Effects of the Nitric Acid Concentrations on the Etching Process, Structural and Optical Properties of Porous Zinc Oxide Thin Films

(Kesan Kepekatan Asid Nitrik Terhadap Proses Pemunaran, Ciri-ciri Struktur dan Optik Filem Nipis Zink Oksida Berliang)

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ABSTRACT

The present study reports on the fabrication of porous zinc oxide by wet chemical etching. ZnO thin films were deposited via radio-frequency magnetron sputtering on p-type silicon with (111) preferred orientation. The etchants used in the present work were 0.1% and 1.0% nitric acid (HNO_3) solutions. ZnO were etched at various times and were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and photoluminescence (PL) spectroscopy to allow the examination of their structural and optical properties. The XRD results revealed that the intensity of ZnO(002) decreased when the thin films were etched in varying HNO_3 concentrations over different periods of time. The above observation is attributed to the dissolution of the ZnO(002). The SEM images showed that the thickness of the ZnO layers decreased over the etching time, which resulted from the isotropic etching by the HNO_3 solution. The PL emission intensity initially increased with increasing etching time. However, with further etching of the samples, the PL spectra showed a decreasing trend in intensity as a result of the decrease in the surface-to-volume ratio. All results lead to the conclusion that 1.0% HNO_3 has the capability to change the ZnO surface significantly.

Keywords: Photoluminescence spectroscopy; scanning electron microscope; wet chemical etching; X-ray diffraction; zinc oxide

ABSTRAK

Penyelidikan ini melaporkan fabrikasi struktur zink oksida berliang melalui proses punaran basah. Filem nipis ZnO dienapkan ke atas substrat silikon (111). Larutan pemunar yang digunakan dalam kajian ini adalah larutan asid nitrik (HNO_3) yang berkepekatan 0.1% dan 1.0%. Filem nipis ZnO dipunarkan selama beberapa jangka waktu yang ditetapkan dan ciri-ciri struktur dan optik dikaji dengan menggunakan pembelauan sinar-X (XRD), mikroskop elektron imbasan (SEM) dan spektroskopi fotoluminesen (PL). Keputusan XRD menunjukkan bahawa keamatan bagi puncak ZnO(002) menurun selepas filem nipis ZnO dipunarkan dalam larutan yang berkepekatan berlainan untuk jangka waktu yang berlainan. Pemerhatian ini adalah disebabkan penguraian ZnO(002) semasa proses punaran filem nipis. Imej-imej daripada SEM pula menunjukkan ketebalan filem nipis ZnO berkurangan dengan peningkatan masa punaran. Pemerhatian ini adalah disebabkan proses punaran isotropik oleh larutan HNO_3. Manakala spektrum PL pada peringkat awal punaran menunjukkan peningkatan keamatan puncak apabila masa punaran meningkat. Namun begitu, proses punaran yang berterusan menunjukkan keamatan puncak PL mula menunjukkan trend menurun dan fenomena ini adalah disebabkan penurunan nisbah luas permukaan terhadap isi padu dalam filem nipis ZnO.

Kata kunci: Mikroskop elektron pengimbas; pembelauan sinar-X; punaran basah; spektroskopi fotoluminesen, zink oksida

INTRODUCTION

Wide-bandgap zinc oxide is a popular material because of its high exciton binding energy, which facilitates a lasing action based on exciton recombination above room temperature (Ozgur et al. 2005). Although research on ZnO started decades ago, the use of ZnO has gained a substantial amount of renewed interest in recent years. This interest stems from the availability of high-quality ZnO substrates owing to the technological advancements and reports on the successful deposition of the p-type conduction in ZnO films. This process allows the wider application of ZnO in the research and development of devices (Chang et al. 2011).

ZnO has been used in numerous areas of technological development, such as biotechnology (Zhao et al. 2010), ultraviolet (UV) applications (Shao et al. 2010), opto-electronics (Sood et al. 2011), electronics and photonics (Yi et al. 2005) because of its potential for a vast array of uses. The fabrication of porous and nanostructured ZnO is another topic of interest because of the capability of this material to alter ZnO optical properties that are suitable for device fabrication, especially for optoelectronic devices (Dubey & Gautam 2009). On the other hand, the research community has taken a great interest in porous ZnO for its large internal surface area and improved mass

transportation that are attributed to the size-controlled macropores (Sumida et al. 2001).

Numerous studies on nanostructures and porous ZnO fabrication focus on such methods as electrochemical deposition (Kim et al. 2010), electrochemical anodization (Basu et al. 2008), unbalanced magnetron sputtering (Sharma et al. 2002) and wet chemical etching (Yoo et al. 2008). Wet chemical etching, specifically known as strain etching is a reliable method for producing porous materials. This method involves a few controlling parameters and is relatively cost-efficient. The study conducted by Yoo et al. (2008) on the etching behavior of two types of etchants (ferric chloride and oxalic acid) is a useful reference. Instead of focusing on the relationship between the etchant pH and concentration and the etching characteristic as reported by Yoo et al. (2008), the present study examined the effects of etchant concentrations on the structural and optical properties of ZnO thin films. Unlike the work by Yoo et al. (2008), the current study used another type of etchant, nitric acid (HNO_3), as the etching medium. Cross-sectional imaging and photoluminescence (PL) were also employed to study how the etchant reacts to the ZnO thin films, as well as to determine the effects of etchant concentrations on the PL emission of ZnO thin films. Such characterizations were not discussed in the study by Yoo et al. (2008). Besides that, a study on the fabrication of porous ZnO via 0.5% HNO_3 wet chemical etching was also carried out (Ang et al. 2011). The main difference between both of this work is the use of 2 relatively extreme concentration of acid solution (0.1% and 1.0% despite of only 0.5% in our previous study. The purpose to employ both acid concentrations was to investigate the effect of high and low concentration on the etching process of HNO_3 solution on ZnO thin films as well as the optical and structural properties of the etched products (porous ZnO thin films).

In the present study, a set of ZnO thin films were deposited on the p-type silicon substrates with (111) preferred orientation [Si(111)] via the radio frequency (RF) magnetron sputtering method. Characterizations of the surface morphology and the average thickness of the ZnO thin films were estimated by scanning electron microscopy (SEM). Nondestructive characterization methods, such as X-ray diffraction (XRD) and PL spectroscopy were utilized to investigate the characteristics of the samples in depth.

EXPERIMENTAL DETAILS

An Edwards Auto 500 RF sputtering system equipped with a QC Scientific Precision chiller was employed to sputter ZnO layers onto p-Si(111). Prior to ZnO sputtering, the p-Si(111) substrates underwent Radio Corporation of America procedures. Two ZnO sputtering targets with a purity of 99.99% and a diameter of 76.2 mm were placed approximately 100 mm away from the Si substrate in the sputter chamber. Prior to the pre-sputtering process, the sputter chamber was vacuumed until the chamber

pressure reached 5×10^{-5} mbar. Subsequently, high-purity (5N) Argon gas was introduced into the chamber through a mass flow controller until the chamber pressure reached 2.0×10^{-2} mbar. The ZnO thin films were deposited with the RF power of 200 W for 2 h. The ZnO deposited on the Si wafers measured about 1.0 μm thick using SEM cross-section measurements.

The deposited ZnO samples were cut into 1 cm × 1 cm pieces before the etching process. In the current study, HNO_3 with concentrations of 0.1% and 1% were used. The samples were immersed in etchants with various etching times, as shown in Table 1. After the etching process, the samples were rinsed with distilled water and dried under nitrogen gas flow to remove any chemical residue on the sample surface.

TABLE 1. Etching parameters

HNO_3 concentration	Etching time (s)		
0.1%	60	120	180
1.0%	15	20	25

The prepared porous ZnO samples were characterized by XRD, SEM and PL spectroscopy to facilitate the examination of their structural properties, surface-morphological and cross-sectional structure and optical properties, respectively. All XRD measurements were conducted using the PANalytical X'pert PRO MRD system comprising $Cu_{K\alpha1}$ and $Cu_{K\alpha2}$ X-ray sources with wavelengths of 1.5406 and 1.5444 Å, respectively. The XRD measurement was performed in 2theta-omega (2θ-ω) scan mode, also known as phase analysis (PA). In this scan mode, the XRD-PA measurements were obtained with the scan in the range of 30° to 40°, in which the axes of omega (ω) and 2theta (2θ) are moved in a coupled manner, such that only the diffracted beams from the crystalline planes that are parallel to the sample surface are detected. The XRD results obtained were analyzed using the X'pert PRO HighScore software to obtain the crystalline details of the samples. For SEM characterization, the images of the samples were obtained using a JSM-6460/ LV (JEOL, Inc.) SEM. In the SEM imaging, the surface morphological images of the samples were taken at 10000 × magnification with an acceleration voltage of 10 kV. The samples were then divided into two to obtain cross sectional images at 20000 × to 30000 × magnification at the same acceleration voltage.

The optical properties of the samples were characterized by PL spectroscopy. The PL was measured using a Jobin Yvon LabRAM HR 800 UV system. A Helium-Cadmium laser source with a wavelength of 325 nm was also used. The samples were scanned in the range of 330 nm to 450 nm to obtain a PL emmision peak that corresponds to ZnO.

RESULTS AND DISCUSSION

This section presents the characterization results for the as-grown and etched ZnO thin films. For clarity, the results are discussed progressively in several parts. The first presents a detailed discussion of the analysis of the XRD spectra of the ZnO sample. Next, the SEM images, including the surface morphological and cross-sectional images will be discussed in detail while the etching behavior and mechanism of HNO$_3$ are presented after the SEM characterization. Finally, the optical properties of the porous ZnO characterized by PL spectroscopy will be discussed in the last part of the results and discussion section.

X-RAY DIFFRACTION CHARACTERIZATION

Figure 1 shows the XRD spectra of the as-grown and etched ZnO thin film deposited on p-Si(111). An intense peak corresponding to the ZnO(002) can be clearly observed at 34.3° for all samples. This peak indicates that the ZnO thin films used in the present study originated from the wurtzite crystal structure. The dominant ZnO(002) peak in the XRD spectra also indicates that the ZnO thin film used in the present study had the preferred orientation along the (002) plane. Apart from the ZnO(002) peak, the minor peak that corresponds to ZnO(101) (at approximately 36.08°) was also detected.

Figure 1 shows that the intensity of ZnO(002) decreased as the thin films were etched in different HNO$_3$ concentrations over different periods of time. The decrease in the intensity of the diffraction peak is attributed to the dissolution of ZnO(002), which decreased the thin films thickness with increasing etching time, as discussed in SEM characterization section (Figure 3). The degree of crystallinity of the thin films after the etching process may also affect the intensity of the diffraction peak. A sudden decrease in the intensity of ZnO(002) for the ZnO thin films etched by 0.1% HNO$_3$ solution for 120 s was observed. However, the main reason for the sudden decrease in peak intensity remains unidentified. Compared with the as-grown ZnO thin film, the intensity of the diffraction peak originating from the ZnO(101) decreased as the samples were etched in different concentrations of HNO$_3$ solution. The decrease in ZnO(101) peak intensity is attributed to the dissolution of the ZnO with (101) orientation during the etching process, whereby the growth of the ZnO with (101) orientation on the thin films was found to be minimal.

SEM CHARACTERIZATION

Figure 2 shows the surface morphological images of as-grown and porous ZnO thin films. Figure 2(a) demonstrates that the as-grown ZnO sample comprised leaf-like particle shapes. When the ZnO samples were etched in 0.1% and 1.0% HNO$_3$ solutions, the etchant had the tendency to attack the thin area or the sharp area on the leaf-like ZnO particle, forming grains and voids that are parts of a porous structure. However, the surface features of the samples varied because of the differences in etchant concentration and etching time.

For the ZnO samples etched in 0.1% HNO$_3$ (Figure 2(b) to 2(d)), voids started to develop when the ZnO thin films were etched for 60 s (Figure 2(b)). However, as the etching time increased to 120 and 180 s, respectively, a slight change on the sample surface was observed. This change may be attributed to the weak concentration of HNO$_3$, which limits the further development of the porous surface on the ZnO thin films. Most of the voids formed on the sample surface are shallow voids. Only small portions of dark spots representing the formation of deep voids were observed (Figure 2(b) to 2(d)). Isotropic etching is believed to occur during the etching process, during which the occurrence of etching is non-directional and non-selective. The capability of the etchant to etch the ZnO layer downward to the substrate is hindered by the low chemical concentration. Likewise, under the isotropic etching effect, the ZnO layer thickness will decrease with the etching time (Figure 3). Subsequently, this decrease in the ZnO layer thickness contributes to the formation of shallow voids. The effects of higher etchant concentration
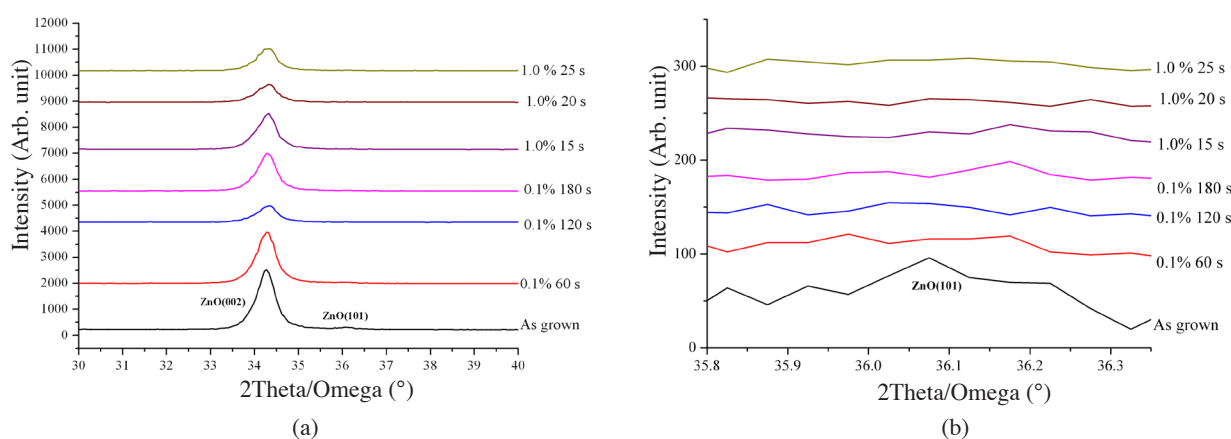

(a)

(b)

FIGURE 1. XRD patterns of as-grown ZnO and ZnO thin films etched in 0.1% and 1.0% HNO$_3$ solutions
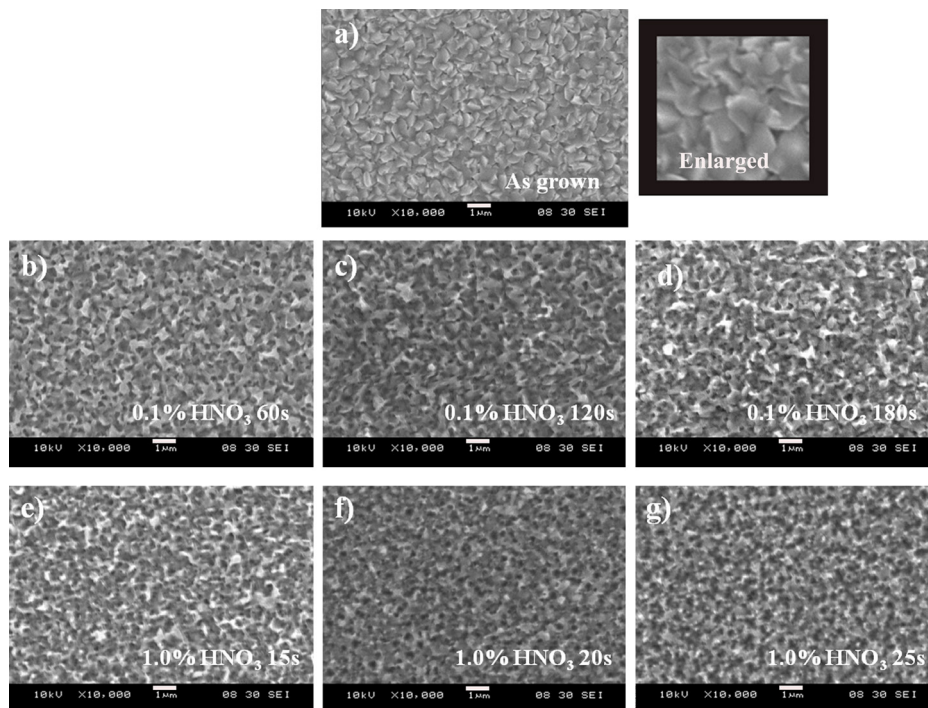
FIGURE 2. Surface morphology of as-grown ZnO and ZnO thin films etched
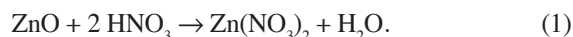in 0.1% and 1.0% HNO$_3$ solutions

on the surface morphology of ZnO layers were observed by immersing the ZnO samples in the 1.0% HNO$_3$ solution for 15, 20 and 25 s. The SEM images in Figure 2(e) to 2(g) reveal that the significant changes in the surface morphology occurred in the samples with a greater number of dark spots. This finding indicates that the fast etching characteristic of 1.0% HNO$_3$ enables the etchant to 'drill' the sample downward to the substrate within a shorter time and increases the number of the deep voids in the sample compared with 0.1% HNO$_3$. When the etching time reached 25 s, the ZnO grains became smaller and the number of dark spots increased. This phenomenon is attributed to the etching of the side wall of the porous structure, aside from the etching toward the substrate.

As shown in Figure 3(a), the thicknesses of the as-grown ZnO layers are even throughout the substrate, suggesting the consistency of the RF sputtering of the ZnO layer on the substrates. Figure 3 also shows that the average thickness of the ZnO thin films decreased over time when etched in 0.1% and 1.0% HNO$_3$ solutions. This observation proves earlier findings that an isotropic etching mechanism occurs with the use of HNO$_3$ etchants. The thickness of the ZnO thin films were also observed to decrease consistently when the films were etched in various concentrations of HNO$_3$ solution. In addition, when the samples were etched in 0.1% HNO$_3$ solution, the valleys (cross-sectional views of voids) formed were shallow. Moreover, only a small portion of the deep valley can be viewed on the ZnO layers. As a higher concentration of etchant was applied, the valley structures on the porous ZnO became deeper and more obvious. For the ZnO samples etched in 1.0% HNO$_3$ solution, a tremendous increase in the deep valleys

was observed. Likewise, the side wall of the valleys became trimmer, i.e. similar to standing sharp pillars. The formation of a pillar-like side wall increased the depth of the voids in the ZnO layers and at the same time, expanded the exposed surface of ZnO. This observation indicates a significant change in the ZnO surface when 1.0% HNO$_3$ solution is employed. From the SEM characterizations, higher concentrations of HNO$_3$ allow for more portions of deep voids in the porous structure.

ETCHING BEHAVIOUR AND MECHANISM OF HNO$_3$ ON ZNO THIN FILMS

The reaction of ZnO thin films with HNO$_3$ solution in the current study can be described by the following equation:

$$ZnO + 2\,HNO_3 \rightarrow Zn(NO_3)_2 + H_2O. \tag{1}$$

Generally, the HNO$_3$ molecules separate to form H$^+$ and NO$_3^-$ ions when dissolved in water. As the acid reacts with the ZnO surface, Zn^{2+} and NO$_3^-$ react to form a Zn(NO$_3$)$_2$ ionic bonding molecule, whereas the remaining O^{2-} ions will react with the H$^+$ from HNO$_3$ to form water. During this process, Zn^{2+} and O^{2-} leave the ZnO surface, thus forming voids.

As indicated by the SEM micrographs, the surface morphologies of the film are significantly affected by the etchant concentration. The surface morphology of the ZnO thin films etched in 0.1% HNO$_3$ differed from those etched in 1.0% HNO$_3$, in which the voids and valleys formed in the cross-sectional view of the thin films. The Si substrate will have the tendency to contain a higher degree of dislocation because of the relatively large lattice mismatch (Ozgur et
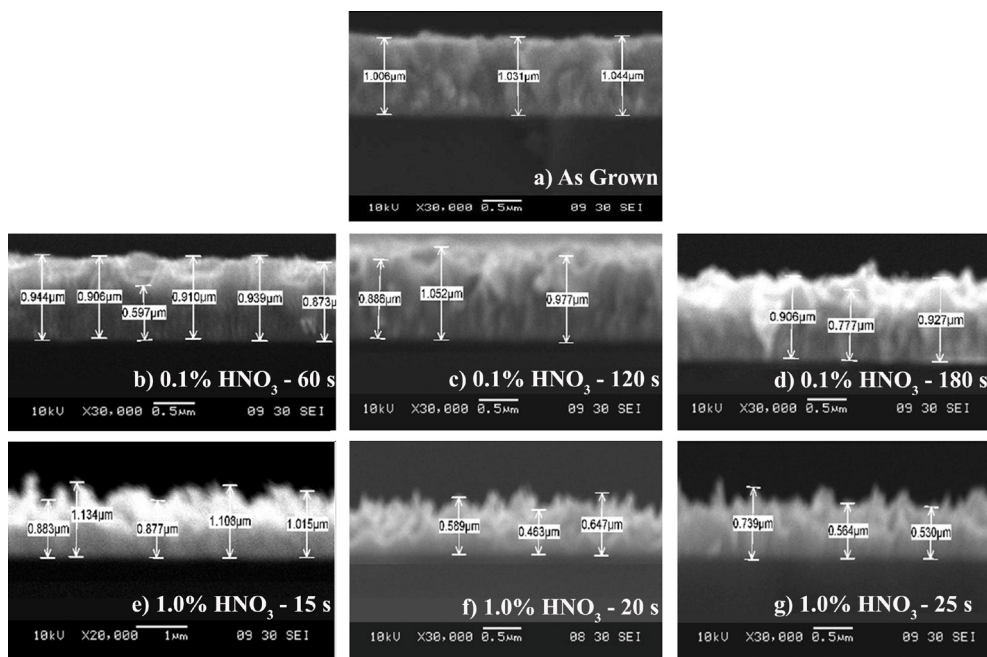
FIGURE 3. Cross-sectional SEM micrographs of as-grown ZnO and ZnO
thin films etched in 0.1% and 1.0% HNO$_3$ solutions

al. 2005) between ZnO and Si substrate. Consequently, the etching operation occurring at the dislocation and the boundary is preferable (Zhao et al. 2006). Hence, the etching rate along the boundary is faster than that in the grain.

All the ZnO thin films showed a degree of surface morphology change after undergoing wet chemical etching. The use of HNO$_3$ tends to reduce the average thickness of the ZnO thin film layer because of the production of porous structures. Hence, a compromise must be found between these two subjects so as to produce a porous ZnO while providing sufficient average thin film thickness.

PL CHARACTERIZATION

Figure 4 shows the PL spectra of the as-grown ZnO and ZnO samples etched in various concentrations of HNO$_3$ solution. The peaks shown in Figure 4(a) to 4(b) are the PL band-edge luminescence peaks of ZnO located at approximately 380 nm. As seen in this figure, all samples etched in the 0.1% and 1.0% HNO$_3$ solutions exhibited a similar behavior with increasing etching time. The intensity of the PL spectra initially increased with increasing etching time increases because of the increase in the surface-to-volume ratio of the ZnO layers. However, as the samples were etched over longer periods of time, the intensity of the PL spectra started to decrease. This behavior is attributed to the decrease in the surface-to-volume ratio of the ZnO layers that resulted in the decrease of the PL band-edge intensity (Shim et al. 2002). However, for the samples etched in 1.0% HNO$_3$, there is only little decrease in PL intensity for the samples etched for 25 s compared with the ZnO layer etched for 20 s. This phenomenon shows that the surface-to-volume ratio decreases slightly despite the decreased in the overall

thickness of the ZnO layers. This condition results from the formation of a greater number of deep voids in the ZnO layers compared with those in the other two samples. Thus, only a slight decrease in the surface-to-volume ratio was observed in the samples. Notably, the ZnO sample etched in 1.0% HNO$_3$ solution exhibited a higher PL intensity compared with the samples etched in 0.1% HNO$_3$. This finding indicates a higher surface-to-volume ratio for the porous structure that has been successfully synthesized, thus confirming the capability of the 1.0% HNO$_3$ solution to facilitate significant changes on the ZnO surface compared with other concentrations of HNO$_3$ solution.

CONCLUSION

The porous ZnO thin films were fabricated via wet chemical etching in 0.1% and 1.0% HNO$_3$. The XRD spectra revealed that the ZnO samples used in the current study have the wurtzite structure, with the ZnO(002) preferred orientation. As the ZnO layers were etched, the intensity levels of ZnO(002) and ZnO(101) were found to decrease. This behavior is attributed to the dissolution of (002) and (101) during the etching process. The surface morphological and cross-sectional SEM images showed that the isotropic etching mechanism during the etching process facilitated changes in the surface morphology of the ZnO samples. The PL characterization indicated that the samples etched in 0.1% and 1.0% HNO$_3$ solutions exhibited a similar behavior; i.e. the intensity of PL peaks initially increased with increasing etching time, but subsequently decreased when the samples were etched for an extended period of time. This behavior results from the decrease in
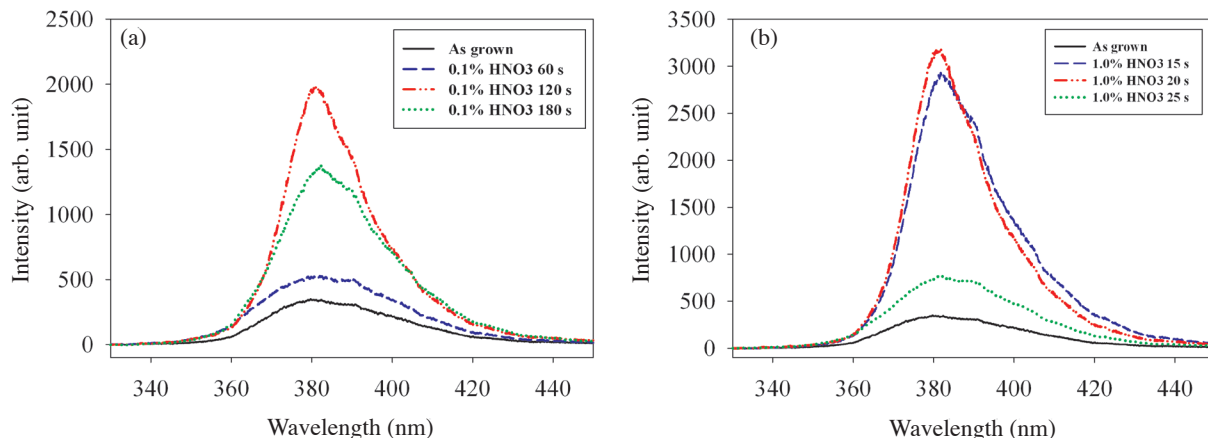
FIGURE 4. PL spectra of ZnO thin films etched in 0.1% and 1.0% of HNO$_3$ solutions

the surface-to-volume ratio attributed to the longer etching time. All results showed that 1.0% HNO$_3$ can significantly change the surface morphology as well as increase the surface-to-volume ratio of ZnO thin films.

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