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Fabrication of Porous ZnO Thin Films via Ammonium Hydroxide: Effects of Etching Time and Oxidizer on Surface Morphology and Surface Roughness

(Fabrikasi Filem Nipis ZnO Berliang melalui Ammonium Hidroksida: Kesan Masa Punaran dan Pengoksida ke atas Morfologi dan Kekasaran Permukaan)

S.S. Ng*, P.K. Ooi, S. Yaakob, M.J. Abdullah, H. Abu Hassan & Z. Hassan

ABSTRACT

The effects of the etching time and oxidizer on the surface morphology and surface roughness of the porous zinc oxide (ZnO) thin films, which were formed using ammonium hydroxide (NH_4OH) were investigated. The etching time was varied from 1 to 5 min. The oxidizer used was hydrogen peroxide (H_2O_2) solution. The ZnO thin films were obtained using radio- frequency magnetron sputtering on n-type silicon (111) substrate. The thickness of the ZnO thin films was approximately 1.34 μm. The morphology, topography and surface roughness of the porous ZnO were characterized using scanning electron microscope (SEM) and atomic force microscope. The SEM results showed that the surface morphology of the as-grown ZnO film has a leaf-like structure. However, this structure transformed into irregularly shaped pores upon exposure of the ZnO thin films to the etchant solutions. Increased etching time corresponded to increased pore size, which concurrently resulted in the formation of granular ZnO. Finally, it was found that the etching rate increases with the addition of H_2O_2 in the NH_4OH solution.

Keywords: Ammonium hydroxide; hydrogen peroxide; porous ZnO; wet etching

ABSTRAK

Kesan masa punaran dan pengoksida ke atas morfologi dan kekasaran permukaan filem nipis zink oksida (ZnO) berliang yang dihasilkan dengan amonium hidroksida (NH_4OH) telah dikaji. Masa punaran diubah daripada 1 ke 5 min. Pengoksida adalah larutan hidrogen peroksida (H_2O_2). Filem nipis ZnO disediakan dengan menggunakan percikan pemagnetan frekuensi radio atas substrat silikon (111) jenis-n. Ketebalan filem nipis ZnO adalah lebih kurang 1.34 μm. Morfologi, topografi dan kekasaran permukaan ZnO berliang dicirikan dengan menggunakan mikroskop elektron imbasan (SEM) dan mikroskop daya atom. Keputusan SEM menunjukkan bahawa ZnO filem yang disediakan terdiri daripada lapisan struktur seperti dedaun. Walau bagaimanapun, struktur ini bertukar kepada bentuk liang yang tidak teratur apabila filem nipis ZnO terdedah kepada larutan pemunar. Peningkatan masa punaran sejajar dengan peningkatan saiz liang, yang serentak mengakibatkan pembentukan ZnO berbutir. Akhirnya, didapati bahawa kadar punaran meningkat dengan penambahan H_2O_2 dalam larutan NH_4OH.

Kata kunci: Amonium hidroksida; hidrogen peroksida; punaran basah; ZnO berliang

Introduction

In recent years, zinc oxide (ZnO) single crystalline films have drawn significant research interest because of its outstanding properties, such as a direct wide band gap (~3.4 eV), large free exciton-binding energy (~60 meV) and high resistance to radiation damage (Look 2001). Due to its unique properties, ZnO films have many applications, such as in piezoelectric transducers, varistors, transparent conducting films, blue and ultraviolet (UV) light emitters and high-temperature and high-power transistors. A new field of study was created to investigate the unique properties of porous materials, such as a high specific surface area, large pore volume, enhanced chemical and photochemical stability, uniform pore size, superior shape selectivity, and rich surface chemistry (Gür et al. 2010). These characteristics make the porous ZnO a promising material for various applications such as sensors, photovoltaic solar cells and ion-insertion batteries.

To date, two methods, namely, dry etching and wet etching, have been used to prepare porous ZnO (Sun et al. 2007). However, the etch process was dominated by dry etching because of its controllable etching rate (Lee et al. 2001; Na et al. 2005; Sun et al. 2007). Nevertheless, wet etching possesses the advantages of easiness and low equipment cost. Moreover, reports have shown that ZnO films can be etched both in acidic and alkaline solutions. Recently, Sun et al. (2007) showed that ammonium chloride is an appropriate candidate for the formation of porous ZnO due to its controllable and moderate etching rate. Meanwhile, Yoo et al. (2008) have employed oxalic acid and ferric chloride in the etching process. The variation in the etching solutions indicates that a specific

etching solution is yet to be established for the formation of porous ZnO. Hence, we are motivated to explore further the formation of porous ZnO using another kind of etching solution.

In the present work, radio frequency (RF) magnetron-sputtered ZnO films were etched in ammonium hydroxide (NH_4OH) solution. The effects of the etching time and the effects of addition H_2O_2 solution on the surface morphology and roughness of porous ZnO thin films were studied comprehensively.

Experimental Details

Prior to the growth of the ZnO films, n-type silicon (Si) wafers with (111) orientation were cleaned using the cleaning process described by the Radio Corporation of America. ZnO was deposited on the substrate using the A500 Edwards RF magnetron-sputtering unit. The substrates were fixed on a rotating substrate holder at 10 cm above the target. Two ZnO sputtering targets with a diameter of 76.2 mm (purity of >99.99%) were used. The sputter chamber was pumped to a pressure of approximately 5×10^{-5} mbar before introducing high- purity (5N) argon gas. During the process, the chamber pressure was maintained at 2.0×10^{-2} mbar and the RF power was regulated at 200 W. The targets were pre-sputtered for 10 min to remove any possible contaminations. The film was deposited at room temperature for 2 h.

Porous ZnO was prepared by wet etching. The ZnO films were etched using NH_4OH (30%) solely, followed by a mixture of 100 mL NH_4OH and 1 mL H_2O_2 (30%) at various etching times. The surface morphology and structure of the porous ZnO thin films were characterized by scanning electron microscope (SEM, JSM6460LV, Jeol Inc.) and the surface topography was measured by atomic force microscope (AFM, Dimension Edge, Bruker) in tapping mode. The AFM scanning areas were set at 10×10 μm.

Results and Discussion

Surface Morphology of Porous ZnO Thin Films

Figure 1(a) shows the SEM surface morphology of the as-grown ZnO film on n-Si(111) substrate. The image shows that the surface morphology of the ZnO film has a leaf-like structure. However, a large quantity of dislocation was observed on the surface of the ZnO film because of the inhomogeneous growth of granular ZnO on the n-Si (111) surface. A similar morphology was reported previously, although with a less prominent leaf-like structure (Lu et al. 2001). The thickness of the as-grown ZnO film was about 1.34 μm as shown in Figure 1(b).

Figure 2(a) to 2(c) shows the SEM surface morphologies of the porous ZnO, which was etched with NH_4OH at various etching times. The results showed that irregularly shaped pores were formed on the ZnO film surface. At 1 min, the pores initially formed between the edges of the leaf structure, as shown in Figure 2(a). When the etching time was increased to 3 min, the pore sizes increased, as depicted in Figure 2(b). Consequently, the granulation on the ZnO film became more prominent.

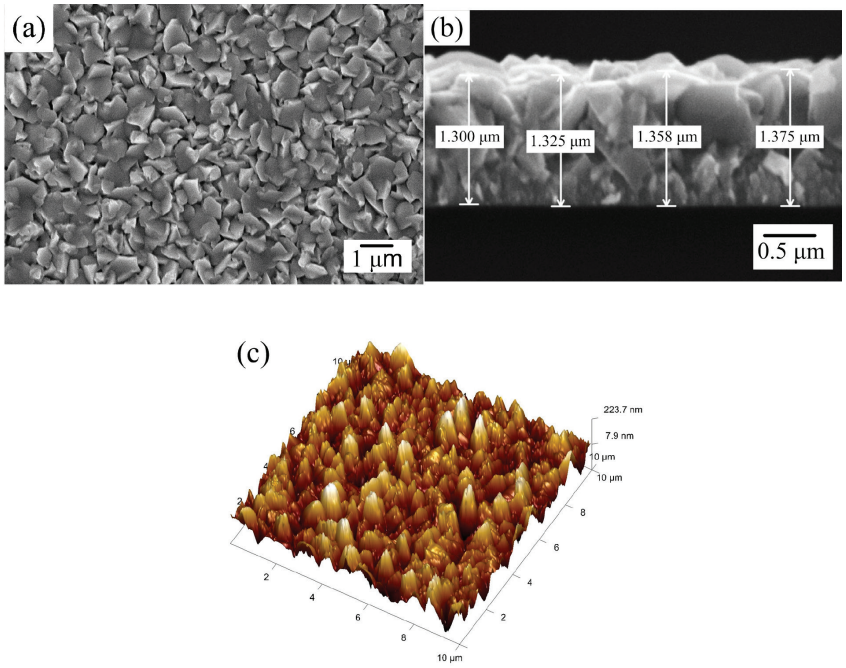

FIGURE 1. Scanning electron microscope (SEM) images of the (a) surface morphology, (b) cross section of the film and (c) atomic force microscope (AFM) topography of as-grown ZnO thin film on n-type Si(111) substrate

However, the grains on the ZnO became smaller and a number of grains were destroyed as the etching process continued to 5 min, as shown in Figure 2(c). Meanwhile, Figure 3(a) to 3(c) shows the SEM cross-sectional images of the porous ZnO layer, which was etched with NH_4OH at various etching times. The thickness of the porous ZnO slightly decreased and became less dense. With a longer etching time, the porosity of the films significantly increased.

The variation in the morphology of the obtained porous ZnO is attributed to the active dissolution of grains ZnO in NH_4OH solution. The etching process is believed to initiate at the defect sites on the ZnO film, namely, the edge of the grains ZnO, as soon as it was exposed to the NH_4OH solution. According to Zhao et al. (2006), the etching operation occurs at the dislocation and boundary. The etching rate at the boundary was faster than that at the grain, as shown in Figure 3. The reaction of ZnO with the NH_4OH solution is described in (1) to (3) (Chang et al. 1992):

$$NH_4OH \rightarrow NH_4^+ + OH^- \quad (1)$$

$$4NH_4^+ + 4H_2O \rightarrow 4NH_3 + 4H_3O^+ \quad (2)$$

$$ZnO + 2H_3O^+ \rightarrow Zn^{2+} + 3H_2O \quad (3)$$

Figure 2(d) to 2(f) shows the SEM images of the surface morphologies of the porous ZnO etched with a mixture of 100 ml NH_4OH and 1 mL H_2O_2 at various etching times. Figure 3(d) to 3(f) shows the SEM cross-sectional images of the corresponding porous ZnO samples. Figure 2(d) shows that small pores were formed on the ZnO film at 1 min etching time. Increased etching time correspond with the formation of larger pores, as shown in Figure 2(e). A longer etching time of 5 min caused the grains on the ZnO to dissolve and become smaller, as shown in Figure 2(f).

In general, the outcomes of etching with the addition of an oxidizer are similar to that of the NH_4OH solution alone but at a faster etching rate. The increment in the etching rate is attributed to the presence of H_2O_2 in the etchant solution, which forms excess oxygen-related defects (Tsai et al. 2010). H_2O_2 acts as oxidizer, which allows the formation of an oxide layer on the ZnO film (Chang et al. 2001). According to Jo et al. (2005), the etching of the O-terminated surface was rapid and uniform, whereas the etching of the Zn-terminated (0001) surface was slow and non-uniform. Therefore, the presence of H_2O_2 in NH_4OH creates more sites for the dissolution of ZnO grain. In addition, H_2O_2 treatment is fairly effective in removing deep-level defects, such as Zn interstitials and Zn or oxygen vacancies near the ZnO surface (Kim et al. 2005).

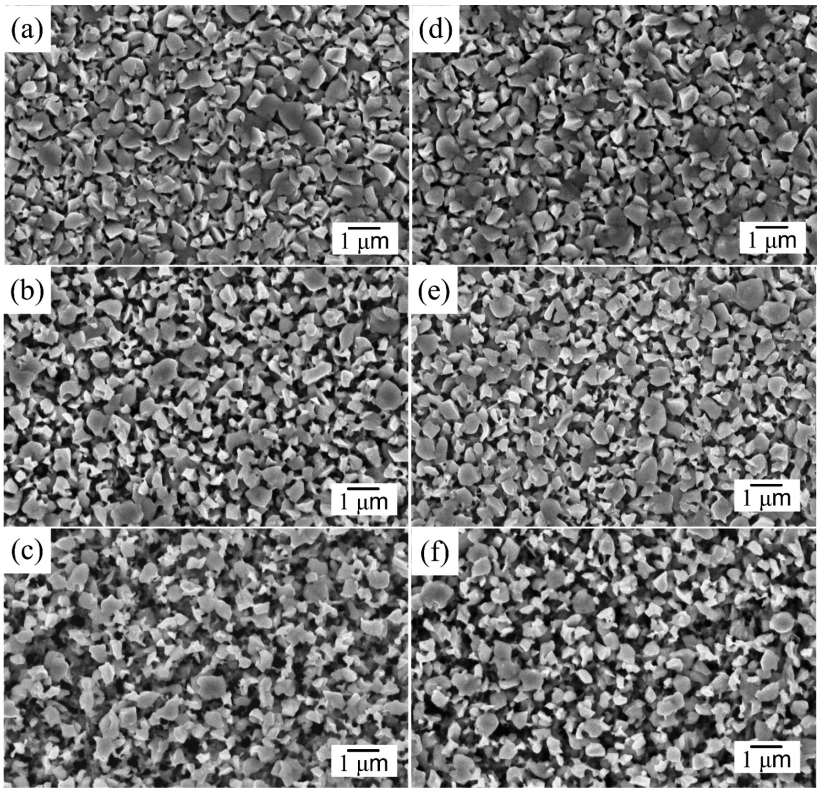

FIGURE 2. SEM images of the porous ZnO surface morphologies prepared using NH_4OH solution at (a) 1, (b) 3 and (c) 5 min etching times and using a mixture of 100 mL NH_4OH and 1 mL H_2O_2 at (d) 1, (e) 3 and (f) 5 min etching times

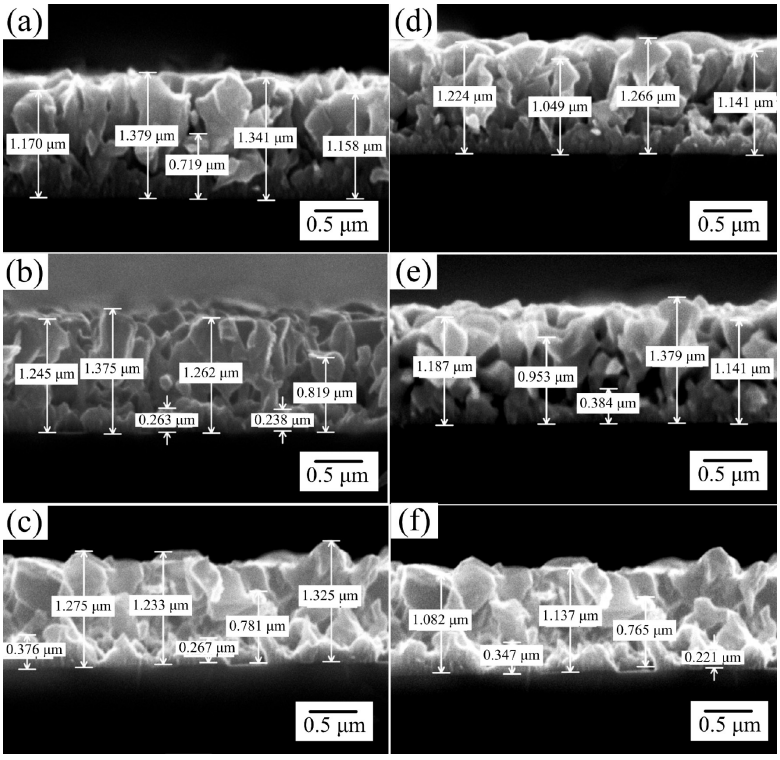

FIGURE 3. SEM cross-sectional images of porous ZnO prepared using NH_4OH solution at (a) 1, (b) 3 and (c) 5 min etching times and using a mixture of 100 mL NH_4OH and 1 mL H_2O_2 at (d) 1, (e) 3 and (f) 5 min etching times

SURFACE TOPOGRAPHY OF POROUS ZNO THIN FILMS

The AFM topography of the as-grown ZnO film and the porous ZnO films etched with NH_4OH solution at different etching times were shown in Figures 1(c), 4(a), 4(b) and 4(c), respectively. The as-grown ZnO consisted of large hillocks in uniform sizes and few voids (valleys between hillocks), as depicted in Figure 1(a). These hillocks represent the granular ZnO. At 1 min etching of the ZnO film, the hillocks reduce in size and the number of voids increased, as shown in Figure 4(a). These effects were more evident as the etching time increased to 3 and 5 min (Figures 4(b) and 4(c), respectively). Similar findings were also found when H_2O_2 was added to the NH_4OH solution, as shown in Figures 4(d) to 4(f). However, in this condition, the hillocks were smaller compared with the results of the dissolution in NH_4OH alone, which resulted in more voids. The above observations were confirmed by the plot of root mean square (RMS) surface roughness versus etching time, as shown in Figure 5. The results indicated that the RMS surface roughness increased with the increase of etching time in NH_4OH alone. On the other hand, with the addition of H_2O_2, the RMS surface roughness increased significantly as the etching time increased from 1 to 5 min. In comparison, the surface roughness of the unetched ZnO is 58.8 nm. The topography and surface roughness of the obtained porous ZnO were attributed to the distribution of the dissolved area and the rate of dissolution. Generally, a longer etching time tends to increase the area to be dissolved. Subsequently, the surface of the porous ZnO film became rougher with increasing etching time. This result is in agreement with the results obtained by Sun et al. (2007) by etching ZnO films using NH_4Cl (5%) alone at longer etching times (3 to 30 min).

Based on Figure 5, the RMS surface roughness of the porous ZnO thin films was higher under the combined action of NH_4OH and H_2O_2 compared with that under NH_4OH alone. This result indicated a faster etch rate with the addition of H_2O_2 to the NH_4OH solution.

CONCLUSION

In summary, the surface characteristics of porous ZnO thin films fabricated at various etching times using NH_4OH and a mixture of NH_4OH and H_2O_2 were investigated. The leaf-like structure of the as-grown ZnO film became irregularly shaped pores following etching treatment. With increased etching time, more areas of granular ZnO were dissolved, resulting in a larger pore size and smaller granules. Furthermore, a longer etching time increased the surface roughness of porous ZnO. Similar observations on the morphology and surface roughness were seen when the ZnO thin films were etched with a mixture of 100 mL NH_4OH and 1 mL H_2O_2. However, the surface roughness was higher under etching with NH_4OH and H_2O_2 solutions. This result showed that adding an oxidizer into the etching solution results in a faster etching rate.

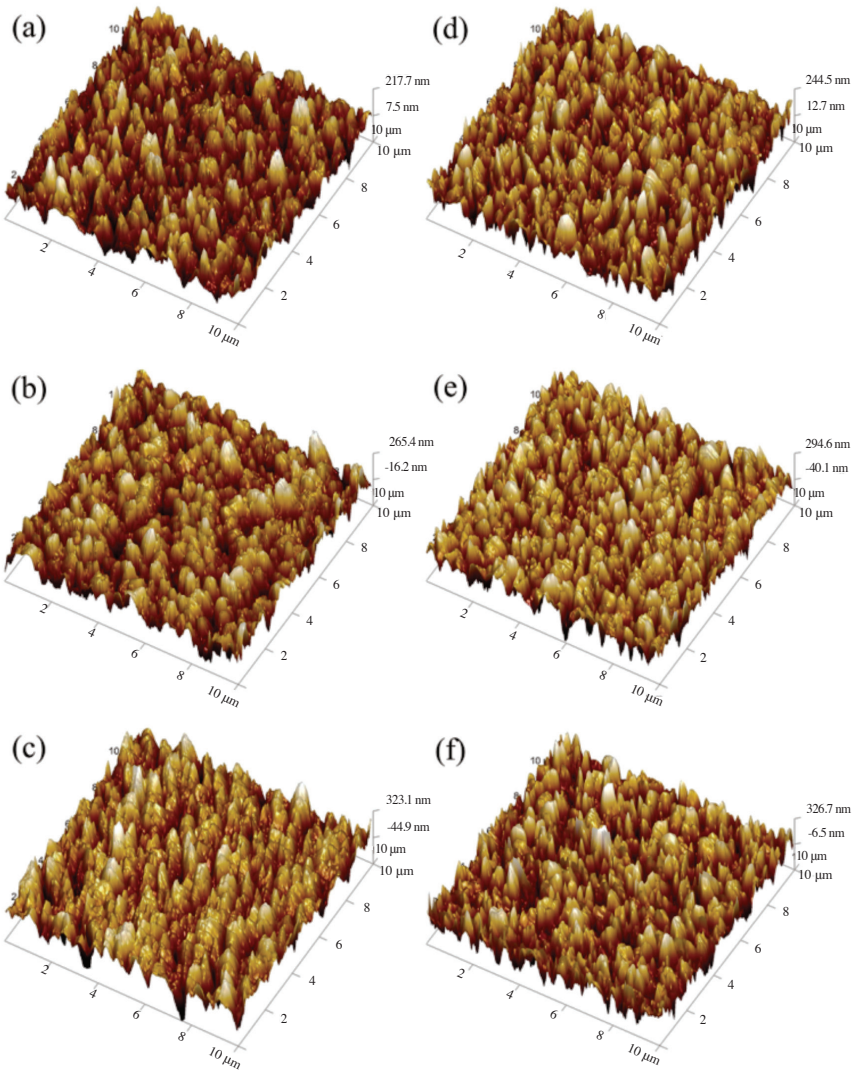

FIGURE 4. AFM topographic images of the porous ZnO thin films prepared using NH_4OH solution at (a) 1, (b) 3 and (c) 5 min etching times and AFM topographic images of porous ZnO prepared using a mixture of 100 mL NH_4OH and 1 mL H_2O_2 at (d) 1, (e) 3 and (f) 5 min etching times

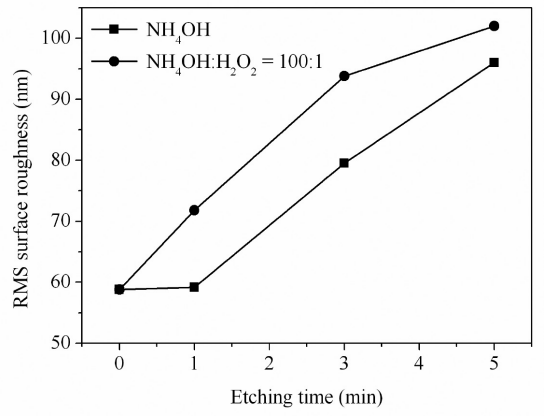

FIGURE 5. Root mean square surface roughness of porous ZnO thin films prepared using NH_4OH solution and a mixture of 100 mL NH_4OH and 1 mL H_2O_2 at various etching times

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Nano-Optoelectronics Research and Technology Laboratory
School of Physics, Universiti Sains Malaysia
11800, Penang
Malaysia

*Corresponding author; email: shashiong@yahoo.com

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