanowires synthesized on the crest of oval shaped structure.

Transmittance spectrum of ZnO nano-structures was measured between 300-800 nm as shown in the figure-5. Changes in transmittance spectrum versus wavelength (λ) of ZnO nanostrurers synthesize on various metal-coated substrates are presented in the figure-5. It is undoubtedly clear that the value of transmittance spectra changes with various metal coated glass-substrates from 300-800 nm. The value of transmittance spectra depends on substrate colour manifestation. Au-coated glass substrate appears yellow and Pt coated substrate appears is dark grey in form. Pt-coated substrate shows 30-54% value of transmittance which lie in the low region of the spectrum. Transmittance for Au coated glass substrate was 31-60%. Hence transmittance value crucially affects the substrate colour appearances [18, 19].

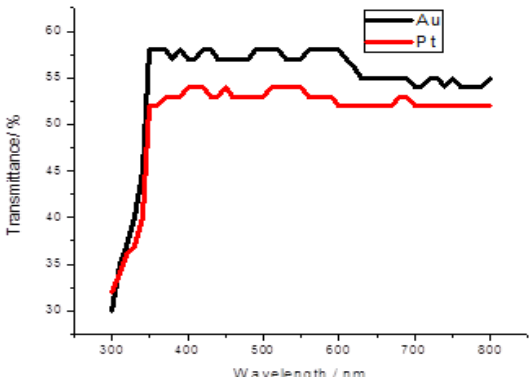


Fig. 5. Distinctive transmittance spectrum of zinc oxide nanostructures grown on various conducting substrates at 90 °C.

Absorption coefficient (α) measured the value of optical band-gap energy (*Eg*). Optical band gap $\alpha = \alpha o\ (hv - Eg)n$. Here Eg is the energy band gap and *hv* photon energy. Here αo = constant and exponent of $n = ½$ is direct allowed transition for zinc oxide. Band-gap energy (*Eg*) can be measured by $(\alpha hv)^2 = 0$, the linear potion of the curves. Energy band gap *Eg* for ZnO has a value of 3.30 eV and 3.29 eV for gold and platinum coated silicon substrates. Eg-values depend on

surface structures, morphologies and crystallite size of the synthesized samples [20-22]. In figure 6 B and C specify the values between *hv versus* $(\alpha hv)^2$ at conducting substrates Pt and Au.

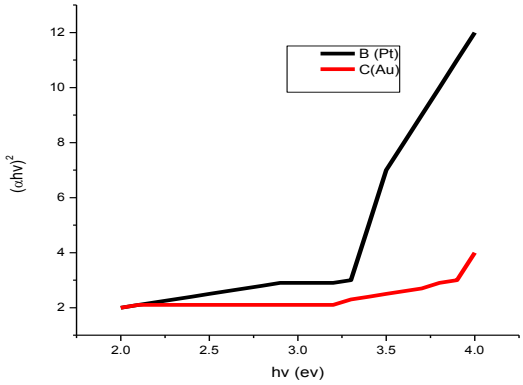


Fig. 6. Graph between hv versus $(\alpha hv)^2$ *of zinc oxide nanostructures synthesized on various conducting substrates at 90°C for 3h. Transmittance/ % versus Wavelength/ nm.*

4. Conclusion

The current work ZnO nanostructures such as nanorods and nanowalls were fabricated on different metal coated silicon substrates by chemical synthesis technique at 95°C. XRD pattern presents well aligned peaks of zinc oxide with no impurities which showed that as growth product is pure. The size of nanowalls and nanorods as grown on gold coated substrate are on the nanoscale. Experimental data repented in the current research investigate various kinds of metal-coating and a reflect an influence on the surface morphology of zinc oxide nanostructures by this method.

It has been investigated that zinc oxide nanostructures grown by this technique present interesting morphologies like hexagonal nanorods and nanowalls. However, zinc oxide nanowalls arrays observed for platinum coated substrate and nanorods and nanowalls both observed for gold coated substrate. Hence, it was discovered from these results that metal coating affects the morphology of zinc oxide surface that are helpful to enhance sensing at room temperature due to reduction in the thickness of nanowalls. Therefore, sensing observed at room temperature. Optical band gap energy (Eg) for zinc oxide nanostructures lie in the range of 3.0 to 3.5 eV. Band gap energy (Eg) 3.37 eV is the bulk value of zinc oxide.

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