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Wet chemical etching of ZnO film using aqueous acidic salt

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Abstract

$FeCl_3 \cdot 6H_2O$ was used in the wet etching of single crystalline ZnO films. The method has great effects on the suppression of the “W” shaped etching profile usually observed when ZnO films were etched by acid. “U” shaped profile and smooth surface morphology were obtained under a wide range of etching rate, as confirmed by stylus profiler and scanning electron microscopy. The ferric deposition detected by the X-ray photoelectron spectra is speculated to be responsible for the formation of suitable solution hydromechanical parameters. The deposited layers can be removed easily by ultrasonic treatment, which makes the process easily controllable. These results show that this method is promising for processing ZnO-based optoelectronic devices.

Keywords: Etching; X-ray photoelectron spectroscopy; Depth profiling; Zinc oxide

1. Introduction

ZnO single crystalline films have attracted great attention these years, mainly because of its direct wide band gap (~3.4 eV), large free exciton binding energy (~60 meV), and consequently its promising applications in short wavelength optoelectronic devices [1–3]. In the fabrication of these devices, such as light-emitting diode (LED) and laser diode, mesa etching method plays an important role. The possibility of wet chemical etching is a fundamental advantage of ZnO over another wide band gap semiconductor GaN.

Various etchants such as HCl, HNO_3, H_3PO_4, or H_3PO_4/HAc/H_2O have been used for the wet chemical etching of ZnO [4–6]. In their studies, a special kind of acid was used as etchant. The mechanism is that the reaction of zinc oxide in acid solution produces zinc salt dissolved in water to make the etched pattern. However, the “W” shaped etching profile observed in the acid etching process [4] makes the device have an open circuit, which hinders the acid etchants to be practically used in the ZnO device fabrications. So far, no comprehensive study has been carried out to solve this problem.

In this study, a novel etchant, $FeCl_3 \cdot 6H_2O$, was used in ZnO etching process. Under a wide range of etching rate, “U” shaped etching profile and smooth etching surface morphology were obtained readily. This etching effect results from ferric deposition produced during the etching process which plays a key role in the formation of suitable solution hydromechanical parameters. After several cycles of ultrasonic treatment, the deposits can be removed completely. This method is expected to be used in fabrication of ZnO-based devices.

2. Experimental details

Wurtzite single crystalline ZnO thin films used in this study were grown on c-plane sapphire substrates using thin AlN layer as buffer by radio-frequency plasma-assisted molecular-beam epitaxy. Details of sample preparation can be found in our previously published work [7], except for that the upper part of the ZnO epilayer was Ga-doped. The thickness of the ZnO:Ga films was about 1 μm. Hall Effect measurements (HL5200, BIO-RAD) were performed at room temperature, and showed that the films have a bulk electron concentration of $\sim 10^{19}$ cm^{-3}, and an electron mobility of ~40 cm^2/Vs.

Photoresist etching mask was made by standard photolithography. About 1 μm thick resist (MEGAPOSIT® S9918M PHOTO RESIST, Shipley Company) was masked on the ZnO

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film surface by spin coating. After pre-baking at 95 °C for 1 min, these samples were exposed to 365 nm ultraviolet light for 25 s. Submicron Ultraviolet Mask Aligner (MA6, Karl Süss Company, Germany) was employed in this step. After being developed in MICROPOSIT® 351 developer (ROHM AND HAAS electronic materials company) and rinsed with deionized water, the patterned samples were obtained.

$FeCl_3\cdot 6H_2O$, a typical aqueous acidic salt, which was reported in MgO crystal etching [8], was used to etch these patterned ZnO samples. 0.8 mmol $FeCl_3\cdot 6H_2O$ was dissolved in 100 mL water at room temperature. The ZnO films were etched in the acidic salt solution for 1 min with persistent stirring. For comparison, hydrochloric acid (HCl) was also used as etchant. 0.4% HCl solution was prepared to etch the ZnO thin film.

Etching profile was characterized by Dektak 8 stylus profiler (DI, Veeco Metrology Group). After removing the mask, scanning electron microscopy (SEM) (XL30 S-FEG, FEI) was used to examine the surface morphology using an accelerating voltage of 5.00 kV. The surface stoichiometry was measured by X-ray photoelectron spectroscopy (XPS). The XPS spectrometer (MKII, VG, Scientific Ltd) includes a hemispherical analyzer (VG-MARK II). Its background pressure is better than 1.0×10^{-10} Torr. All spectra studied here were corrected by refining C_{1s} core level.

3. Results and discussion

Fig. 1(a) shows a typical etching profile of the ZnO film using hydrochloric acid (HCl) as etchant. A “W” etching profile is observed, which results from the faster etching rate near the mask edge than that in the center. This “W” shaped profile was also observed previously [4]. Such kind of etching profile will deteriorate device performance. For instance, the disconnection between the n-type region and p-type region will occur if there is “W” shaped etching profile in LED structure as illustrated in Fig. 1(b), which shows the schematic drawing of a LED structure with “W” shaped etching profile.

The etching profile is improved greatly when $FeCl_3\cdot 6H_2O$ is used. “U” shaped profile is obtained on the etched ZnO film (see Fig. 1(c)). The sample shows a smooth surface and sharp etching step as shown by the SEM image (Fig. 1(d)). The smooth surface morphology in the etched area indicates that the etching rate is almost homogeneous over the entire sample surface.

Fig. 2 shows the etching rate as a function of $FeCl_3\cdot 6H_2O$ concentration. Under a wide range of etchant concentration, the etching rate shows almost linear behavior, and the slope is about 32 nm/min mM. It should be noticed that the etching rate was measured from the profiler data. Considering that the $FeCl_3$ solution does not react with the photoresist S9918 which was

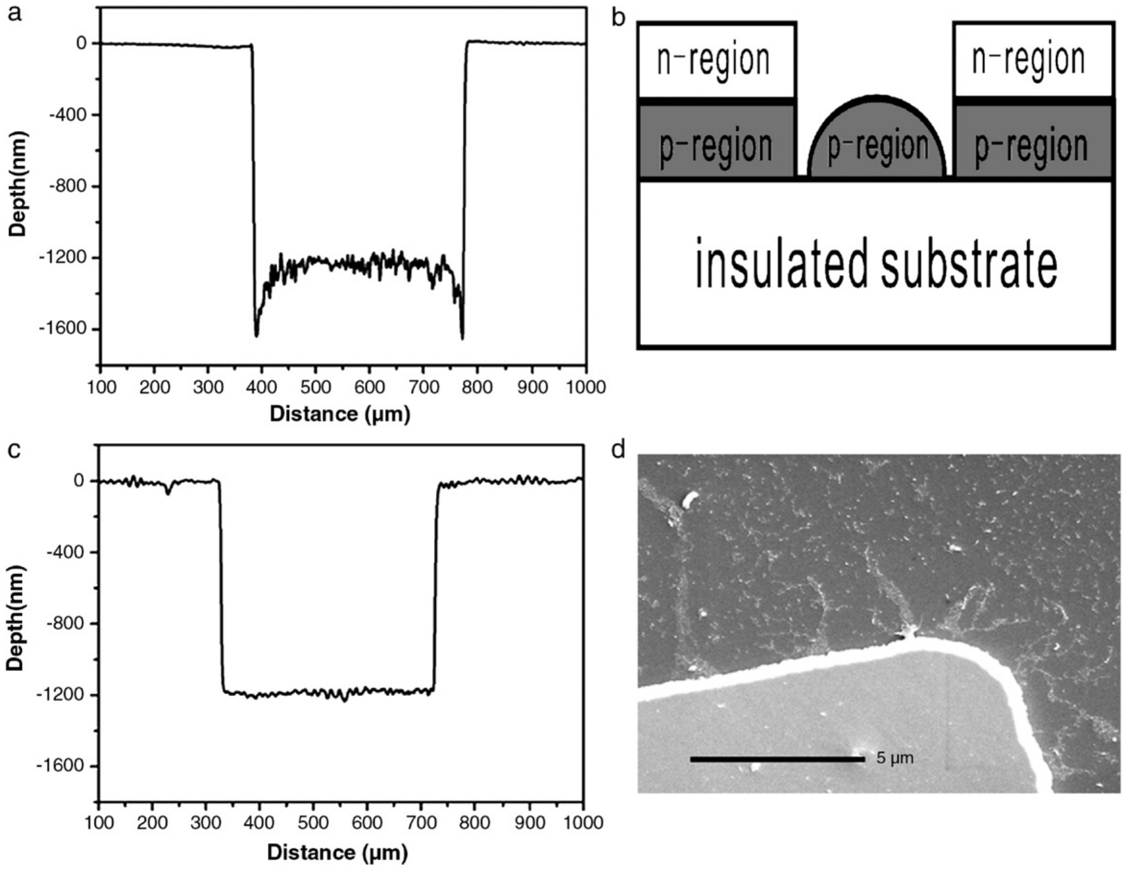

Fig. 1. (a) “W” shaped profile etched by 0.4% HCl solution measured by stylus profiler. (b) Schematic drawing of a LED structure with “W” shaped etching profile. (c) “U” shaped profile etched by 8 mM $FeCl_3$ solution measured by stylus profiler. (d) The SEM image of the ZnO film with smooth surface etched in 8 mM $FeCl_3$ solution for 1 min. The dark region is the etched region, and the bright one is unetched. The SEM was operated at 5.00 kV.

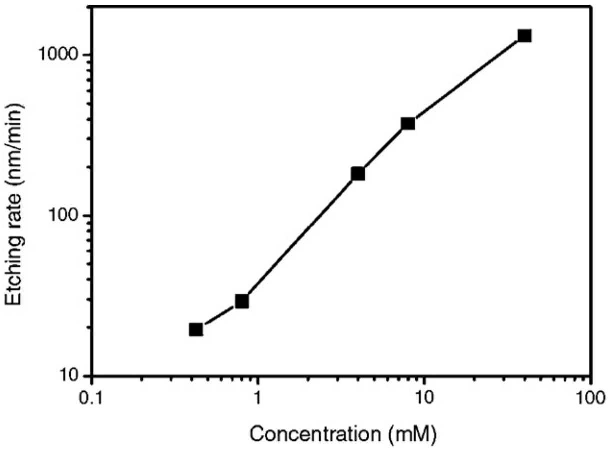

Fig. 2. The relationship between the etching rate and $FeCl_3$ concentration.

proved already by many of our experiments, it is reasonable to determine the etching depth simply by measuring the total depth from the photoresist surface to the etched surface and the thickness of the photoresist.

The effects of $FeCl_3{\cdot}6H_2O$ etchant on the suppression of "W" shaped profile in ZnO film can be explained qualitatively as follows. In the $FeCl_3{\cdot}6H_2O$ solution, the reaction between ZnO and etchant produces dissolvable $ZnCl_2$ salt and $Fe(OH)_3$ deposits (though the indescriptible ferric compound may be more complicated, it does not change our explanation). This reaction could be expressed as:

$$3ZnO + FeCl_3 + 3H_2O = Fe(OH)_3\downarrow + 3ZnCl_2$$

The wet chemical etching is a very complicated process. It is affected by many factors such as the geometric conformation of the pattern, the microcosmic structure of the film surface, the hydromechanical parameters and so on. Here we only consider a simple model in terms of the mass transport limit. In this model, the streamline and the Reynolds number (*Re*) play an important role in the formation of etching profile. During the ZnO reaction with $FeCl_3$, the resultant deposition changes Re, then the streamline, and makes the etching profile more controllable than using acid as etchant [9]. In this case, the "U" shaped etching profile was readily obtained. Recently, Harush et al. discussed the similar phenomenon in GaN film etching process [10]. In their work, a mass transport limited model was proposed as a possible mechanism, similar to the theoretical study of the patterned growth of GaAs film by using metal–organic chemical vapor deposition [11].

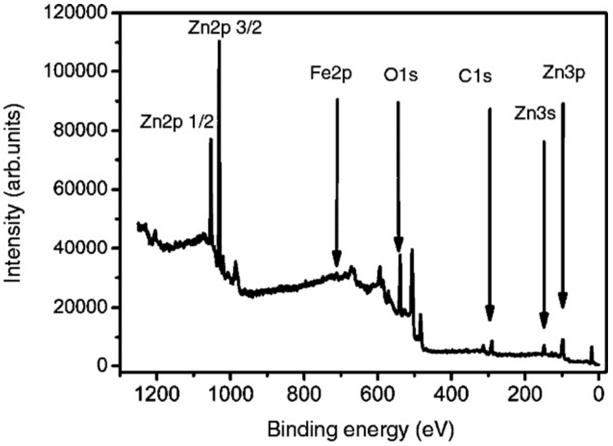

Fig. 3. XPS spectrum of the ZnO etched by $FeCl_3$ solution.

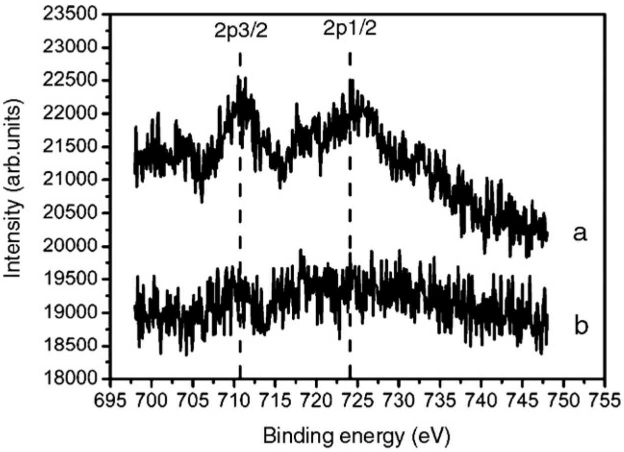

Fig. 4. XPS spectrum of Fe_{2p} peaks. Curve (a) is measured from the as-etched sample, and curve (b) from the sample after 3 cycles of 5 min ultrasonic treatment.

The deposition of ferric compound on the etched ZnO surface was confirmed using XPS. Fig. 3 shows the XPS spectrum with energy resolution of 1.0 eV. This spectrum was obtained from the etched ZnO film surface after removing the mask. We could observe a weak peak at the Fe_{2p} core level position, but no peak for Cl appears. So some $Fe(OH)_3$ deposits did cover on the surface but the quantity was very little. These deposits could be removed after three times of 5 minute ultrasonic cleaning, which was confirmed by the XPS spectrum as shown in Fig. 4, where no signal for Fe_{2p} was observed. An Ohmic contact with low resistance can be achieved from these samples after this treatment. The fabrication of metal electrode on this surface will be reported elsewhere.

The most advantage of our work is that the "U" shaped etching profile can be realized under a relatively wide range of $FeCl_3{\cdot}6H_2O$ concentration, i.e. we could delicately control the etching rate without any change to the etching profile. In contrast, a "U" shaped etch profile on GaN surface could be obtained only when the high etchant concentration, i.e. under high etching rate, was used [10]. A high etching rate, however, would give rise to a shorter etching period, and make the process difficult to control. This problem becomes more serious in the fabrication of device with a multilayer structure where an accurate control of etching depth is critical. In addition, a rough surface caused by faster etching process would be unfavorable for the formation of low resistance Ohmic contact.

4. Conclusion

We found a practical etching process for ZnO single crystalline film: etching in $FeCl_3{\cdot}6H_2O$ solution followed by several cycles of ultrasonic cleaning. By using this method, "U" shaped etching profile was readily obtained. The etched ZnO samples show very smooth surface morphology under different etching rates. This method does not change the electrical properties significantly and is promising for the fabrication of ZnO-based devices.

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