Surface Topology and Optical Properties of Nanostructured Zinc Oxide Thin Films Prepared Using Two-Stage Solution Immersion Method

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Abstract. Nanostructured zinc oxide (ZnO) films were prepared using two-stage immersion process. The properties of the prepared films were investigated using atomic force microscopy and ultraviolet-visible spectroscopy. The root-mean-square surface roughness of the nanostructured ZnO film was 79 nm. The average optical transmittance of the film was 72% in the visible spectrum. The prepared nanostructured ZnO film also has high ultraviolet absorbance.

1. Introduction

Recently, research on metal oxide nanostructured semiconductors shows fascinating results due to the unique physical and chemical properties of nanomaterials. Among the metal oxide nanostructure that has been extensively studied is zinc oxide (ZnO). The ZnO nanostructures have been applied for various electronic devices such as sensors, solar cells, and field emission devices owing to their distinctive structures and tunable conductivity and properties [6, 13, 14]. Various methods have been used to fabricate ZnO nanostructures including hydrothermal [1], chemical vapor deposition (CVD) [15], electron beam evaporation [5], radio frequency (RF) magnetron sputtering [9], thermal oxidation [2], and sol-gel methods [4].

In this paper, we reported a solution immersion method to synthesize nanostructured ZnO films on the glass substrates. The films were prepared through two stages of immersion process. The first stage of immersion process is to produce ZnO nanorod arrays, while the second stage of immersion process is to deposit nanostructured ZnO on ZnO nanorod arrays. The motivation of this research is to produce higher surface area through the introduction of ZnO nanostructures on nanorods. In addition, the study also to seek novel nanostructures configuration, which could improve electronic device performance particularly humidity sensor. The use of ZnO nanostructures such as assembled nanoflakes, nanograin, or nanoplatelets structure is likely to improve structural-mechanical stability in comparison to one-dimensional (1D) and zero-dimensional (0D) nanoparticles structures [7].

2. Experimental procedure

2.1. Preparation of First ZnO seed layer

The preparation of solution for the first ZnO seed layer used zinc acetate dihydrate ($Zn(CH_3COO)_2.2H_2O$; 99.5% purity; Aldrich), monoethanolamine (MEA, $H_2NCH_2CH_2OH$; 99.5% purity; Aldrich), aluminum nitrate nanohydrate ($Al(NO_3)_3.9H_2O$; 98% purity; Analar), and 2-methoxyethanol as a precursor, stabilizer, dopant source, and solvent, respectively. The solution was prepared at 0.4 M. The solution was stirred and heated at 80 °C for 3 hours before aged for 24 h at room temperature. The prepared homogeneous solution was spin-coated on glass substrates at 3000 rpm for 1 min. Then, the film-coated substrates were heated and dried at 150°C for 10 min. Subsequently the thin films were annealed for 1 h at 500 °C in a furnace after the procedure was repeated for a five times to increase the thickness.

2.2. Preparation of ZnO Nanorods Growth

The solution for ZnO nanorod was prepared using zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$; 98.5% purity; Schmidt), hexamethylenetetramine (HMT, $C_6H_{12}N_4$; 99% purity; Aldrich), and aluminum nitrate nanohydrate ($Al(NO_3)_3.9H_2O$; 98% purity; Analar),as a precursor, a stabilizer, and a dopant source, respectively. The solution was prepared at 0.1 M. The solution were prepared by mixing and dissolving the reagents into deionized (DI) water and then sonicated at 50 °C for 30 min. Then, the solutions were aged at room ambient for 2 h. Next, the solutions were poured into Schott bottles; the seed layer-coated glass substrates were placed at the bottom of the bottles. The bottles were then immersed in a water bath immersion tank at 95 °C for 2 hour. Subsequently, the obtained films were cleaned with DI water and dried at 150 °C for 10 min. Finally, the films were annealed at 500 °C for 1 h after the thin films

2.3. Preparation of Second ZnO seed layer

For the preparation of solution for the second ZnO seed layer, zinc acetate dihydrate ($Zn(CH3COO)2.2H_2O$; 99.5% purity; Aldrich), mono-ethanolamine (MEA, $H_2NCH_2CH_2OH$; 99.5% purity; Aldrich), aluminum nitrate nonahydrate ($Al(NO_3)_3.9H_2O$; 98% purity; Analar), and 2-methoxyethanol were used as a precursor, stabilizer, dopant source, and solvent, respectively. The solution was stirred and heat at 80 °C for 3 hours before aged for 24 h at room temperature. The prepared homogeneous solution was spin-coated on ZnO nanorod array-coated glass substrate at 1000 rpm for 1 min. Next, the coated nanorod films were heated and dried at 150°C for 10 min. Finally, the samples were annealed for 1 h at 500 °C.

2.4. Preparation of ZnO nanostructures on ZnO nanorod arrays

The solution was prepared using zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$; 98.5% purity; Schmidt), hexamethylenetetramine (HMT, $C_6H_{12}N_4$; 99% purity; Aldrich), and aluminum nitrate nanohydrate ($Al(NO_3)_3.9H_2O$; 98% purity; Analar),as a precursor, a stabilizer, and a dopant source, respectively. The solutions were prepared by mixing and dissolving all the reagents into DI water. Then, the solution was sonicated at 50 °C for 30 min and aged at room temperature for 2 h. Next, the solutions were poured into Schott bottles; the coated nanorod films on glass substrates were placed at the bottom of the bottles. The bottles were immersed into water bath immersion tank at 95 °C for 2 h. The obtained nanostructured films were cleaned with DI water and heated at 150 °C for 10 min. Next, the obtained nanostructure films were annealed at 500 °C for 1 h.

2.5. Characterization

The surface topology of nanostructured ZnO films were characterized using atomic force microscopy (AFM) and the optical properties of the samples characterized using ultraviolet-visible (UV-Vis; Varian Cary 5000) spectrophotometer.

3. Result and Discussion

Fig. 1 shows surface topology of nanostructured ZnO film prepared using solution method. Fig.1 (a) and (b) show two-dimensional (2D) and three-dimensional (3D) AFM images of nanostructured ZnO film, respectively. The images were obtained using contact mode AFM. The scanning area of the images was 10 µm x 10 µm. The figures reveal that the sample surface is relatively rough. The measured value of root-mean-square (RMS) surface roughness was 79 nm. Our previous experiment showed that after the first immersion process, the nanorod were grown uniformly on the glass substrate [8, 10, 11]. However, after the second immersion process, the nanorod structure was not observed in the AFM images. This condition was due to the secondary growth of ZnO nanostructures on ZnO nanorod arrays after second time immersion process. These nanostructures can be observed clearly in the AFM images as shown in the circle in Fig. 1(a). In addition, the coating process of second ZnO seed layer on the nanorod arrays, which deposited on top of the nanorods, may hinder the visibility of the nanorod structure. The high surface roughness of deposited films also influenced by the chemical species presence in the films and the physical aspects during the deposition process.
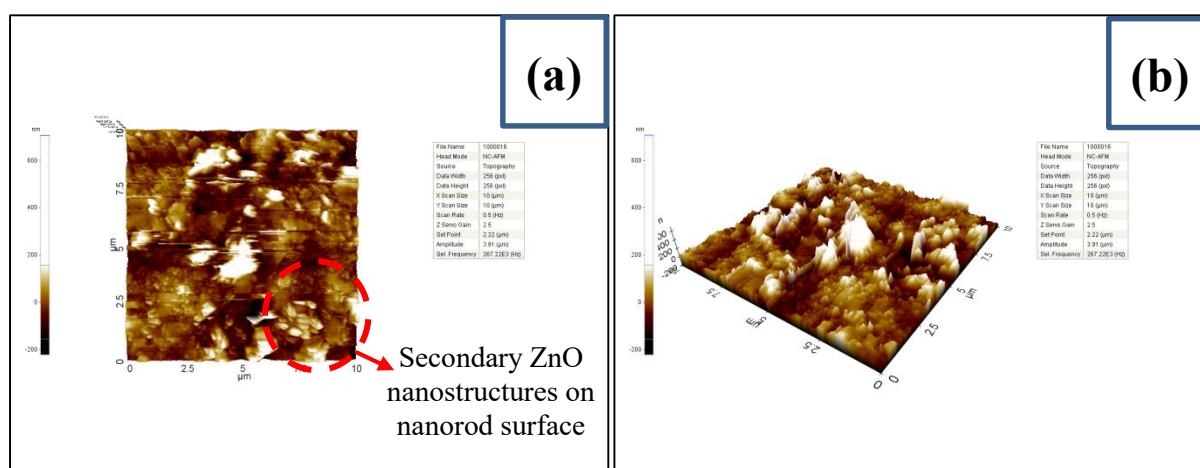

Fig. 1. (a) 2D and (b) 3D AFM images of nanostructured ZnO film prepared using solution immersion method.

Fig 2 shows the optical measurement results of nanostructured ZnO film. The results for ZnO nanorod arrays coated with second ZnO seed layer was also shown for comparison. Fig. 2(a) displays the transmittance spectra of nanostructured ZnO film at wavelength of 350 to 800 nm. The films showed good transmittance properties in the visible region (400-800 nm) with average transmittance approximately 72 %. This transmittance value was slightly lower than that of the ZnO nanorod arrays coated with second ZnO seed layer (78 %). This condition was due to decrease in void of the film after second time immersion process [3]. Furthermore, the scattering of light might be prevalent in the nanostructured ZnO film due to rough surface induced by secondary nanostructured ZnO growth [12].

Figure 2(b) shows the absorbance spectra of nanostructured ZnO film and film of ZnO nanorod arrays coated with second ZnO seed layer. The results show that both films have high absorbance properties in the UV region below 400 nm. However, the nanostructured ZnO film possess higher light absorbability in the UV region. This condition might be due to light scattering effects as discussed previously. The light scattering phenomenon results in longer transmission path of the light in the film. This condition enables the light absorbance at the optimum capacity by nanostructured ZnO due to light traveling across more ZnO surfaces. In addition, the higher fraction of nanostructured ZnO film as compare to film of ZnO nanorod arrays coated with second ZnO seed layer enables UV light to be absorb efficiently. It also can be observed that the ZnO films shows a cut-off wavelength at 380 nm. The band gap energy of ZnO were reported to be in the region between 3.2 to 3.3 eV, which matches with cut-off wavelength of

nanostructured ZnO in this study. The cut-off wavelength observed through UV-vis spectroscopy result can be as a preliminary tool for material bandgap estimation.
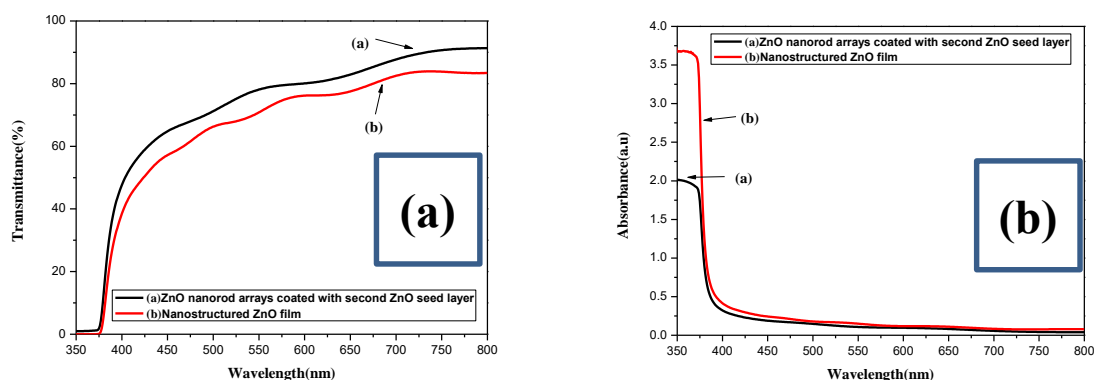

Fig. 2. (a) Optical transmittance and (b) absorbance spectra of nanostructured ZnO film and film of ZnO nanorod arrays coated with second ZnO seed layer.

4. Conclusion

In summary, nanostructured ZnO film have been successfully synthesized by two-stage immersion method on glass substrate. The structural and optical properties of the film were investigated using AFM and UV-vis spectroscopy, respectively. The nanostructured ZnO film has high surface roughness with RMS roughness value of   79 nm. The optical transmittance spectra revealed that nanostructured ZnO films exhibit high transparency in the visible region with average transmittance of 72 %. Moreover, the absorbance of nanostructured ZnO film in the UV region below 400 nm improved compare to that of film of ZnO nanorod arrays coated with second ZnO seed layer. These results due to light scattering effect induced by rough surface area and the existence of secondary ZnO nanostructures on the nanorod surfaces.

5. Acknowledgement

6. References

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