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Zinc Oxide Nanowires Prepared by Oblique Angle Deposition Method

This paper presents a detailed study of the oblique deposition effect on the morphology, structure and optical properties of ZnO nanowires (NWs) prepared by the deposition of zinc metallic films on glass substrates at different angles (0, 50 and 70°) and then oxidized in air at 650°C. Highly transparent ZnO thin films were successfully prepared by the oblique angle deposition (OAD) technique on glass substrates at room temperature. Atomic force microscopy (AFM) results show that the sample obliquely deposited presented greater roughness as compared with normally deposited ZnO NWs ($\theta=0$). Optical measurements showed a sharp absorption edge, near 380 nm, in both normal and oblique films. When the oblique angle increased, the absorption edge of spectra demonstrated a red shift with a direct band gap (3.11eV). Scanning electron microscopy (SEM) results show that the OAD led to the formation of bent columnar ZnO NWs. These NWs were inclined from the substrate normal in a direction opposite to the incident vapor beam. Due to the OAD technique, surface diffusion enhanced the self-shadowing effect. When oblique Zn thin film was later oxidized in air at 650°C for a longer time, the ZnO NWs had a needle-like structure, as was clearly shown by SEM images obtained.

Keywords: Oblique deposition; GLAD technique; ZnO thin films; ZnO Nanowires

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1. Introduction

The oblique angle (OAD) is a useful geometrical arrangement for the deposition of nanostructured thin films. OAD is a physical evaporation method for synthesizing materials with controlled nanostructure, where the self-shadowing effect and limited diffusion of adatom are the requirements to achieve the controlled nanostructures [1]. Many methods utilized for the OAD of thin films such as, vapor–liquid–solid deposition [2], magnetron sputtering [3], pulsed laser deposition [4], and Plasma-assisted deposition [5]. In recent years OAD has been drawing attention due to its applications in solar cells and LED devices [6], photovoltaic applications [7], biosensors and gas sensors [8,9], photonic devices [10], hydrogen generation [11], and liquid crystal displays [12].

Transparent conductive oxide (zinc oxide) is a unique material that exhibits semiconducting and piezoelectric properties, and has a very rich family of nanostructures, both in their properties and structures. Various ZnO nanostructures, such as nanobelts, nanorings, nanohelices, nanosprings, nanowires, etc., are touted to have applications in optoelectronics, sensors, transducers, and the biomedical sciences [13,14]. Among these, aligned one-dimensional ZnO nanostructures have attracted much attention in recent years, especially as electron-accepting semiconductors in organic photovoltaic cells [15-17] and other applications in electro-photo mechanical nano-devices [14]. The most common method to synthesize ZnO nanostructures utilizes a vapor transport process,

where the vapor species are first generated by evaporation, chemical reduction and gaseous reaction, and are then transported and condensed onto a cooler substrate. In this work, ZnO thin films were deposited on glass substrates by the thermal deposition process, and the structural and optical properties of those thin films were then investigated. The aim of this article is to show the influence of the incident angle on the surface morphology, optical and chemical properties of zinc-oxide nanostructure.

2. Experimental Part

The deposition of metallic Zn thin films were performed in a vacuum chamber onto unheated glass substrates by the oblique angle deposition (OAD) technique at room temperature. The chamber was evacuated using a diffusion pump to a base pressure of 1×10^{-5} torr. The evaporation was carried out using a molybdenum boat heater. The zinc metallic films were deposited at different angles (0, 50 and 70°) between the normal to the substrate and the incidence direction of the evaporated atoms. The deposited normal and oblique Zn films were oxidized in a conventional furnace at 650°C for one and a half hours, in order to prepare ZnO nanowires (NWs). Longer time was used for oxidation an oblique Zn film at 650°C, in order to prepare ZnO NWs needle-like structure. Figure (1) shows the schematic diagram of the evaporative deposition system (oblique angle deposition system). The deposition angle, θ , defines the incidence angle of vapor flux, where θ of 0 happens when the substrate normal is pointed directly at the vapor source, where

θ of 90° happens when the substrate normal is perpendicular to a line between the center of the substrate and the center of the vapor source. Zinc oxide film thickness was determined by a weight method using the formula [18]:

$$t = m / A \rho \quad (1)$$

In this formula, t is the film thickness, m is the weight gain, A is the area of the coated film, and ρ is the density of ZnO

The film thickness was determined to be approximately 300, 290 and 270 nm for oblique angles ($\theta=0, 50$ and 70°) respectively (this decrease in ZnO film thickness are due to geometrical consideration in the oblique angle deposition technique).

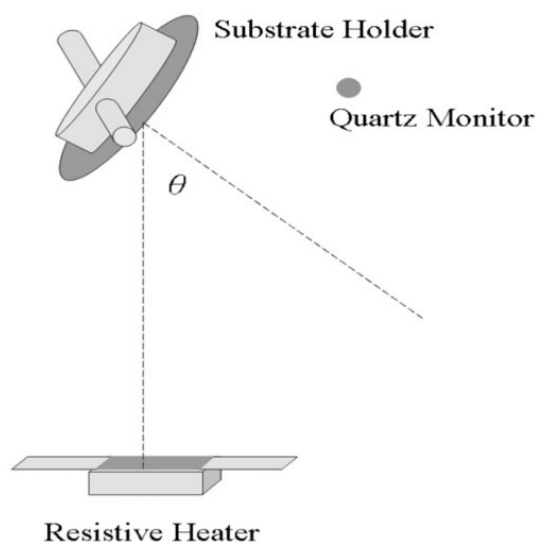


Fig. (1) The typical arrangements of OAD technique

The optical transmittance of the ZnO thin films were carried out at room temperature using Shimadzu UV-VIS 2450 spectrophotometer, and the optical band gap energy was calculated from the data of the optical transmittance and wavelength. Atomic force microscopy (AFM) operating in contact mode was used for the observation of the surface morphology for the ZnO films deposited

with different angles. The morphology of the product was observed with a Tescan Vega II-Cheek scanning electron microscope (SEM). The size and distribution of ZnO nanowires were characterized by AFM with an Angstrom Advanced AA300 scanning probe microscope (SPM). By means of SEM and AFM techniques, the nanostructure characteristics and their enhancement of oblique incident on ZnO films were investigated. Besides, the influence of the deposition angle of the optical and composited properties is also observed.

3. Results and Discussion

SEM analysis surface morphology of thin films is very important tool to investigate microstructure of thin films. Figure (2) shows the top-view SEM images of OAD-ZnO NWs prepared by zinc metal that is deposited at various incident angles and then oxidized in the air (at 650°C for one hour and 30 min). The top view of the normal deposition ZnO (Fig. 2a) shows the commonly observed, featureless structure that is characteristic of a thermal evaporated film, while the top views of the oblique deposition ZnO films at 50° (Fig. 2b) and 70° (Fig. 2c) show the columnar nanostructure (nanowires) growth on film surface more oriented in one and the same direction – in comparison with the structures of the normal deposition shown in Fig. (2a). The inclination angle caused by the shadow effect increases with the increase in the flux arrival angle [19]. This feature can be associated with the oblique position of the film substrate during the deposition process which may favor the respective orientation. Indeed, in the case of obliquely deposited films, certain crystalline planes may be favored in growth over the other, and therefore, the crystallites may grow with other planes parallel to the substrate [20,21].

As can be seen in Fig. (2a), the surface of the film deposited at angle of 0 is semi-smooth with smaller grains, whereas pinholes, voids and large grains are observed in the case of the films deposited at angles of 50° and 70° , as shown in Fig. (2a,b), these pinholes and voids were increased with the increase in the deposition angle. Larger separations between neighboring columns, and highly porous thin films of the OAD ZnO films occur due to shadow effects and limited the mobility of the deposited atoms on the substrate surface [22].

As shown in Fig. (3), ZnO NWs with needle-like structure, that prepared by oxidation of zinc thin films at 650°C for long oxidation time (four hours), which results in good agreement with previous work by Chen et al. [23]. The diameter and the length of the NWs are 50nm and $1\mu\text{m}$, respectively, and they had randomly distribution. The OAD leads to the formation of a bent columnar ZnO, inclined from the substrate normal in the opposite direction, towards the incident vapor beam, owing to surface diffusion enhanced self-shadowing effect [22]. Also, observed

the rods like needle are randomly distributed of ZnO NWs with high porosity as observed. One prominent characteristic of an OAD technique, it is much reduced density, and increased porosity as compared to films grown at normal incidence [23].

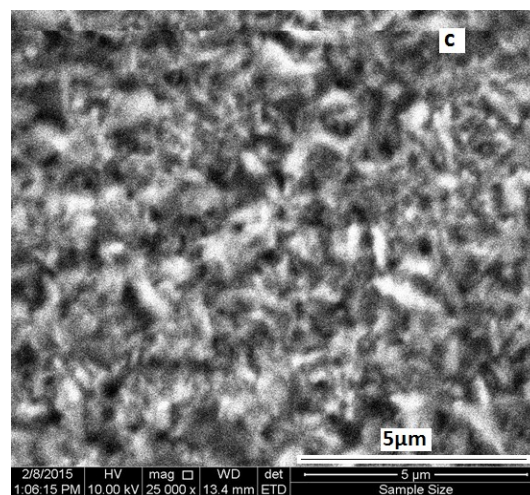
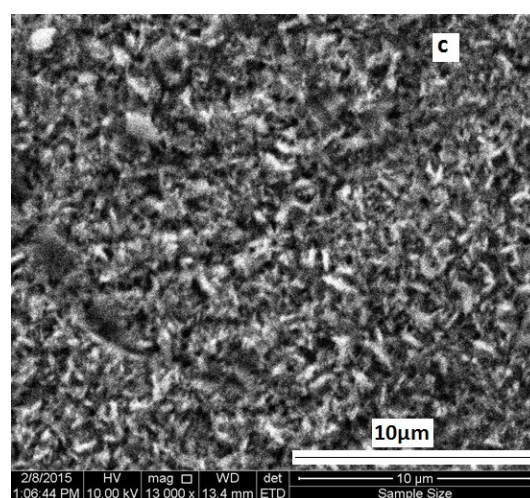
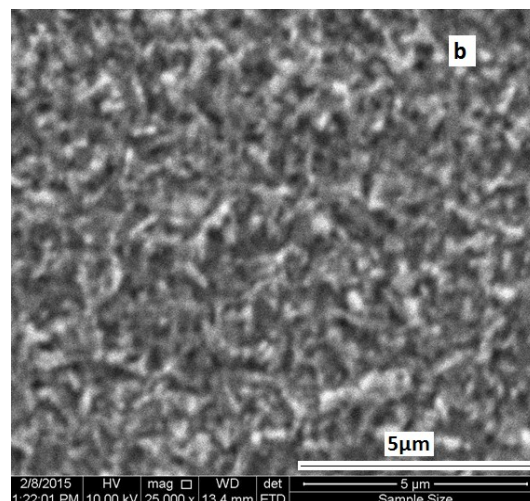
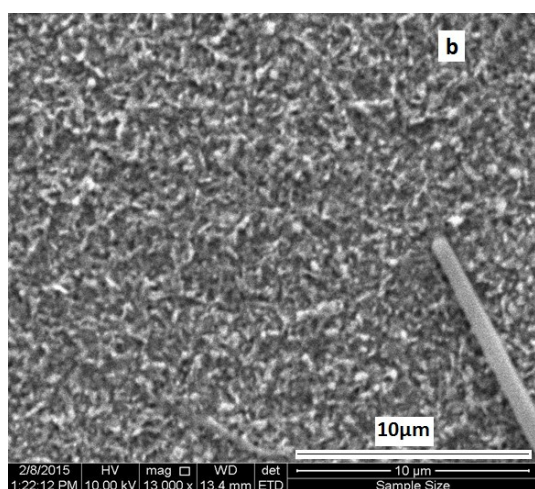
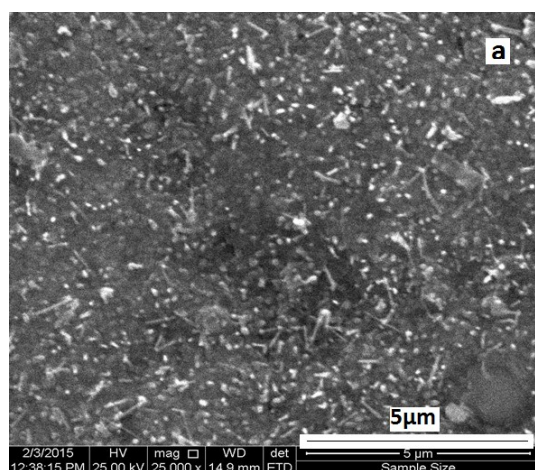
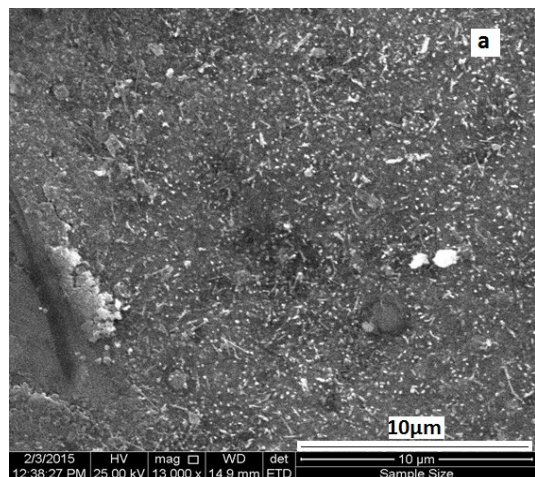


Fig. (2) Different magnification Surface morphology of the ZnO films at deposition angles of (a) 0°, (b) 50° and (c) 70°, oxidized in the air (at 650°C for one and half an hour)

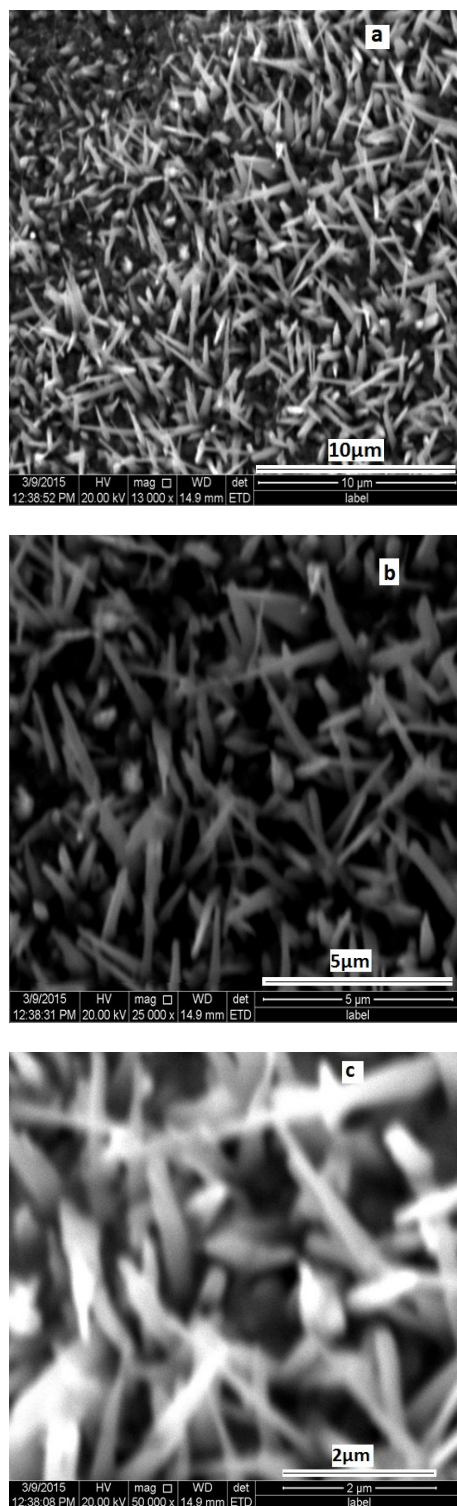


Fig. (3) Different magnification Surface morphology of the ZnO NWs needle like structure at deposition angle of 70°, oxidized in the air (at 650°C for 4 hours)

To investigate the surface morphology of deposited films, the surface was examined by AFM technique. Figure (4) presents a selection of 10×10μm sized atomic force micrographs of, respectively, studied normal ($\theta=0$) and oblique ($\theta=70^\circ$) ZnO NWs films. Some quantitative data about the surface roughness and the wires height

distributions for respective samples are presented in Fig. (4).

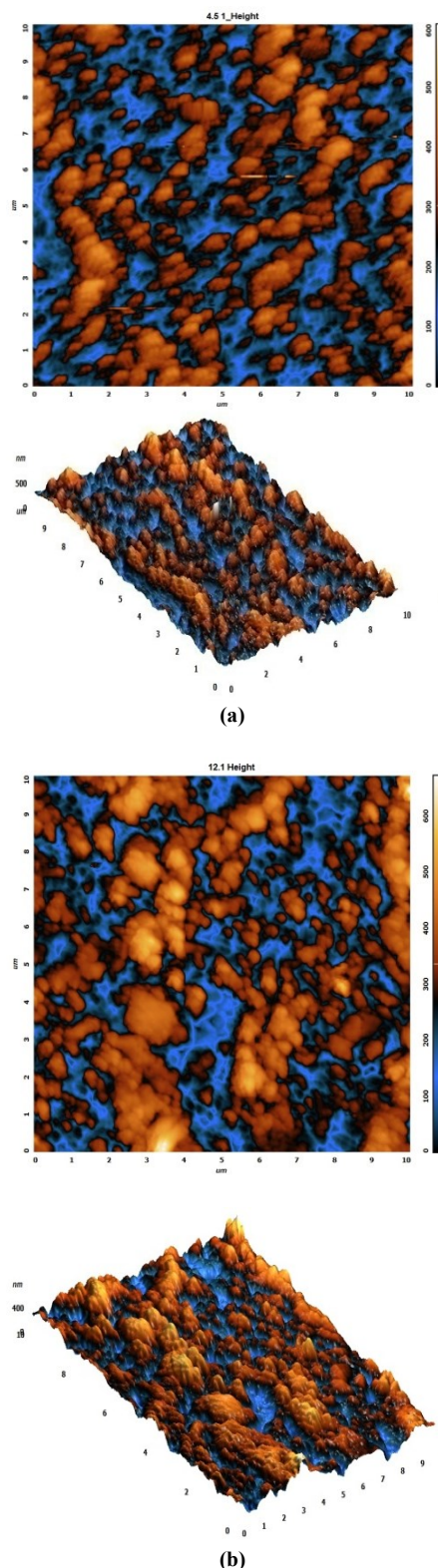


Fig. (4) Two and Three dimension AFM surface micrographs of ZnO NWs (a) $\theta=0$ and (b) $\theta=70^\circ$ prepared at oxidation temperature of 650°C for 1.5 hr

It is clearly visible that the growth of zinc thin film under oblique deposition conditions led to the formation of a columnar structure. These columns

are perpendicular to the surface of the substrate. The arrival of vapor flux and formation of film nuclei is a random process. Atomic shadowing occurs when the substrate fixed at a large oblique angle relative to the incident vapor flux. Atomic shadowing occurs when oblique vapor flux is shadowed deposited film material from reaching areas on the substrate. Therefore; the nuclei grow into columns and developed shadows. These columns are in different lengths. As a result, some columns will screen neighboring area from incoming vapor flux. For sufficient time, there is no growth in the shadow areas and results in a porous structure with isolated columns of zinc material growing towards the vapor source [24]. The analysis of these data indicates that the deposition conditions and the oblique angle influence the surface morphologies of the as-deposited ZnO films. Thus, the sample obliquely deposited presents a greater roughness (41-55nm) and a larger wires height distribution, as compared with the normally deposited sample. Consequently, other texture orientations of the nanowires on the film surface may occur.

The compositions of the normal ($\theta=0^\circ$) and oblique ($\theta=70^\circ$) ZnO NWs respectively were examined by EDX. The zinc oxide nanowires were identified by EDX and the result is shown in Fig. (5). The EDX analysis provided the precise composition of the tip. The EDX spectra in Fig. (5) feature peaks corresponding to elements oxygen (O), zinc (Zn), silicon (Si) and carbon (C) (The appearance of Si peak in the spectrum is due to the glass substrate, and the C coming from the system of measurement), which depict the characteristic composition of a tip of a Zinc Oxide. Moreover, the EDX measurement for the Zinc Oxide NWs shows that the ratio of (Zn/O) in the oblique incident ($\theta=70^\circ$) has lower values as compared with normal incident ($\theta=0^\circ$). This is because the absorption of residual gases into the film during condensation is greatly enhanced when the vapor atoms arrive on the surface at high angles of incidence [14].

The UV-absorption spectra of the normal ($\theta=0^\circ$) and oblique ($\theta=70^\circ$) ZnO NWs prepared at oxidation temperature 650°C for one hour and a half shown in Fig. (6).

It is clear from this figure that a prominent exciton band at 380nm, corresponds to the ZnO nanostructures in both normal and oblique deposited films. This absorption peak is red-shifted, as compared to the bulk exciton absorption of ZnO (373nm) [25], which is due to the size effect of the nanostructures. This absorption in the visible range of wavelength implies that there exist more defect energy levels in the synthesized ZnO nanostructures, which are due to the specific experimental synthesis conditions. The normal and oblique deposited films absorb the radiations in the UV range up to 380nm and almost all the visible spectrum radiations are transmitted by the ZnO nanowires. May be

attributed to the Burstein-Moss effect where an increase of the oxygen content in the OAD-ZnO film [26]. Also and due to rod-like formation, structure in the oblique deposited film combined shadowing effect. The absorption magnitude increases with increasing deposition angle – which is a result that well agrees where this result is in a good agreement with literature [23].

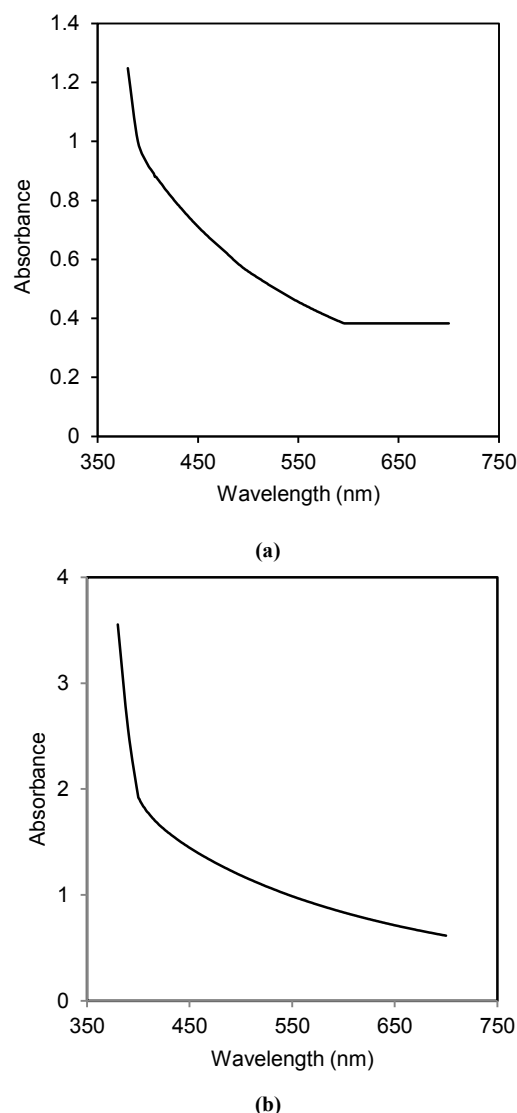


Fig. (6) UV-visible absorption spectroscopy of the ZnO NWs, (a) normally deposited and (b) obliquely deposited thin films at $\theta=70^\circ$ oxidized at 650°C for 1.5 hr

Figure (7) shows the plot of $(\alpha h\nu)^2$ vs. $h\nu$, for both normal and oblique ZnO films respectively, where $h\nu$ is the energy of the incident photon. The energy gap (E_g) was estimated by assuming a direct transition between valence and conduction bands from the expression:

$$(\alpha h\nu) = A (h\nu - E_g)^{0.5} \quad (2)$$

where A is a constant, E_g is the energy band gap, which is determined by extrapolating the straight line portion of the spectrum to $\alpha h\nu = 0$

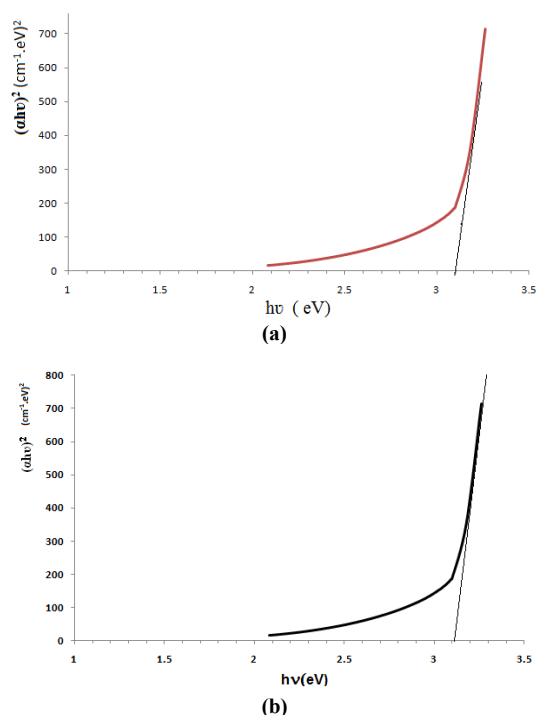


Fig. (7) Variation of $(\alpha h\nu)^2$ vs. photon energy ($h\nu$) for (a) normally deposited and (b): obliquely deposited ZnO NWs, both oxidized at 650°C for 1.5 hr

From this drawing, the optical energy band gap $E_g=3.11$ eV is deduced for both normal and oblique deposition. This value is slightly smaller than the bulk value of 3.31 eV [27], and is in good agreement with previously reported data of ZnO thin film [28].

4. Conclusion

ZnO nanowires prepared by oblique angle deposition technique (OAD), when high purity Zn metal deposited normally ($\theta=0$) and obliquely at ($\theta=50$ and 70°) onto glass substrates at room temperature and oxidized in air at 650°C for different time periods. By means of SEM and AFM techniques, the incident angle has a great effect on the morphology, optical and chemical properties. The AFM investigations revealed a more orientated arrangement of the surface roughness in obliquely deposited ZnO films in comparison with those from normally deposited films and the oblique angle influence the surface morphologies of the as deposited films. SEM shows ZnO nanowires and coalminer growth with needle-like structure in obliquely prepared ZnO at oxidation temperature 650°C for 4 hours.

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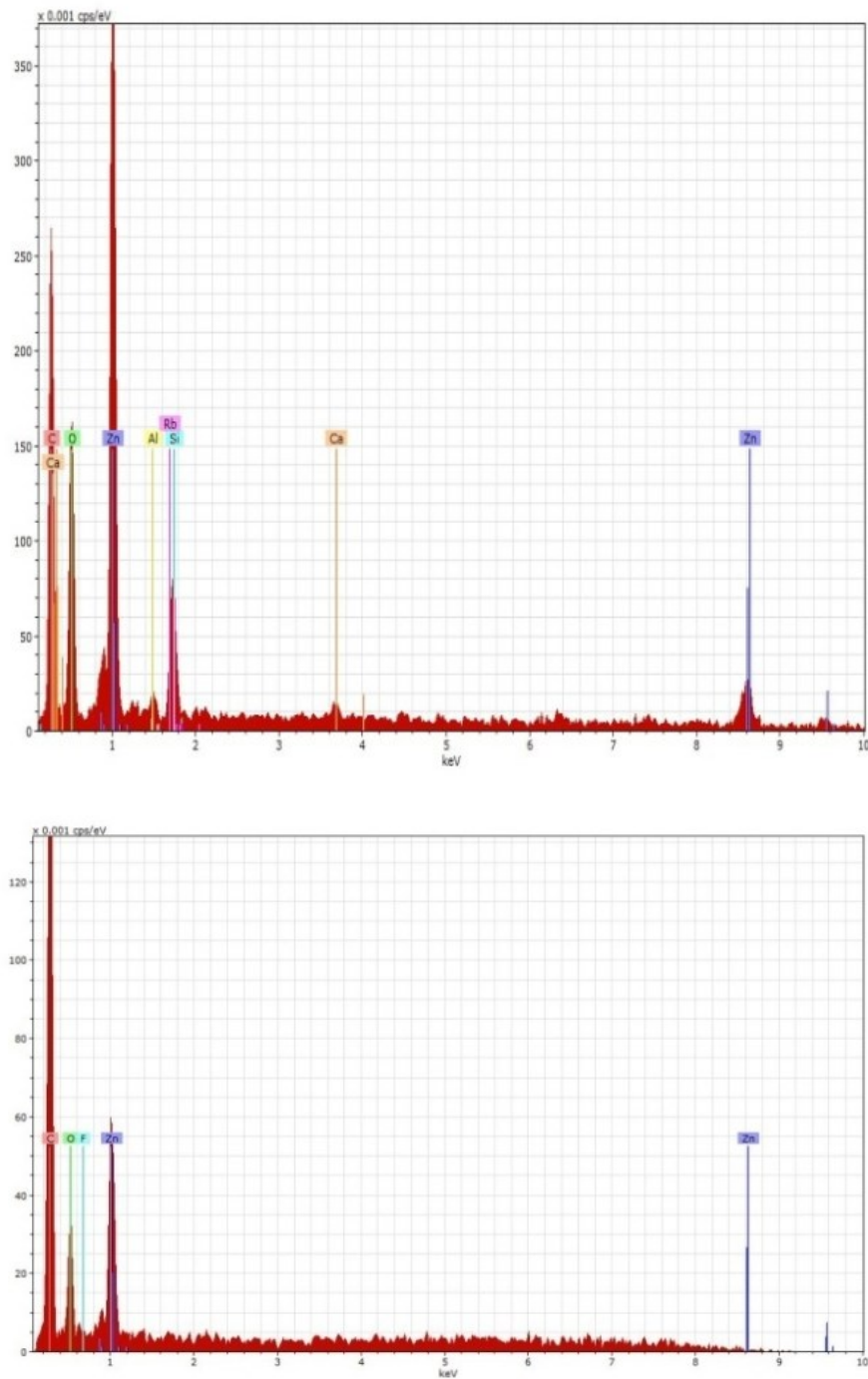


Fig. (5) The composition analysis of ZnO NWs (a) normally deposited ($\theta=0^\circ$) and (b) obliquely deposited at $\theta=70^\circ$ and oxidized at 650°C for 1.5 hr