Wet Etching Behaviors of Transparent Conducting Ga-Doped Zinc Oxide Thin Film by Organic Acid Solutions

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Abstract

150 nm thick Ga-doped ZnO thin film, which was deposited by a sputtering process, was wet-chemically etched by using various organic acids such as oxalic, citric and formic acid. Wet etch parameters including etchant concentration and temperature are investigated for each etchant, and their effects on the etch rate and the feature of edge line are compared.

1. Introduction

Because of its low resistivity and high visible light transmittance, indium tin oxide (ITO) has been extensively used as a transparent electrode in solar cells and flat panel displays. However, ITO is faced with critical problems such as the shortage and toxicity of indium [1]. Ga- or Al-doped zinc oxide (ZnO) thin film has been coming into the spotlight as a promising transparent conducting oxide (TCO) alternative to ITO. ZnO film can be anisotropically etched by various wet etchants including HCl, HNO_3, H_3PO_4, NH_4Cl and so on [2]. It was found that ZnO film is too easily etched in most of above solutions even if the solution concentration is significantly reduced, typically leading to uncontrollable etch rate and edge line shape [3]. In our study, various organic acid-based etching solutions including oxalic, citric, and formic acid were used for the systematic investigation of their effects on morphology, wet etch kinetics, and optical/electrical properties of ZnO thin film.

2. Experimental

Ga-doped zinc oxide (GZO) thin film was deposited on glass substrate at 200°C using a sputtering process. Its thickness and resistivity are ~150 nm and ~4.0×10^{-4} Ωcm, respectively. Photoresist etch mask was formed on GZO film by a conventional photo-lithography. Subsequently, GZO film was soaked in various etching solutions and placed in an oven. Etchant concentration and temperature for each etching solution were varied 0.1–2 wt% and 30–60°C, respectively. The etched surfaces were inspected using field emission-scanning electron microscopy (FE-SEM) and atomic force microscope (AFM). The etching depth was measured with Tencor profilometer.

3. Results and discussion

A GZO thin film was deposited by a sputtering process on glass substrate. The optimized parameters to obtain a high quality GZO thin film include substrate material, substrate temperature, pressure, ratio of argon and oxygen and film thickness. The x-ray diffraction pattern of GZO films deposited at growth temperature of 473 K is shown in Fig. 1. A prominent (002) peak indicates that the crystalline structure of the films are oriented with c-axis perpendicular to substrate surface [3]. A high

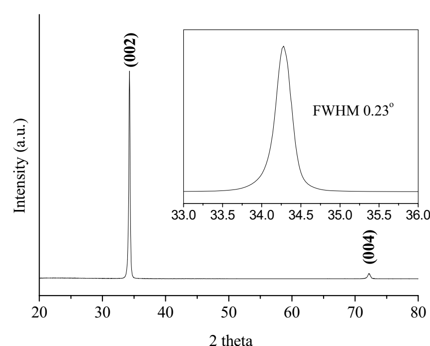


Fig. 1. XRD pattern of a typical GZO thin film. The inset shows a high resolution diffraction pattern with a FWHW of 0.23°.

resolution diffraction pattern in the inset of Fig. 1 exhibits the full-width-at-half-maximum (FWHM) of 0.23°, demonstrating a highly ordered columnar structure of the GZO film.

For GZO thin film, different etching solutions of weak acids such as oxalic acid, citric acid and formic acid generated different etching slopes of the line pattern, surface morphologies, and etching rates. Preliminary etching results using etchant concentrations of 0.1 wt% (0.01 M) oxalic acid, 0.1 wt% (0.08 M) citric acid, and 0.1 wt% (0.02 M) formic acid under the fixed etching temperature of 30°C are shown in Fig. 2, which presents SEM images of the mid-period of etching and overall etching for each organic etchant. Based on the results from mid-period etching, all organic etchants led to the formation of crater-like spots. And overall etching could be divided into two kinds of etching behaviors. In the case of oxalic and citric acid etching, aggressive expansion of spots in a lateral dimension causes a non-uniform edge line. However, in the case of formic acid etching, tiny and numerous spots were generated instead of widened spots, ultimately leading to uniform and sharp edge line.

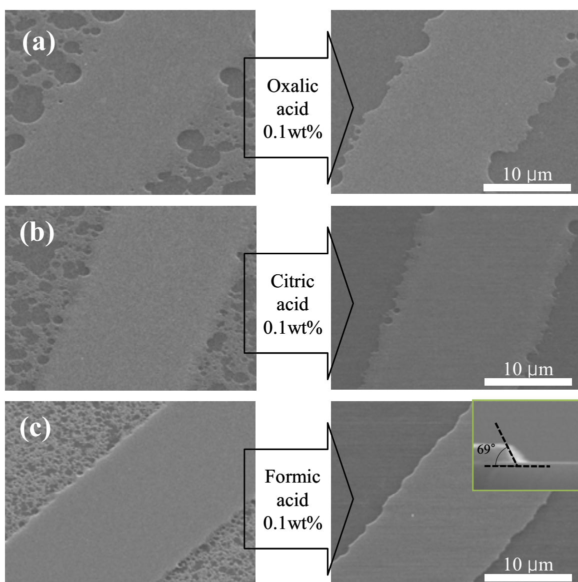


Fig. 2. SEM images of mid-period (left side) and overall etching (right side) behaviors by (a) oxalic acid 0.1 wt%, (b) citric acid 0.1wt%, and (c) formic acid 0.1 wt% at 30°C. The insert in Fig. 1(c) presents a cross-sectional image.

Oxalic and citric acid are stronger than a formic acid. Thus, these acids can produce many hydronium ions in water. Zhu et al. reported that hydronium ions penetrating below the mask are relatively slower in weak acid. In other words, the in-plane lateral-etching rate of weak acid is limited in comparison to the case of the strong acid [4]. On this account, etching of formic acid could lead to steep angle of patterned line (69°) as shown in the inset of Fig. 2(c).

Etch rate can be controlled by changing the etchant concentration and reaction temperature. It was reported that compared to etchant concentration the reaction temperature is a predominant factor in determining an etch rate. Fig. 3(a) shows the lateral and vertical etching rate of formic acid-based GZO film with different temperatures, indicating that the higher temperature leads to rapid etching that causes increased attacking rate between hydronium ions and GZO surface. It is reported by Kwon et al. that the lateral etch rate is at least several times higher than the vertical etch rate due to the preferential orientation of the grain [5]. Based on our experiments and calculated data, the lateral etch rate is faster by 6 times than vertical etch rate. The logarithm of etching rate versus reciprocal temperature in 0.1 wt% formic acid was

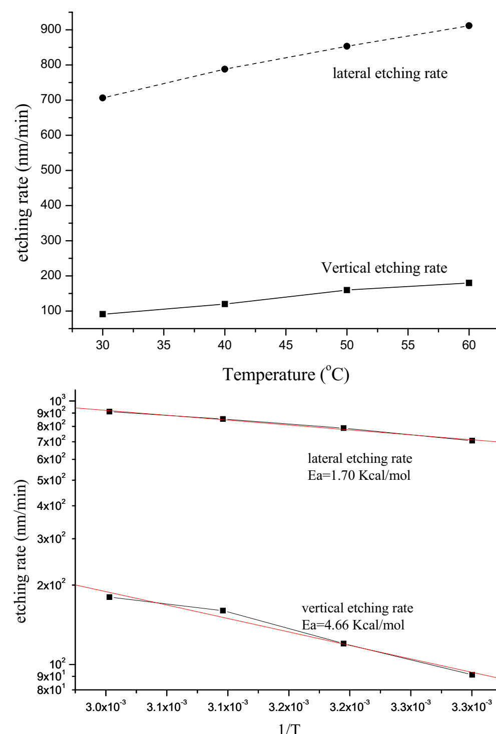


Fig. 3. (a) Calculated vertical and lateral etch rates with different temperatures and (b) Arrhenius plot of etch rates of GZO in 0.1 wt% formic acid etching solution.

potted in Fig. 3(b). The calculated activation energies for vertical and lateral etch rate were found to be 4.66 and 1.70 Kcal/mol, respectively. A lower activation energy of lateral etch rate than that of vertical etch rate indicates that etching reaction in lateral direction occurs quickly and easily due to the textured columnar structure of GZO film.

When used an increased concentration (1.0 wt%) of formic acid at 30°C, we observed the sloped edge line (Fig. 4(b)), similar to the case shown in Fig. 2(a,b) of 0.1 wt% oxalic and citric acid etching. As mentioned previously, a sloped edge phenomenon can occur under a high concentration of hydronium ions. When used a higher temperature of 50°C, the sharpness and uniformity of edge line became worse presumably due to uncontrolled etching behavior at that high temperature.

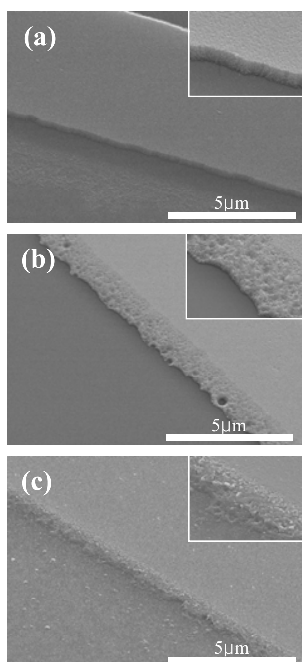
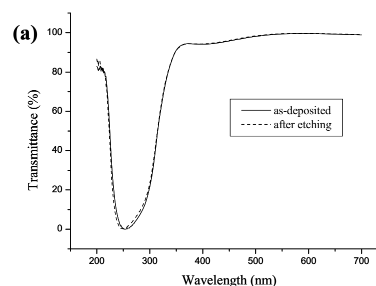


Fig. 4. (a) SEM images of GZO film etched by 0.1 wt% formic acid at 30°C for 4min 30s, (b) 1.0 wt% formic acid at 30°C for 2min. (c) 0.1 wt% formic acid at 50°C for 2min.

Fig. 5 shows the variations of transmittance and surface roughness of GZO film before and after etching process under 0.1 wt% formic acid at 30°C. These transmittance and AFM analyses revealed that photoresist removal and etching processes do not modify the optical and surface properties of GZO film. As expected, the GZO film surface resistivity did not change significantly after those processes.



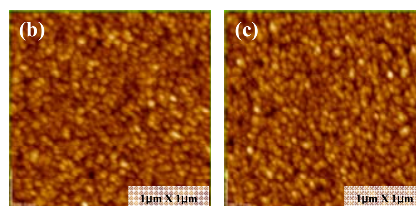


Fig. 5. (a) Optical transmittance spectra and (b,c) AFM images of unetched GZO film before and after etching process under 0.1 wt% formic acid at 30°C.

4. Summary

Etching behaviors of Ga–doped zinc oxide thin film has been studied by using weak organic acids. The steep and sharp edge line of GZO film could be obtained by using 0.1 wt% of formic acid at 30°C. Etch rates could be readily controlled by varying a concentration and temperature. It was found that the line shape of patterned film is strongly affected by the reaction kinetics that is controlled by the etchant concentration and etching temperature.

5. Acknowledgment

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6. References

[1] Y.C. Lin, Y.C. Jian, J.H. Jiang, *Appl. Surf. Sci.*, **254**, 2671 (2008).

[2] H. Zheng, X.L. Du, Q. Luo, J.F. Jia, C.Z. Gu, and Q.K. Xue, *Thin Solid Films*, **515**, 3967 (2007).

[3] J. Sun, J. Bian, H. Liang, J. Zhao, L. Hu, Z. Zhao, W. Liu, and G. Du, *Appl. Surf. Sci.*, in press.

[4] J. Zhu, N.W. Emanetoglu, Y. Chen, B. V. Yakshinskiy, Y. Lu, *J. Electro. Mater.*, **33**, 556 (2004).

[5] J.W. Kwon, E.S. Kim, *J. micro-. Electromech. syst.*, **14**, 603 (2005).