ASM Sc. J., 14, Special Issue 1, 2021 for ICSTSS2018, 76-80

Comparison on Structural, Topological and Optical Characteristics of Pure ZnO and Ag/ZnO Nanorod Films

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Synthesised of Zinc oxide (ZnO) and Argentum (Ag) doped ZnO (Ag/ZnO) nanorod films were successfully deposited on glass substrate coated with ZnO seeded layer prepared using immersion technique. The structure of ZnO and Ag/ZnO nanorod films were investigated using X-Ray diffraction (XRD) and Field emission scanning electron microscopy (FESEM). The topology and optical characteristics were analysed by Atomic Force Microscopy (AFM) and UV-Vis NIR spectroscopy, respectively. Based on the XRD results both the nanorods were in polycrystalline structure. The highest peak intensity for both nanorod films was along (002) c-axis plane. The diameter of ZnO and Ag/ZnO nanorod films were about 77 and 65 nm, respectively. The diameter is reduced when Ag was introduced into ZnO lattice. The surface roughness of Ag/ZnO nanorod films is higher compared to ZnO nanorod films. The average transmittance of Ag/ZnO nanorod films between visible region is reduced compared with ZnO nanorod films. The results obtained show that introducing Ag dopant has significantly changed the structure, topology and optical characteristics of ZnO.

Keywords: Argentum; doped; nanorods; films; zinc oxide

I. INTRODUCTION

The unique properties of zinc oxide (ZnO) semiconductor makes this material is widely used in many application such as solar cells (Moret *et al.*, 2014), sensors (Hijri *et al.*, 2014), light emitting diodes (Li *et al.*, 2018), varistor (Hembram *et al.*, 2018) and photocatalyst (Chang *et al.*, 2018). The band gap energy for ZnO is 3.37 eV, while the exciton binding energy is 60 meV (Razeen *et al.*, 2018). This material is non-toxic, inexpensive, abundant, has good chemical stability with higher electron and is a good transparent at room temperature. The properties of ZnO can change if added or doped with other metal oxide depending on the requirement of an application. Argentum (Ag) one of the transition metals that has been used to dope with ZnO films. It can act as an acceptor and has shown to possess good chemical and electrical properties (Razeen *et. al.*, 2018; Xue *et al.*, 2008).

The use of Ag has also been reported to increase the efficiency of luminescence and photocatalytic activity of ZnO films (Zhang *et al.,* 2005). Ievtushenko *et al.* (2018) studied on the structure and optical characteristics of pure and Ag doped ZnO that was prepared using MOCVD technique on si substrate. They found that the structure of

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ZnO was influenced by Ag doping which altered nucleate mode to heterogeneous and thereby converting polycrystalline to nanorods structure along c-axis plane. It was also found, that the emission of near-band edge of ZnO nanorods was improved when Ag is doped into ZnO.

Various techniques have been used to synthesise ZnO films such as vapour phase epitaxy, RF magnetron sputtering, chemical vapour deposition and aqueous solution method (Razeen *et. al.*, 2018; Ievtushenko *et al.*, 2018). In this study, the nanorod samples were prepared on ZnO coated glass substrate using solution immersion method. This method was chosen due to its simplicity and ability to operate at low temperature. Furthermore, this technique is cheap with mass production. The structural, topological and optical characteristics of nanorod samples were observed and deliberated.

II. MATERIALS AND METHOD

ZnO which acted as seed layer was deposited on a glass substrate using sol gel spin coating technique. A precursor (Zinc acetate dehydrate, 99.5 %, Merck) and stabiliser (monoethanolamine, 99.5 %, Aldrich) was mixed at 1:1 ratio in 2-methoxyethanol solvent. Then, magnesium acetate tetrahydrate (1 at %) and aluminium nitrate nonahydrate (1 at %), which acted as dopant were mixed into the precursor solution. The next process is to deposit the solution onto glass substrate using spin coating method which has been explained in detail by Mohamed *et al.* (2017).

Immersion technique is used to grow the ZnO nanorod arrays on the ZnO seeded layer. 0.1 M zinc nitrate hexahydrate with purity of 98 % from Systerm was used as a precursor. 0.1 M hexamethylenetetramine with 99 % purity from Aldrich was used as a stabiliser. As for Ag/ZnO nanorod films, 1 at.% of Ag nanopowder with 99.5 % purity from Aldrich, which functioned as dopant, was mixed to the solution. The precursor, stabiliser and dopant chemicals were dissolved in DI water. Then the mixed solution was sonicated using ultrasonic water bath by Hwashin Technology Powersonic 405 for about 30 min at 50 ^{o}C. The solution continues to be stirred and let the solution at room temperature for 3 h. The glass substrate that was coated with ZnO were placed on the bottom of vessels. The solution was poured into the vessels at volume of 100 ml. The immersion process was done by placing the sealed vessels in a hot water bath at 95°C for 30 min. After immersion process, ZnO nanorod films was rinsed with DI water. Then the samples were ready to be dried in the furnace at 150 ^{o}C for 10 minutes. Lastly, the synthesised samples underwent annealing process at 500 °C for 1 h in ambient conditions. The synthesised samples were characterised using XRD by PANalytical X'Pert PRO, FESEM by JSM-7600F and AFM by Park System. The optical characteristic of thin film samples were investigated using UV-Visible (UV-Vis) spectroscopy by Varian Cary 5000 brand.

III. RESULTS AND DISCUSSION

The structural characteristic of ZnO and Ag/ZnO nanorod films was investigated using XRD. The XRD patterns of pure ZnO and Ag/ZnO nanorod films was presented in Figure 1. The films sample shows the diffraction pattern for (100), (002), (101), (102) and (103) plane was belonging to ZnO wurtzite hexagonal structure that matches with JCPDS: 361451. Both samples show the strongest diffraction intensity along (002) plane orientation. It can be seen that Ag/ZnO nanorod films shows the highest peak intensity of (002) plane orientation compared to ZnO nanorod films, which indicates the nanorods grew along c-axis due to the minimum energy of the plane. It was found that the (002) peak intensity of Ag/ZnO films has shifted to a higher angular position compared to the ZnO thin film peak. The (002) peak intensity was shifted from 34.26 to 34.87^{o} for ZnO and Ag/ZnO, respectively. The peak shift is possibly due to the incorporation of Ag into the ZnO lattice as a substituent for Zn^{2+} or as an interstitial atom which was also reported by (Rafaie *et. al.*, 2017; Karunakaran *et al.*, 2010).

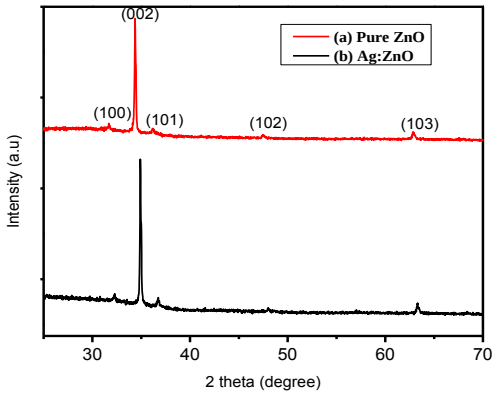

Figure 1. The XRD spectrum of (a) ZnO and (b) Ag/ZnO nanorod films

FESEM was used to see the change of morphology of pure ZnO and Ag/ZnO nanorods films. Figure 2 shows the morphology at 10 K magnification for pure ZnO and Ag/ZnO films. The obtained results illustrate that the films were in nanorods shape with diameter of pure ZnO and Ag/ZnO nanorod films were 77 and 65 nm, respectively. The nanorods diameter reduced when Ag was doped into ZnO lattice. The dense and thin nanorod arrays was obtained for both samples. However, Ag/ZnO has more pores compared to ZnO nanorod arrays. This might be due to the higher difference in the atomic radii between Zn and Ag. The ionic radii of Ag^{+} (0.126 nm) is bigger than that of Zn^{2+} (0.074 nm) (Hosseini *et al.*, 2015).

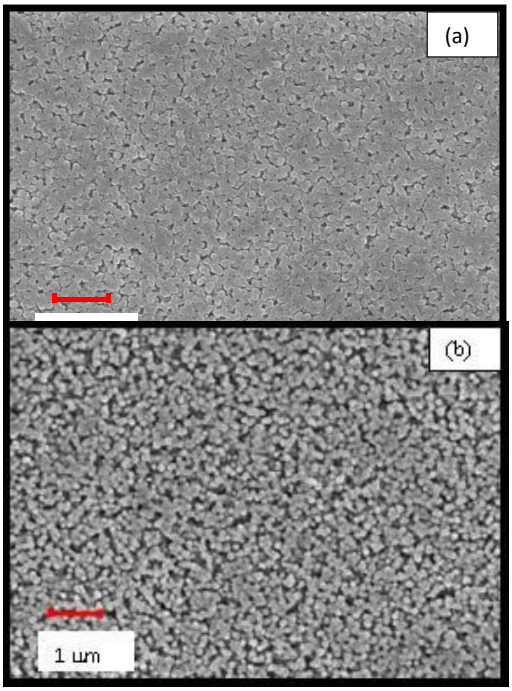

Figure 2. FESEM images of (a) ZnO and (b) Ag/ZnO nanorod films XRD spectrum of (a) ZnO and (b) Ag/ZnO nanorod films

The topological characteristic of ZnO and Ag/ZnO nanorod films in two dimensional (2D) is presented in Figure 3(a) and (b). Figure 3(a) presents compact granular topology compared to Ag/ZnO nanorod films. The surface roughness of ZnO and Ag/ZnO nanorod films are 4.961 and 5.225 nm, respectively as shown in Table 1. High surface roughness contributes to enhance the surface volume and might suitable for dye absorption which is essential for solar cell application (Hosseini *et. al.*, 2015; Ilican *et al.*, 2018).

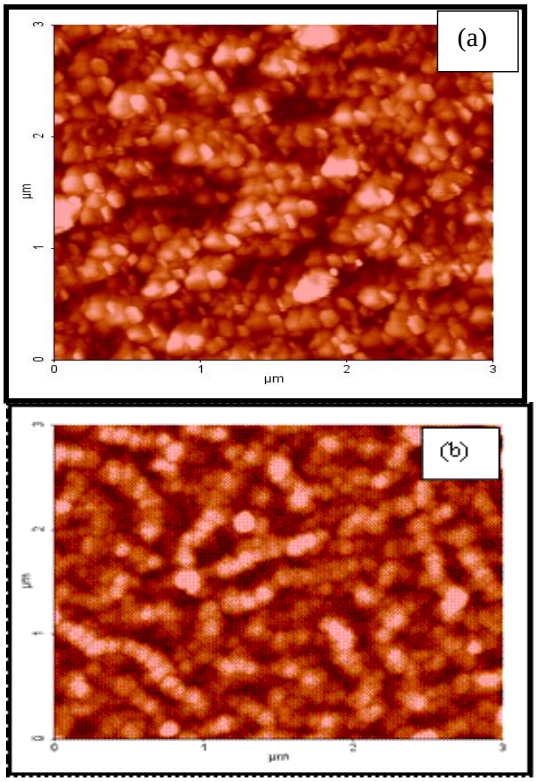

Figure 3. AFM topology of (a) ZnO and (b) Ag/ZnO nanorods films

Table 1. Surface roughness of ZnO and Ag/ZnO nanorods films

Samples	Surface roughness, Ra (nm)
ZnO	4.961
Ag/ZnO	5.225

Figure 4 presents the transmittance spectra of ZnO and Ag/ZnO nanorod films. The average transmission value of ZnO and Ag/ZnO nanorod films is beyond 75 % in the range of visible emission (> 400 nm). It was found that the transmittance value of Ag/ZnO nanorod films was slightly

reduced compared to ZnO nanorod films. This might be caused by the increased scattering caused by pores present in the films (Arunachalam *et al.*, 2017). Moreover, the reduction of transmittance was probably due to high surface roughness of the nanorod arrays as shown for Ag/ZnO nanorod films (Zhang *et al.*, 2010).

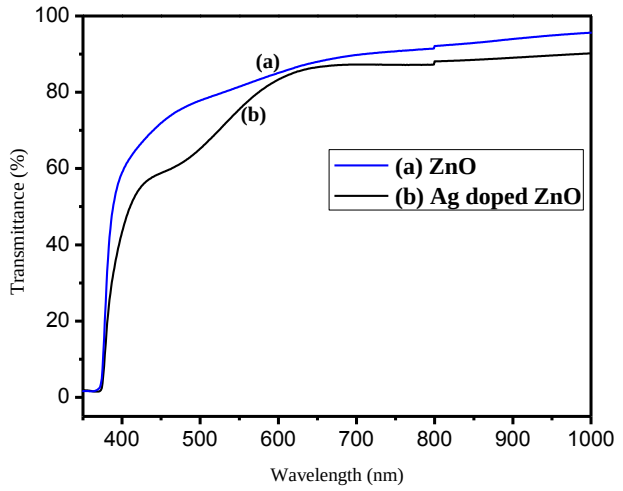

Figure 4. Transmittance spectra of (a) ZnO and (b) Ag/ZnO filmsESEM images of (a) ZnO and (b) Ag/ZnO nanorod films

IV. CONCLUSION

Comparison study have been done on the structural, topological and optical characteristics of ZnO and Ag/ZnO nanorod films on the ZnO coated glass substrates prepared using solution immersion method. Ag/ZnO nanorod films shows the highest peak intensity along (002) plane orientation which indicates the nanorods grown along c-axis. FESEM images shows the ZnO nanorods diameter reduced when Ag was doped into ZnO lattice. Ag/ZnO nanorod films also showed higher surface roughness compared to ZnO nanorod films. The average transmittance also reduced for Ag/ZnO nanorod films compared to ZnO nanorod films. As a conclusion, the properties of ZnO changed when Ag was doped in ZnO. The change in ZnO properties might be suitable for some electronic device applications.

V. ACKNOWLEDGEMENT

The authors gratefully acknowledge support from Universiti Teknologi MARA Pahang, NANO-Electronic Centre, Faculty of Electrical Engineering and NANO-SciTech Centre, Institute of Science, Universiti Teknologi MARA, Shah Alam.

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