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A Comparative Study on Structural and Optical Properties of ZnO Micro-Nanorod Arrays Grown on Seed Layers Using Chemical Bath Deposition and Spin Coating Methods

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In this study, Zinc Oxide (ZnO) seed layers were prepared on Indium Tin Oxide (ITO) substrates by using Chemical Bath Deposition (CBD) method and Sol-gel Spin Coating (SC) method. ZnO micro-nanorod arrays were grown on ZnO seed layers by using Hydrothermal Synthesis method. Seed layer effects of structural and optical properties of ZnO arrays were characterized. X-ray diffractometer (XRD), Scanning Electron Microscopy (SEM) and Ultraviolet Visible (UV-Vis) Spectrometer were used for analyses. ZnO micro-nanorod arrays consisted of a single crystalline wurtzite ZnO structure for each seed layer. Besides, ZnO rod arrays were grown smoothly and vertically on SC seed layer, while ZnO rod arrays were grown randomly and flower like structures on CBD seed layer. The optical absorbance peaks found at 422 nm wavelength in the visible region for both ZnO arrays. Optical bandgap values were determined by using UV-Vis measurements at 3.12 and 3.15 eV for ZnO micro-nanorod arrays on CBD seed layer and for ZnO micro-nanorod arrays on SC-seed layer respectively.

Keywords: ZnO, micro-nanorod, chemical bath deposition, spin coating, hydrothermal synthesis.

1. INTRODUCTION

In the past decades, well aligned nanostructures with controlled surface area and crystal morphologies have attracted a great interest, based on the fact that the morphologies of most nanostructures can effectively tune their intrinsic chemical and physical properties [1]. Zinc oxide (ZnO), as a wide and a direct bandgap (3.37eV) semiconductor, has attracted much attention due to its novel optical and electronic properties [2]. While there are various ZnO nanostructures such as nanowire, nanorod, nanobelts, nanotube and nanoflowers, ZnO nanorod arrays draw attention because of their optical and electrical characteristics [3]. Well-aligned ZnO nanorod arrays are very popular due to their unique applications particularly for gas sensor [4], photoelectrochemical [5], photocatalytic devices [6], solar cells [7]. Some techniques, such as VLS [8], CVD [9], hydrothermal methods [10, 11] were used for synthesis of ZnO arrays.

The CBD method has many advantages such as simplicity, low cost [12]. The sol–gel SC method has several advantages such as a broad deposition area, low cost for the technological applications and easy of use [13]. Hydrothermal synthesis which is a simple, easy and low cost method, is used for obtaining nanostructures in specific shape and size at lower temperatures (lower than 100 °C) [10, 14].

In order to prepare ZnO seed layers, SC method is generally used in the literature [14 – 17]. In addition, CBD method is not used as a seed layer synthesis method according to the research mentioned in the literature.

In this study, ZnO seed layer was synthesized by using CBD and SC methods. Then, ZnO micro-nanorod arrays were grown successfully on seed layers by using Hydrothermal Synthesis method.

The fundamental aim of this study is to investigate the effect of seed layer prepared with CBD method and SC method on ZnO micro-nanorod arrays.

2. EXPERIMENTAL DETAILS

In this study, ZnO seed layers were synthesized on Indium Tin Oxide (ITO) substrates, ITO has a high electrical conductivity, high optical transparency in the visible range and high infrared reflectivity for wavelengths higher than 1 µm [18]. Therefore, it is used widely as transparent conducting oxide.

The first method is the CBD to grow ZnO seed layers on ITO substrates (ZSCBD). ITO substrates were immersed in aqueous solution of 0.1 M Zinc Acetate Dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$, Sigma-Aldrich) and 0.1 M hexamethylenetetramine ($C_6H_{12}N_4$, Sigma-Aldrich) (VL : 1 : 1) at room temperature for 15 min. After immersing process, substrates are heated at 100 °C for 15 min. The process is repeated 10 times for achieving seed layers.

Another method is SC to obtain ZnO seed layers on ITO substrates (ZSSC). 1 g Zinc Nitrate Hexahydrate

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($Zn(NO_3)_2 \cdot 6H_2O$, Sigma-Aldrich) was dissolved in 10 ml ethanol (C_2H_5OH). Ammonia (26 %) was added until getting a clear solution. After preparing the solution, ZnO seed layers were deposited on ITO substrates. The rotation rate was 3000 rpm up to 25 s. The as-deposited ZnO seed layers were sintered at 220 °C for about 2 – 3 minutes and deposited procedure was repeated at 10 times. Seed layers were annealed at 400 °C for 2 h.

ZnO arrays were grown by Hydrothermal Synthesis method at 90 °C on the seed layers. A prepared solution for hydrothermal process contained 0.1 M Zinc Nitrate Hexahydrate and 0.1 M hexamethylenetetramine (VL : 1 : 1). The solution was transferred into Teflon-lined stainless steel autoclave and the seed layers were remained in the autoclave at 90 °C for 4 h.

The properties of ZnO micro-nanorod arrays were characterized by XRD, SEM and UV-Vis measurements.

The structural properties of samples were studied using a Panalytical Empyrean X-ray diffractometer operated at 45 kV, 40 mA with CuKα radiation (λ = 1.5406 Å). The morphologies of the samples were studied using a FEI Quanta 550 FESEM Model Scanning Electron Microscope. The optical properties of the samples were studied using a PerkinElmer Lambda-35 UV-Vis spectrophotometer.

3. RESULTS AND DISCUSSION

Fig. 1 shows the XRD patterns of the seed layers. The peak of ZSSC along the (002) plane which is in good agreement with wurtzite ZnO crystal structure [13], is sharper than the same peak of ZSCBD for the same plane. Furthermore, ITO peaks have emerged sharply in each seed layer. ZSSC, which is thinner and smoother, has given higher ITO peak intensity than the ZSCBD.

Fig. 2 shows the XRD patterns of the ZnO micro-nanorod arrays. (002) diffraction peak of ZnO micro-nanorod arrays grown on seed layer synthesized by using SC (ZRSC) has a much higher intensity than (002) diffraction peak of ZnO arrays grown on seed layer synthesized by using CBD (ZRCBD). Intensities of the other peaks are rather low than (002) peak for each sample and intensities of the other peaks for ZRSC are lower than ZRCBD. The obtained single crystalline wurtzite ZnO structure is in good agreement with the literature [19, 20]. Additionally, it is reported that 2 theta degree of (002) peak for ZnO hydrophobic film growth by using CBD is identified between 50° – 55° with highly intensity [19]. However, 2 theta degrees of (002) peaks for ZRCBD and ZRSC which is identified approximately at 35°, is in good agreement with hydrothermal studies [11, 21].

The crystallize sizes were calculated using Scherer equation:

$$D = k\lambda/(\beta\cos\theta), \quad (1)$$

where λ is the X-ray wavelength; k is the constant (0.9 value); θ is the Bragg angle and β is the full width at half maximum. The results are shown in Table 1. The diffraction peaks of wurtzite (hexagonal crystal system) structure are detected, and the peak positions are in good agreement with the values of data card (98-016-1836) [22].

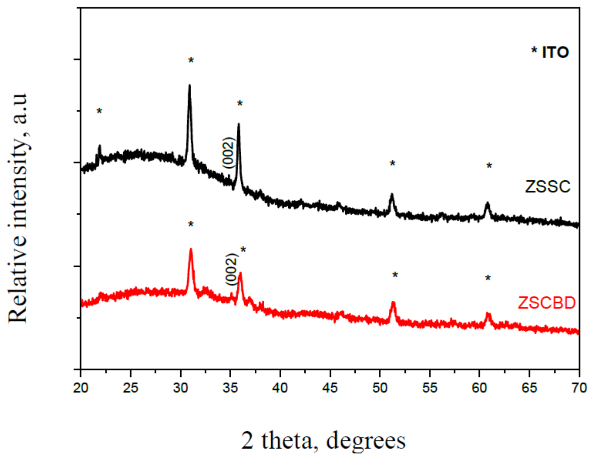


Fig.1. XRD spectra of ZnO seed layers

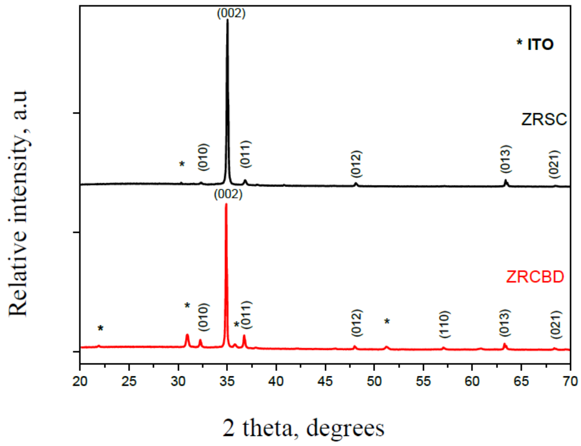


Fig. 2. XRD spectra of ZnO micro-nanorod arrays

SEM images of seed layer are shown in Fig. 3 for different magnifications. It is obvious that ZSSC has a smoother and less rough surface than ZSCBD.

SEM images of ZnO micro-nanorod arrays are shown in Fig. 4 for different magnifications. ZRSC exhibits vertically well-arranged growth direction, which are consistent with the XRD results, while ZRCBD exhibits randomly flower like structure in micro-nano size. Vertically well-aligned ZRSC arrays oriented at (002) plane and (0001) direction are in good agreement with the literature [11, 21]. Most of these rods have approximately 15 – 20° deflection angles from the vertical axis and this result is in good agreement with the literature [21]. However, flower like ZRCBD arrays were grown randomly oriented due to high porosity seed layer.

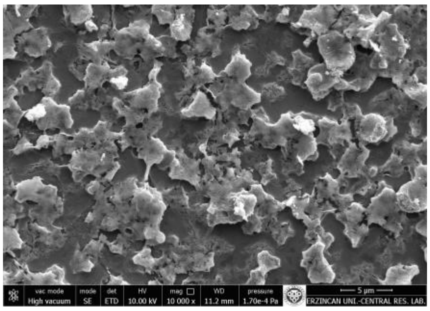
The effects of the differences in the surface morphology on optical characteristics and optical bandgap are discussed in optical results.

Fig. 5 and Fig. 6 show the UV-Vis absorption and optical bandgap spectra of the ZnO micro-nanorod arrays on different seed layers. In Fig. 6, blue lines are fitting line for curve to determine the optical bandgap values.

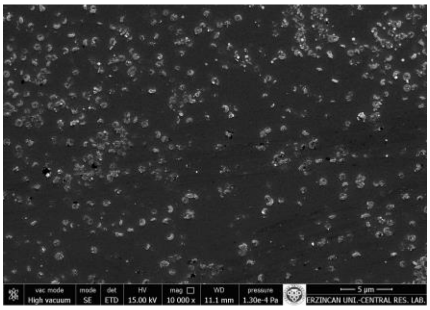
As seen from Fig. 5 and Fig. 6, the UV-Vis absorption spectra of two kinds of samples were different intensity peaks. But, ZnO arrays displayed a sharp absorption onset at about 422 nm for each sample. The optical bandgap for ZRSC (3.15 eV) is in better agreement with the literature [23, 24] than optical bandgap for ZRCBD (3.12 eV).

Table 1. XRD data of ZnO micro-nanorod arrays

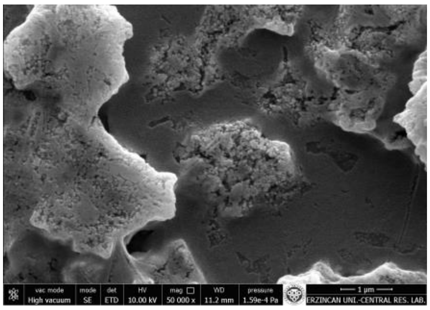
ICSD collection card: 98-016-1836 [22]			XRD Parameters of ZRCBD				XRD Parameters of ZRSC			
2 θ, °	d, Å	h k l	2 θ, °	FWHM	d, Å	D, nm	2 θ, °	FWHM	d, Å	D, nm
31.439	2.8431	0 1 0	32.240 (1)	0.144 (8)	2.77437	60.9	32.309 (5)	0.24 (2)	2.76858	30.7
34.889	2.5695	0 0 2	34.8740 (1)	0.1056 (7)	2.57060	186.6	34.9897 (2)	0.1434 (6)	2.56237	84.5
36.074	2.4878	0 1 1	36.7126 (7)	0.130 (8)	2.44597	73.9	36.803 (2)	0.236 (6)	2.44017	38.5
47.666	1.9063	0 1 2	47.99 (1)	0.1 (2)	1.89436	78.7	48.093 (2)	0.153 (7)	1.89040	67.0
55.973	1.6415	1 1 0	57.034 (3)	0.18 (4)	1.61347	49.1	57.08 (2)	0.60 (8)	1.61222	11.6
63.335	1.4672	0 1 3	63.274 (4)	0.14 (4)	1.46853	76.9	63.3856 (9)	0.133 (3)	1.46622	79.2
68.418	1.3701	0 2 1	68.354 (4)	0.14 (6)	1.37125	82.0	68.447 (5)	0.20 (1)	1.36960	54.2



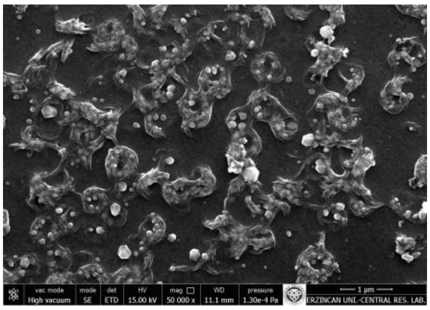
ZSCBD



ZSSC



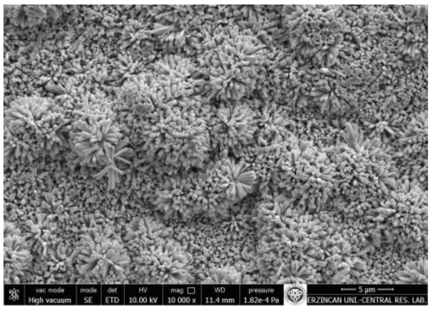
ZSCBD



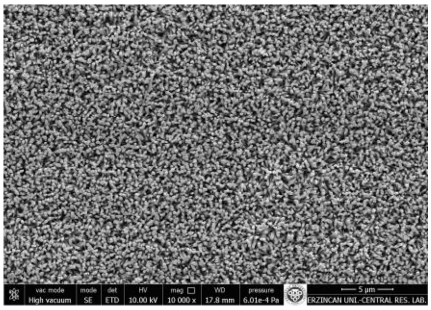
ZSSC

Fig. 3. SEM images (10000 – 50000 magnifications) of ZnO seed layers

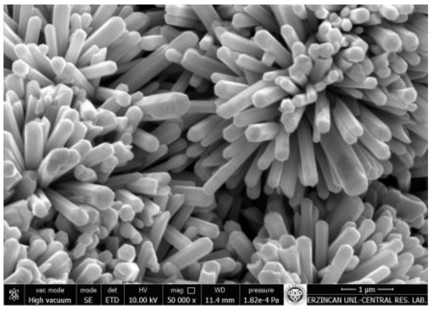
Also, it is reported that high quality ZnO arrays have a narrower bandgap than bulk ZnO (3.37eV) and it is explained that while large bandgap for ZnO structure limits its photoresponce to only the UV solar spectrum region. ZnO structure with narrow bandgap provides effectively to be used solar energy for solar applications [25].



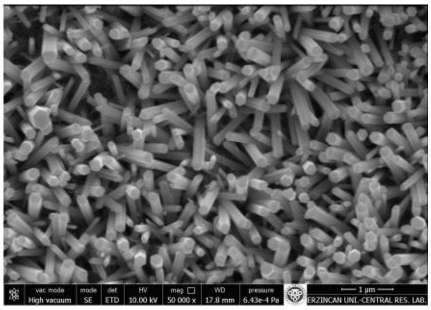
ZRCBD



ZRSC



ZRCBD



ZRSC

Fig. 4. SEM images (10000 – 50000 magnifications) of ZnO micro-nanorod arrays

As seen from results, the seed layer played important roles in morphology, crystal structure and optical properties of ZnO micro-nanorod arrays.

The reason for the strong tendency to uniformity is the way the two main forces balance; they are the rotation-induced centrifugal force, which drives radially outward flow, and the resisting viscous force, which acts radially inward for the SC method [26]. Besides, the major problem of the CBD method is the inefficiency of the process which converts the precursor materials into useful deposits; firstly, homogeneous nucleation leads to rapid formation of large particles throughout the solution, as precipitate, conversely, heterogeneous nucleation occurs at the substrate surface and particles grow slowly to form a film [27]. As a result, morphology of seed layer is strongly related with coating method.

Therefore, ZSSC has smooth and uniform surface that is provided to be synthesized vertically aligned high crystallinity wurtzite ZnO rod arrays on this seed layer. ZSCBD has highly porosity that is caused to be synthesized flower like and randomly oriented ZnO rod arrays on this seed layer.

Additionally, it is reported that highly porous surfaces play an important role in the synthesis of ZnO flower like rod arrays [28]. Porous ZnO nanostructures exhibit highly sensitive performance for metal oxide gas sensor [29], while vertically aligned nanorod arrays are promising candidates for optoelectronic applications [30].

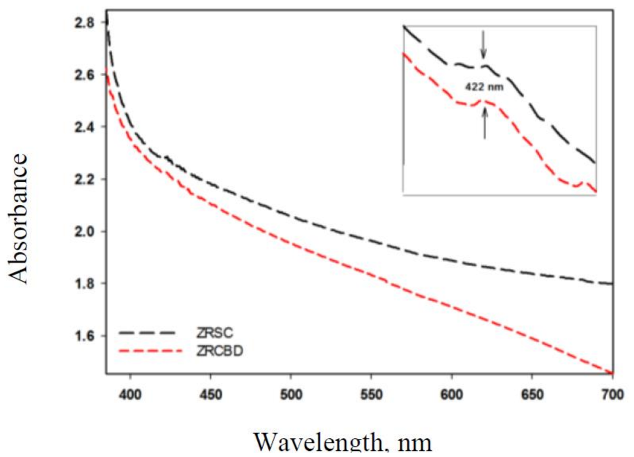


Fig. 5. UV–Vis absorption spectra of ZnO micro-nanorod arrays

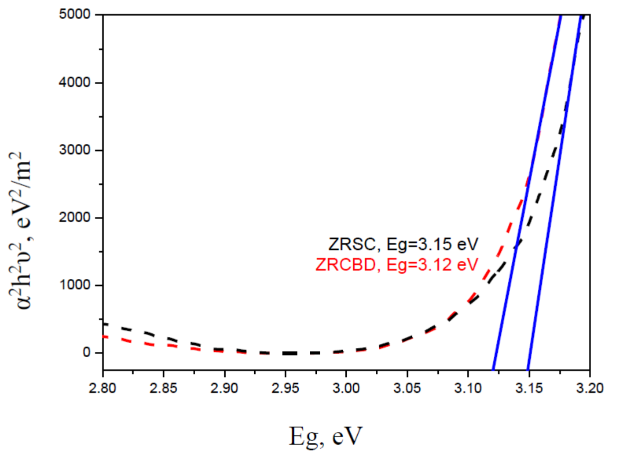


Fig. 6. Optical bandgap spectra of ZnO micro-nanorod arrays

4. CONCLUSIONS

In this study, ZnO micro-nanorod arrays were synthesized on seed layers that were prepared by using two different methods.

The Spin Coating is a better seed layer growth method than the Chemical Bath Deposition method to grow vertically and well-arranged single crystalline wurtzite ZnO micro-nanorod arrays by hydrothermal method. Also, the optical measurements show that optical bandgap of ZnO micro-nano arrays grown on SC seed layer is in good agreement with the literature. Furthermore, the Chemical Bath Deposition method is good seed layer method to obtain flower like ZnO nanostructures.

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