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# Potentiostatic Deposition of ZnO Nanowires: Effect of Applied Potential and $ZnCl_2$Concentration

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***Abstract***-In this work we report on potentiostatic deposition of Zinc oxide (ZnO) nanowires on fluorine-doped tin oxide (FTO) covered glass substrates from electroreduction of molecular oxygen. The influence of applied deposition potential, and the concentrations of zinc precursor ($ZnCl_2$) on the properties of ZnO nanowires was investigated.SEM results revealed that ZnO nanowires electrodeposited at applied potential -0.85Vhave high density and good alignment. The diameters and densities of the electrodeposited ZnO nanowires are strongly dependent on the zinc ion concentrations and well aligned nanowires with uniform diameter can be obtained when the concentration of zinc ions is between 0.5 mM and 1 mM.

## I. INTRODUCTION

Among transparent semiconducting oxides, zinc oxide (ZnO) is probably the most commonly studied material because of its unique characteristics. Besides being a wide band gap (3.37 eV) material, it has a relatively large free exciton binding energy of 60 meV, thus making the excitons stable even above room temperature [1]. In this way ZnO NWs are superior material for fabricating light-emitting diodes (LEDs)[2]. ZnO also has a great potential for applications in microelectronics, spintronics, piezo-electronics, gas sensing, solar cells etc. [3-5].

ZnO nanowires showed attractive characteristics for certain applications [6–10]. This is because nanowires show high aspect ratio, quantum confinement, and direct path for electrons promoting higher electron diffusion coefficient of ZnO nanowires arrays with respect to nanoparticles films with multiple trapping/detrapping events occurring within grain boundaries [11–14].

Several growth techniques have been employed to deposit ZnO nanowires such as vapor deposition, pulsed laser deposition, molecular beam epitaxy, metal organic chemical vapor deposition (MOCVD), sputtering, electron beam evaporation, spray pyrolysis, sol–gel processing, chemical, and electrochemical deposition [15-17]. Among various deposition techniques, electrochemical deposition (ECD) has become attractive for fabricating ZnO nanowires owing to its simplicity, cost-efficiency, large-area deposition and high-quality nanowires can be grown at relative low deposition temperatures [18-20].

In this work, we study the effect of applied potential and zinc chloride concentration on the morphology, structural, and optical properties of electrodeposited ZnO nanowires.

## II. EXPERIMENTAL WORK

A custom-designed 3-electrode cell consists of fluorine-doped tin oxide ($SnO_2$: F, FTO) coated glass substrates as a working electrode, silver-silver chloride (Ag/AgCl) as a reference electrode and platinum wire as a counter electrode was used for thedeposition of ZnO nanowires. ZnO nanowires were prepared using solution of $ZnCl_2$ saturated with bubbling oxygen 20 min before and during the deposition process.

In order to investigate the effect of applied potential on the properties of electrodeposited ZnO nanowires, a series of samples were prepared by varying the applied potential from -0.7 to -1.1 V (vs. Ag/AgCl) where the $ZnCl_2$ concentration is fixed at 0.5 mM and KCl concentration is kept at 0.1M. The growth temperature and time were fixed at 80°C and one hour, respectively for all samples. Another series of ZnO nanowire samples were electrodeposited at constant concentration of KCl (0.1 M) and $ZnCl_2$ concentration was varied from 0.05 mM to 1 mM in order to investigate the effect of $ZnCl_2$ concentration. All ZnO nanowire samples were potentiostatic electrodeposited at fixed potential -0.85 V (vs.Ag/AgCl) using Bio-Logic Sb-50 potentiostat.

The morphology of the deposited nanowires was characterized by JEOL JSM 651 OLV scanning electron microscopy (SEM). Crystal structures and phase compositions of the films were studied by X-ray diffraction analysis using XRD-6000 Shimadzu diffractometer using Cu $K_\alpha$ radiation (40Kv, 30 mA). Optical studies were carried out by recording the optical absorption spectra of the films using JASCOV 630 spectrophotometer.

## III. RESULTSANDDISCUSSION

In order to study the structural properties of the zinc oxide nanowires, i.e. to investigate the crystallographic phase, the overall crystalline quality, and the possible texture of those electrochemically grown nanowires, X-ray diffraction experiments were carried out. The zinc chloride concentration and deposition potential were maintained at 0.5 mM and -0.85 V. The X-ray diffraction patterns (Fig.1) reveal the presence of diffraction peaks related to the hexagonal wurtzite phase [21] and also those corresponding to the tetragonal $SnO_2$ phase of FTO/glass used as a substrate. Moreover, no spurious phases were detected by XRD indicating high purity of the hexagonal ZnO phase. Lattice constant calculated from peak angles is 5.22 Å in the c-axis.

Fig.2shows the bright-field TEM images of ZnO nanowires. The lengths of these nanowires cannot be taken as the average size of all the nanowires constituent networks because of the method of sample preparation for TEM analysis (there are very high chances that nanowires are broken at different places on the base of the nanowire). As against, the diameter corresponds to the actual size because the nanowire fracture was perpendicular to the longitudinal axis. The diffraction pattern shows the high quality of the prepared nanowires, and it is clear from this Fig that the growth of the nanowires is along the axis [0001].

Electrodeposition of ZnO nanowires is generally based of the generation of hydroxide ions ($OH^-$) at the surface of the FTO conducting substrate by cathodic reduction of molecular oxygen. The molecular oxygen has been the most commonly used in the electrodeposition of ZnO nanowires [22]. The reduction of oxygen can take place by two different methods i.e. two electron (equation 1) or four electron processes (equation 2) according to the used electrolyte and cathode properties.

$$O_2 + 2H_2O + 2e^- \rightarrow H_2O_2 + 2OH^- \quad (1)$$
$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad (2)$$

The electrochemical reaction represented in equation 2 is mainly related to the theoretical reduction potential of oxygen (0.16 V vs. SCE). However, the potential of oxygen reduction is sometimes more negative than the theoretical value due to the high overpotential on oxygen reduction of the selected electrode.

Fig.3 (a-e) represents SEM results of ZnO nanowires samples electrodeposited under different applied potential from -0.7V, to -1.1V vs. Ag/AgCl. According to equation 2 the relatively more negative applied potential would lead to generate more hydroxide ions and in the meantime zinc ions in the electrolyte easily diffused to or absorbed on the cathode surface due to the stronger electrical field intensity. All these phenomena would promote the electrodeposition proceeding, and the growth rate of the electrodeposition of ZnO nanowires would increase. As is shown in Fig.3 (a) the nanowires were formed on the substrate when the applied potential was controlled at -0.7 V and the prepared nanowires have uniform diameter and length, not all the nanowires were perpendicular to the substrate and some gaps appeared. When the electrodeposition potential became more negative the density of the electrodeposited nanowires increased where the gaps disappeared and the alignment of the nanowires was enhanced Fig.3 (b-e). From these results we find that samples electrodeposited at applied potential -0.85V have high density and good alignment. So another series of ZnO samples have been electrodeposited at fixed applied potential of -0.85V but at different concentration of $ZnCl_2$.

Fig.4 represents SEM results of ZnO nanowires electrodeposited at different concentration of $ZnCl_2$ from 0.05 mM to 1 mM the applied potential was fixed at -0.85 V (vs. Ag/AgCl). The KCl concentration was kept constant at 0.1 M and the deposition temperature was 80 $^oC$. The solution was bubbled with oxygen 20 min before and during the deposition process and the deposition time was one hour for all samples. As we can see, the diameters and densities of the electrodeposited nanowires are strongly dependent on the zinc ion concentrations. This is predicted result because increasing the size of the particles normally synthesized in solution technique increases with the precursors concentration [23,24]. Lionel Vayssieres [25] showed by chemical solution deposition, using relatively high concentrations (> 1 mM), of zinc precursors increases the diameter of the nanowires. When the zinc ions concentration is low (0.05 mM, 0.1mM) the deposits present as thin nanowires lay on the substrate Fig.4 (a-b). By increase zinc ions concentration the deposits became dense and the diameter of the electrodeposited nanowires increased Fig.4 (c-e). These results indicated that the compound formation mainly depends on the zinc ions concentrations and well aligned nanowires with uniform diameter can be obtained when the concentration of zinc ions is between 0.5 mM and 1 mM.

Fig.5 shows the relation between the average diameter of ZnO nanowires and nanowires density as a function of $ZnCl_2$concentration. This figure shows that the nanowire diameter is more sensitive to $ZnCl_2$ concentration at low than at high concentrations. Actually, for the lowest concentration the most important part of $Zn^{+2}$ react with $OH^-$ ions adsorbed on the nanowire tips because they are more easily reached. The lateral growth of nanowires is very slow resulting in thin nanowires. By increasing the $ZnCl_2$ concentration, there are not enough $OH^-$ ions adsorbed on the nanowire tips to react with all $Zn^{+2}$ ions close to them, this increase of $Zn^{+2}$ concentration around the entire nanowire surface, enhancing the lateral growth. The increase of $[Zn^{+2}/OH^-]$

ratio smoothed the effect of $ZnCl_2$ concentration on the nanowire diameter as can be observed for high concentration values.

We can conclude that the ZnO nanowire growth is mainly limited by $Zn^{+2}$ ions in the low concentration of $ZnCl_2$ system. As $ZnCl_2$ concentration increase the oxygen reduction becomes important, being probably determined by the preferential adsorption of OH- ions on (0001) ZnO face due to its polar nature. Finally, we can say that the variation of $ZnCl_2$ concentration is an effective way to control the ZnO nanowire diameter.

The optical properties of ZnO nanowires were studied in the spectral range of 300–800 nm using V 630 spectrophotometer. FTO/glass substrates were used as reference samples when measuring the optical absorbance spectra.

Fig.6 shows the different absorbance of ZnO nanowires electrodeposited under different deposition potential. It is demonstrated that the absorbance variation trend of ZnO nanowires was uniform and all of them showed high optical absorbance values in the visible range of 400-700 nm and there was an absorption band between 365 and 370 nm corresponding to electron transitions from the valence to the conduction band. At the absorbance edge the absorption coefficient satisfies the equation $(\alpha h\nu)^2 = A\,(h\nu - E_g)$ for direct band gap materials. The optical band gap $E_g$ of the zinc oxide nanowires was determined using the previous relation [26]. If it was difficult to determine the zinc oxide layer thickness, e.g., as in the case of 1D nanocrystalline formation, $E_g$ was determined according to [27] by extrapolating the linear portion of the dependence $(\alpha h\nu)^2$ on hν to the energy axis.

Fig.7 represents the different absorbance spectrum of ZnO nanowires electrodeposited under different concentration of Zinc chloride. From this Fig we find that the absorption intensity increased by increasing the zinc chloride concentration and it reaches maximum at $ZnCl_2$ concentration of 1mM. Fig.8 shows that when the $ZnCl_2$ concentration increased from 0.05mM to 1mM the band gap of ZnO nanowires increased from 3.075 to 3.267 and 3.27 eV respectively, which agrees well with the documented room temperature value (3.2-3.4 eV) of the band gap of bulk ZnO except for the sample electrodeposited at very low concentration (0.05 mM) of $ZnCl_2$.

## IV. CONCOLUSION

A systematic study of the role of deposition potential and $ZnCl_2$concentration on the properties of electrodeposited ZnO nanowires from oxygen electroreduction is reported. The applied potential was varied from -0.7 to -1.1V vs. Ag/AgCl. SEM results revealed that ZnO samples electrodeposited at applied potential -0.8V, -0.9V have high density and good alignment. Also, the diameters and densities of the electrodeposited ZnO nanowires are strongly dependent on the zinc ion concentrations and well aligned nanowires with uniform diameter can be obtained when the concentration of zinc ions is between 0.5 mM and 1 mM.

## V. ACKNOWLEDGMENT

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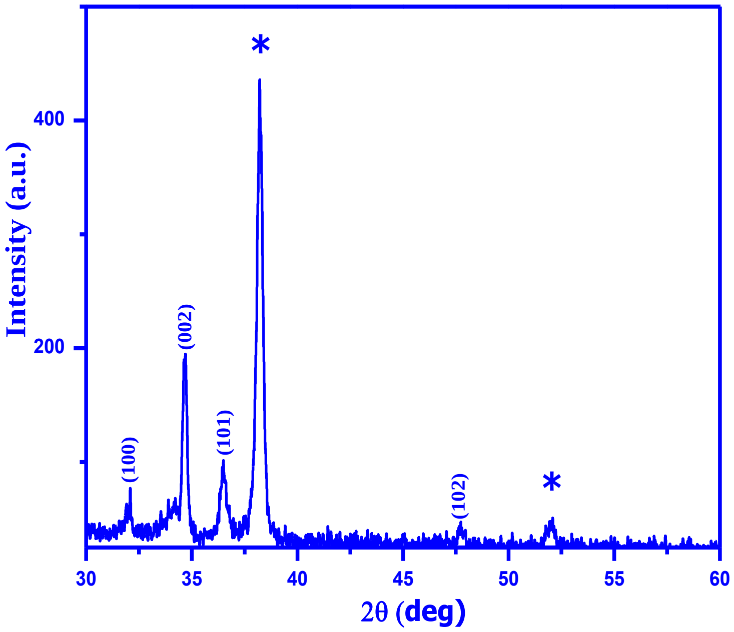

**Fig.1:** XRD pattern of electrodeposited ZnO nanowires. (* refers to FTO substrates).

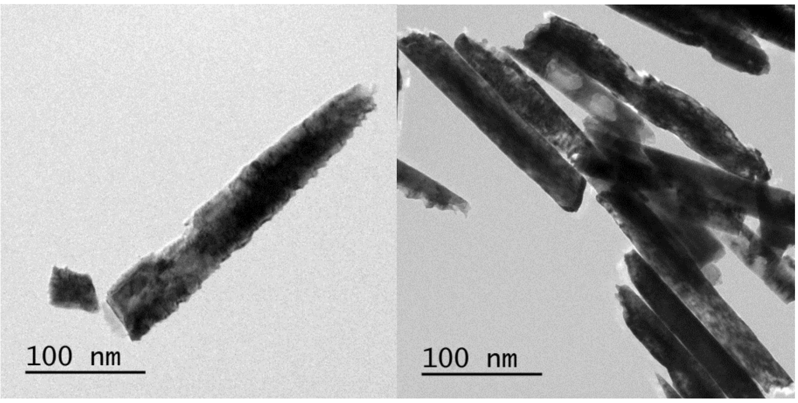

**Fig.2:** Bright-field TEM images of ZnO nanowires.

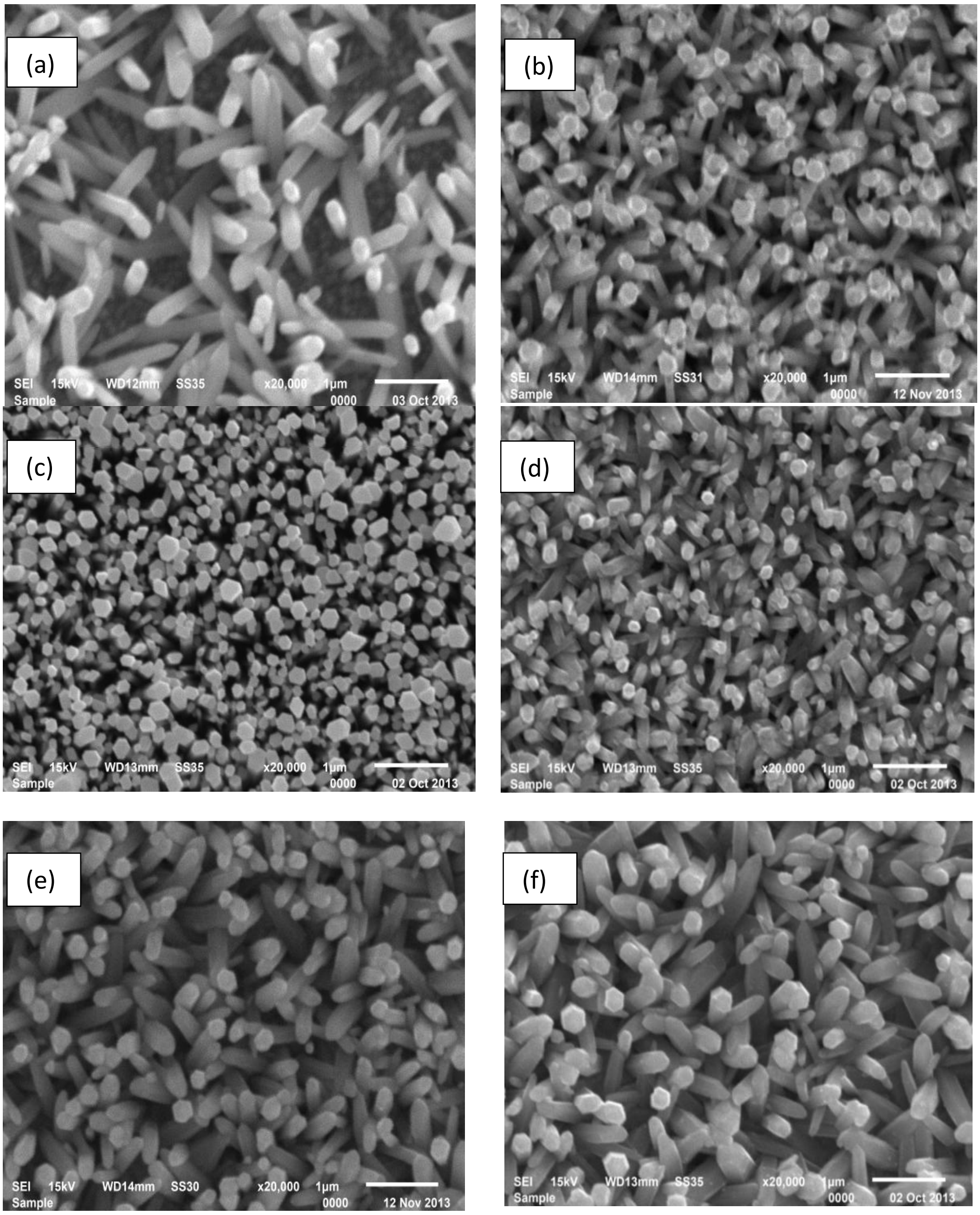

**Fig.3:** SEM photographs of ZnO nanowires electrodeposited at different applied potential (a) -0.7 V, (b) -0.8, (c) -0.85, (d)-0.9, (e) -1, and (f) -1.1V.

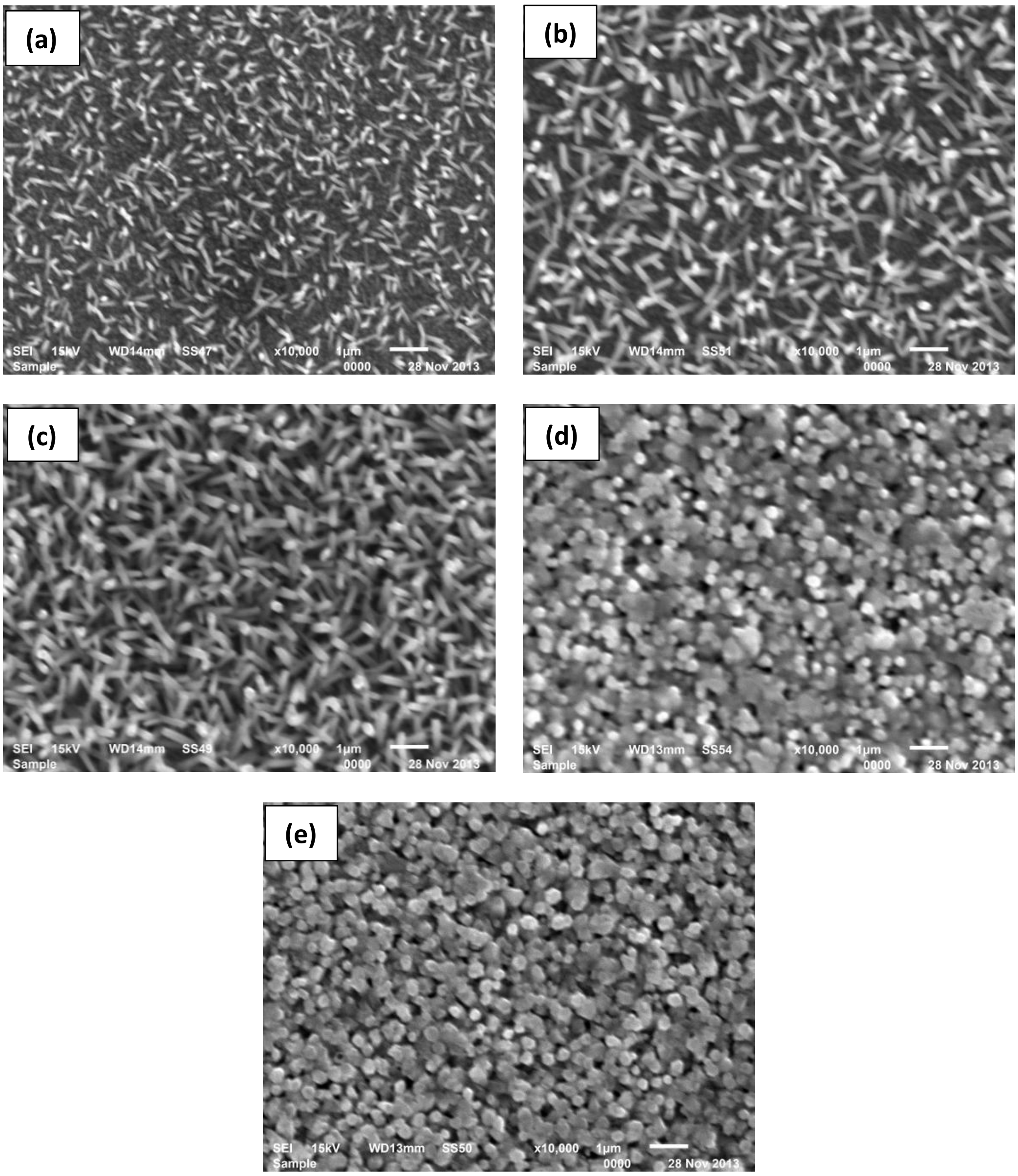

**Fig.4:** SEM photographs of ZnO nanowires electrodeposited at different $ZnCl_2$ concentrations (a) 0.05 mM, (b) 0.1 mM, (c) 0.25mM, (d) 0.5 mM, and (e) 1mM.

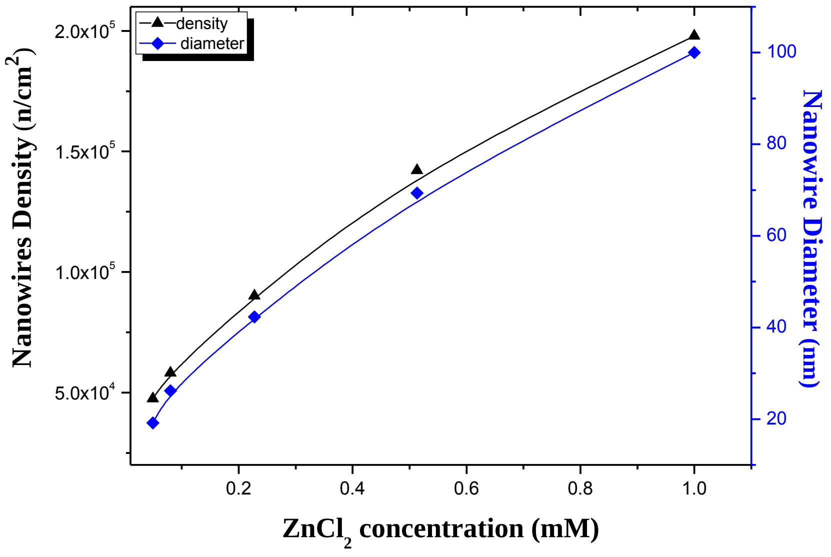

**Fig.5:** Nanowires diameter and density as a function of ZnCl$_2$ concentration.

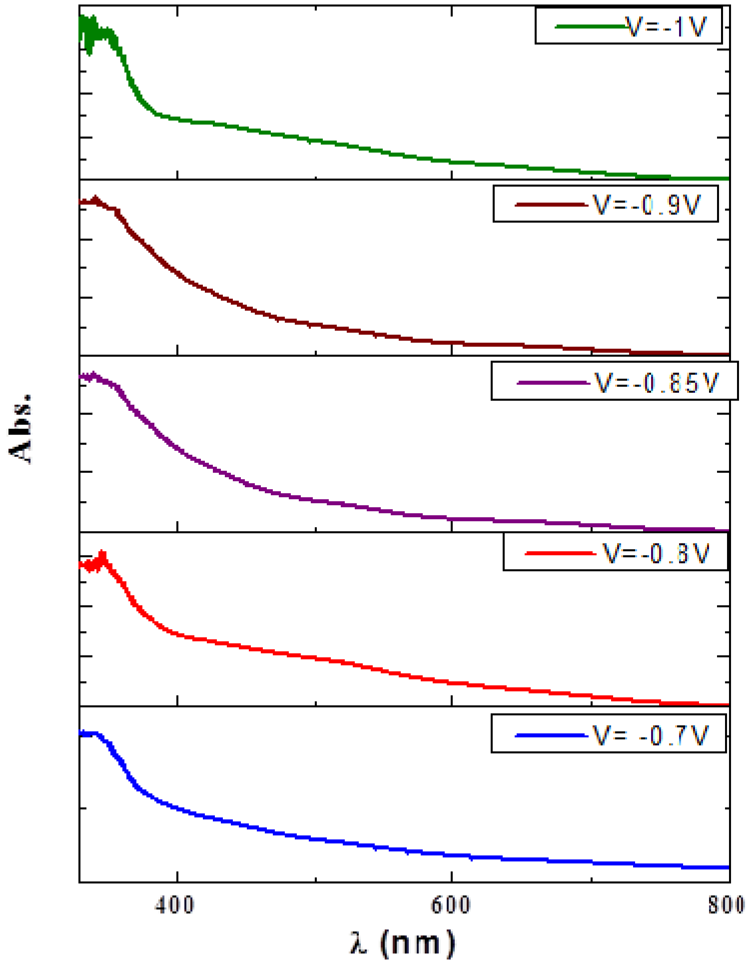

**Fig.6:** Absorption spectrum of ZnO nanowires electrodeposited at different applied potential vs. Ag/AgCl.

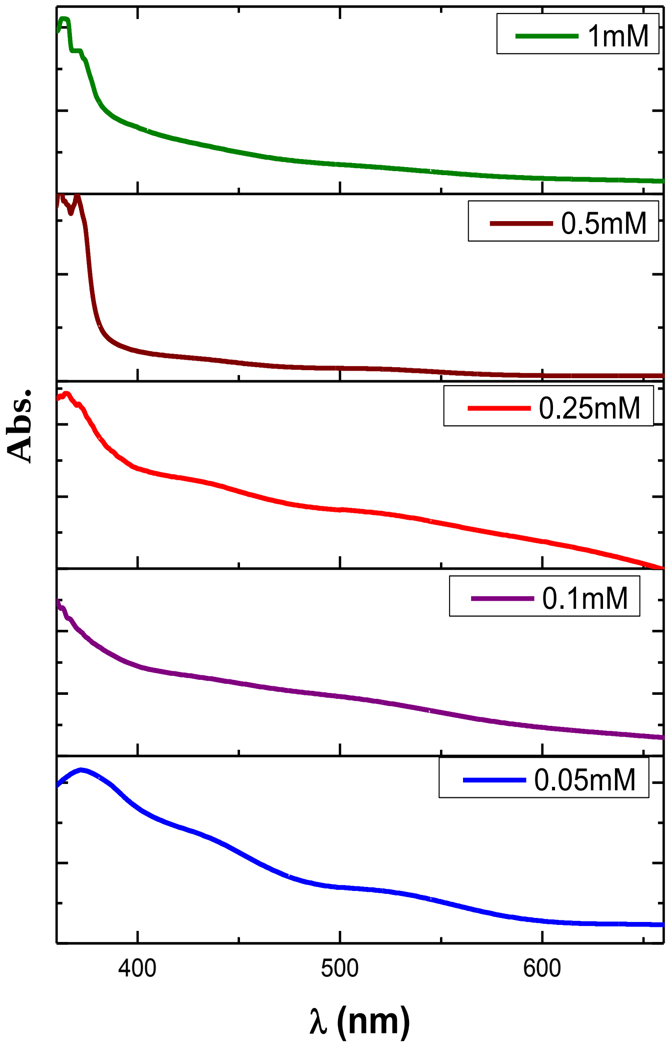

**Fig.7:** Absorption spectrum of ZnO nanowires electrodeposited at different $ZnCl_2$ concentrations.

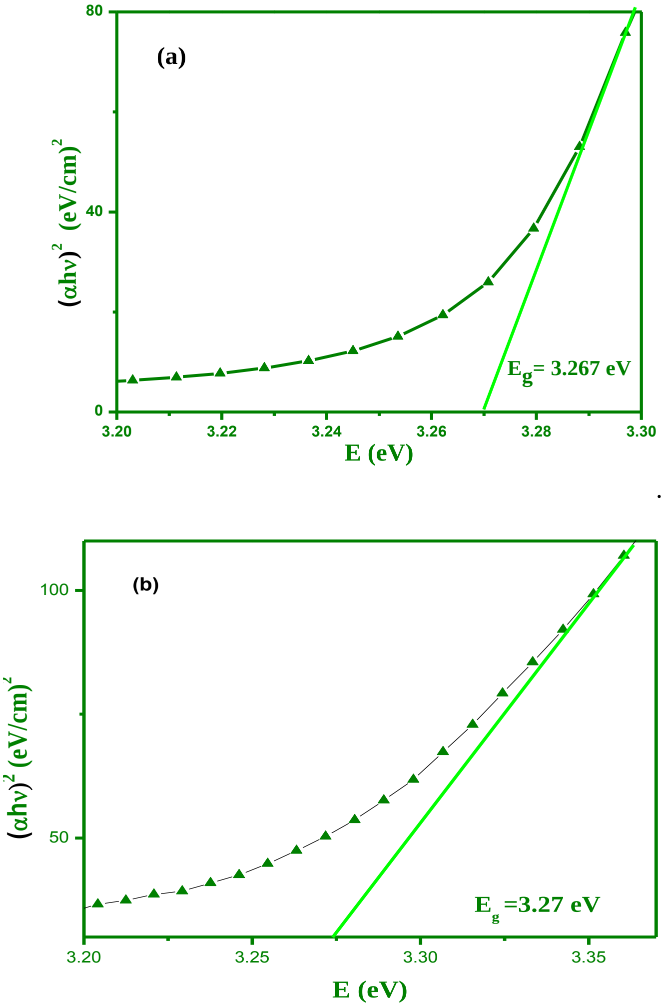

**Fig.8:** Band gap of ZnO nanowires electrodeposited at different concentrations of $ZnCl_2$ (a) 0.5mM, and (b) 1mM.