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Optical and Electrical Performance of ZnO Films Textured by Chemical Etching

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Zinc oxide (ZnO) films were prepared by radio frequency (RF) magnetron sputtering on the glass substrate as transparent conductive oxide films. For silicon solar cells, a proper surface texture is essential to introduce light scattering and subsequent light trapping to enhance the current generation. In this study, the magnetron-sputtered ZnO films were textured by wet-chemical etching in diluted hydrochloric acid (HCl) for better light scattering. The diffuse transmittance of the surface textured ZnO films was measured to evaluate the light scattering. The influence of hydrochloric acid concentration on the morphology, optical and electrical properties of the surface-textured ZnO film was investigated. The ZnO film etched in 0.05M HCl solution for 30 s exhibited average diffuse transmittance in the visible wavelength range of 9.52 % and good resistivity of 1.10 x 10^{-3} Ω·cm while the as-deposited ZnO film had average diffuse transmittance of 0.51 % and relatively high resistivity of 5.84 x 10^{-2} Ω·cm. Experimental results illustrated that the optical and electrical performance of ZnO films can be significantly improved by introducing the surface texture through the wet-chemical etching process.

Keywords: zinc oxide, surface texture, light scattering, diffuse transmittance, resistivity.

1. INTRODUCTION

The use of transparent conductive oxide (TCO) films with textured surfaces is becoming an issue of great interest in thin film silicon solar cell technology. As the incident light reaches the textured surface, it can be scattered from the rough surface. This results in the light trapping inside the solar cell, which improves the current output and consequently the conversion efficiency of solar cells [1]. Textured interface can be fabricated using either a textured substrate [2] or hot-embossing lithography [3], or a transparent conductive oxide, which has a roughness surface [4]. Zinc oxide (ZnO) films have been widely applied in solar cells as standard front transparent conductive oxide. Magnetron sputtering with high deposition rate, high reliability and good control of the film properties is the most attractive and common use technique. The magnetron sputtered ZnO films are optically smooth, thus do not scatter the light. There are various methods to prepare textured ZnO films, such as sandblast process [2], chemical vapor deposition [5], metal-organic chemical vapor deposition [6], pulsed DC magnetron sputtering [7] and chemical etching [8]. Sputter deposition and post deposition wet chemical etching have emerged as an easy method to prepare ZnO films for silicon thin film solar cell application. Fernández et al. [9] proposed a two-step chemical etching process in diluted aqueous solution to achieve efficient textured surfaces for light trapping. Berginski et al. [10] textured the magnetron-sputtered ZnO:Al (AZO) thin films by wet-chemical etching with diluted hydrochloric acid (0.5 % HCl). Yen et al. [7] etched AZO films in three different aqueous solutions, 0.5 % HCl, 5 % oxalic acid and 33 % KOH, to study the effect of structural, electrical and optical properties of AZO films as a function of texturing medium and time period to achieve the desirable front electrode materials with good light-trapping properties for thin film silicon solar cell applications. Fernández and Gandía [11] established the relationship between etch parameters such as etchant concentration and etching time, and the structural, electrical and optical properties of AZO films. The wet chemical etching involves the reaction between a liquid (solution) and solid (thin film). The mechanism of the etching process includes: transport of reactants to the surface; surface reaction; transport of products from the surface. The etching rate can be controlled by changing the solution concentration and reaction temperature. Increasing the solution concentration can accelerate the etching activity and the speed the reactants reach and leave the etched surface [12].

In this work, the ZnO films were prepared on the glass substrate by radio frequency magnetron sputtering system in an argon atmosphere at substrate temperature of 275 °C. The as-deposited ZnO films were etched in diluted hydrochloric acid to fabricate the surface-textured ZnO. The influence of morphology, optical and electrical properties of the resultant films as a function of etchant concentration was investigated to obtain the efficient surface-textured ZnO films with good light trapping properties.

2. EXPERIMENTAL METHODS

2.1. Film preparation

A series of ZnO films were prepared by radio frequency magnetron sputtering system (ULVAC MB06-4703) on the glass substrate at substrate temperature of 275 °C. The dimensions of the glass substrate are 25.4 x 25.4 x 2 mm. The target is a ZnO disk (2 inch diameter) with a purity of 99.995 %. The distance between

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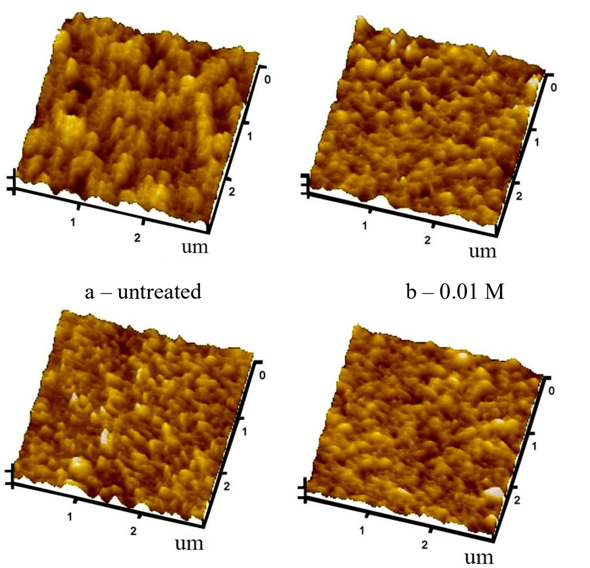
the target and substrate is approximately 10 cm. The target was sputtered in high purity argon (99.999 %) and nitrogen (99.999 %) plasma. Prior to deposition, the substrates were cleaned in soap solution, submerged in acetone and ethanol solutions and in an ultrasound bath for 10 min after rinsing with distilled water. Then the substrates were dried in an oven at the temperature of 50 °C for 30 min before the application of deposition. The chamber is equipped with a rotary vane pump and a turbo pump. After a pumping time of two hours, the chamber was evacuated down to a base pressure of 1.2×10^{-3}Pa. Before the application of deposition, the ZnO target and substrate were sputter-cleaned to remove the oxide and contaminant. ZnO films were deposited at an operation pressure of about 2×10^{-1}Pa with the duration of 60 min for all the prepared samples. In this work, the thicknesses of ZnO films were measured by surface profiler (KLA Tencor P16). To obtain the film thickness, a small tape was placed at the substrate prior to deposition to get a step on the sample surface. The step height was measured in different points on the sample surface and the film thickness was taken as the average of these values. The as-prepared films were etched in diluted hydrochloric acid for 30 s with various concentrations ranging from 0.01 to 0.05 M. The thickness of the ZnO films about 560 nm after the chemical etching. In this study, the influence of the hydrochloric concentration on the morphology, optical and electrical properties of ZnO films was investigated.

2.2. Microstructure and surface topography

The microstructure and surface topography of ZnO films were examined using atomic force microscopy AFM (Seiko Instruments Inc. SPA 400). The AFM was operated in the tapping mode. Typical AFM images of etched ZnO films are presented in Fig. 1.



a – untreated   b – 0.01 M

c – 0.03 M   d – 0.05 M

Fig. 1. Surface topography of ZnO films etched with various HCl concentrations

The surface roughness (root mean square) of ZnO films etched in hydrochloric acid with concentrations of 0.0 M, 0.01 M, 0.03 M and 0.05 M are 5.03 nm, 5.08 nm, 5.22 nm and 5.38 nm, respectively. The surface roughness of the textured ZnO film is increasing with the increase of the hydrochloric acid concentration. The films exhibit fine polycrystalline grains with collar clusters. It reveals that the films are highly dense and compact in nature. The crystalline structure and preferential orientation of ZnO films were examined by X-ray diffraction (XRD) using Shimadzu LabX XRD-6000 with CuK_α radiation ($\lambda = 0.154$ nm) and scanned from 20 to 80° at a rate of 2°/min. The XRD spectrum is quite similar for all the ZnO films. A typical XRD spectrum of ZnO film is illustrated in Fig. 2.

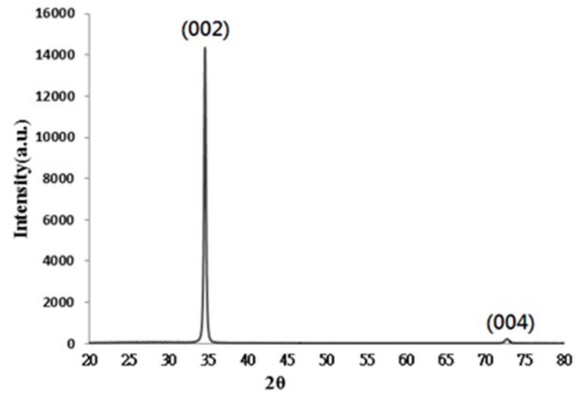


Fig. 2. XRD pattern of ZnO film without etching

The film shows strong peak in (002) direction, implying a polycrystalline hexagonal wurzite crystal structure with a preferred c-axis orientation. In the case of polycrystalline hexagonal structure, the most closely packed and with the lowest free surface energy is the (002) plane, which will favor the grain growth in this direction [13]. The grain size of ZnO films can be determined from the XRD spectrum by using Scherrer equation. Another low intensity peak corresponding to (004) direction is also observed indicating that the films have a preferred orientation with c-axis perpendicular to the substrate.

3. RESULTS and DISCUSSIONS

3.1. Optical properties

Spectroscopic ellipsometry is widely used to determine the optical properties of the films. In this work, the transmittance spectra measurement was performed with the double beam spectrometer Lambda 750 from Perkin Elmer. Measurements were made using a scanning spectrophotometer fitted with an integrating sphere. By placing the test sample at the entrance of the sphere, transmitted light enters the sphere. The sphere collects all the light passing through the sample to obtain the total transmittance. For the measurement of diffuse transmittance, there is a hole in the integrating sphere so that light passing directly through the sample is not collected as shown in Fig. 3. The total transmittance spectra in the wavelength range 300-1200 nm for etched ZnO films is plotted in Fig. 4. The average transmittances of these films are summarized in Table 1. No apparent changes of the average transmittance are observed for the etched ZnO films in the studied hydrochloric acid concentrations. The films have 76 % of average transmittance in the wavelength range 300 – 1200 nm and increase transmittance values up to 83 % in the visible wavelength range 400 – 800 nm. The light scattering of the surface-textured ZnO films can be evaluated by the diffuse transmittance.

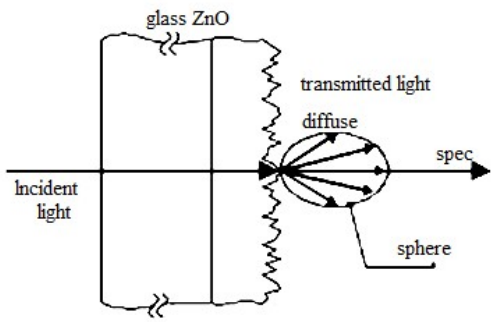


Fig. 3. Measurement of total and diffuse transmittance [14]

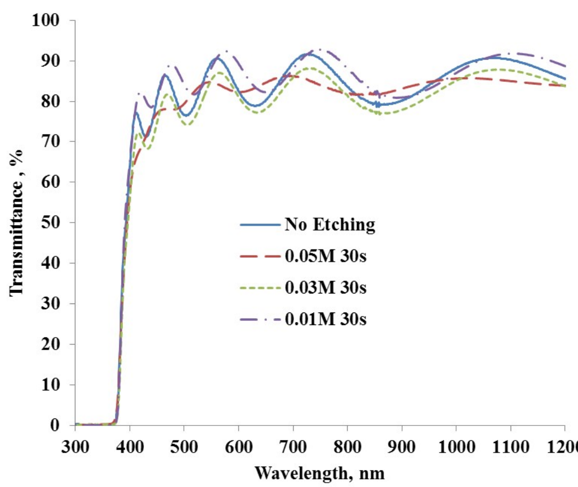


Fig. 4. Total transmittance spectra of ZnO films etched with various HCl concentrations

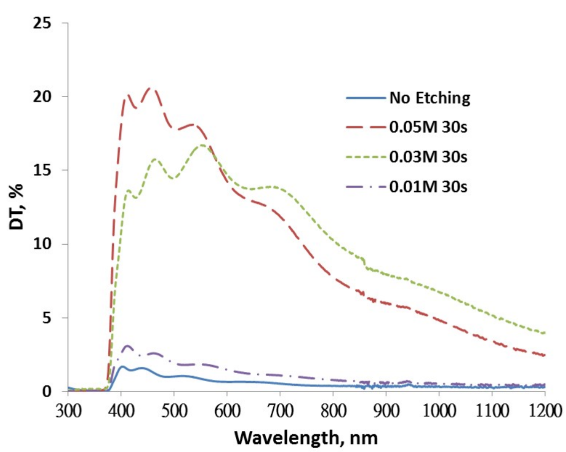


Fig. 5. Diffuse transmittance spectra of ZnO films etched with various HCl concentrations

Fig. 5 depicts the diffuse transmittance spectrum in the wavelength range 300 – 1200 nm for the etched ZnO films with various hydrochloric acid concentrations. It shows that the diffuse transmittance of the surface-textured ZnO film is significantly increasing with the increase of the hydrochloric acid concentration. The average diffuse transmittances of these films are listed in Table 1. It can be observed that the average diffuse transmittance in the visible wavelength is increasing up to 9.52 % for the ZnO film with the concentration of 0.05 M, while the average diffuse transmittance for the as-deposited ZnO film is only 0.51 %. This demonstrates that the light scattering of ZnO film can be significantly improved by surface textured ZnO through the wet-chemical etching process.

Table 1. Average total transmittance and diffuse transmittance of ZnO films etched with various HCl concentrations

Wavelength range, nm	Hydrochloric acid concentration			
	0 M	0.01 M	0.03 M	0.05 M
	total transmittance			
300 – 1200	76.5 %	76.9 %	75.1 %	75.1 %
400 – 800	83.6 %	84.8 %	82.2 %	82.6 %
	diffuse transmittance			
300 – 1200	0.51 %	0.91 %	9.38 %	9.52 %
400 – 800	0.75 %	1.49 %	14.0 %	14.8 %

3.2. Electrical properties

The electrical properties of the surface-textured ZnO films were investigated by Hall effect measurement using an Ecopia HMS-300 system. The electrical resistivity and Hall mobility of surface-textured ZnO films varied with hydrochloric acid concentration and are presented in Fig. 6. The resistivity of the films decreases from 5.84×10^{-2} Ω·cm to 1.10×10^{-3} Ω·cm as the hydrochloric acid concentration increases from untreated to 0.05 M. The Hall mobility increases from 4.66 cm^2/V_S to 14.6 cm^2/V_S as the hydrochloric acid concentration increases from 0.0 M to 0.05 M. The decrease of the resistivity is attributed to the increase in the extent of the crystallization and orientation [15], which causes an increase of the mobility. The carrier concentration increases from $1.33 \times 10^{-19} cm^{-3}$ to $4.31 \times 10^{20} cm^{-3}$ as the hydrochloric acid concentration increases from untreated to 0.05 M. The increase in the intensity of the diffraction peak and also the narrowing of the peak, i.e., decrease in full width at half maximum (FWHM) of the peak with the increase of the HCl concentration indicates the improvement in crystallinity of the films [16]. This leads to a decrease of the resistivity as the HCl concentration is increasing.

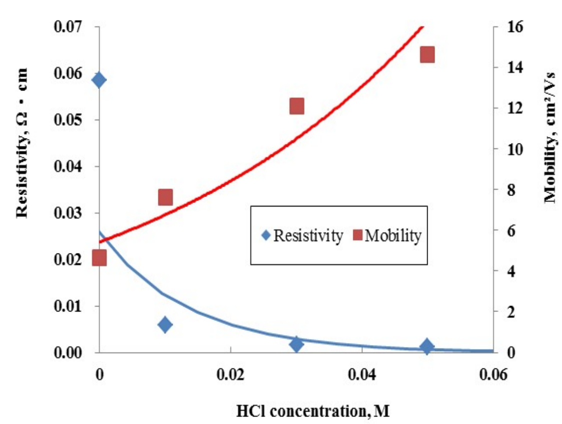


Fig. 6. Resistivity and mobility of ZnO films etched with various HCl concentrations

4. CONCLUSIONS

The morphology, optical and electrical properties of ZnO films etched with hydrochloric acid were investigated in this paper. Experimental results show that hydrochloric acid concentration plays an important role in modifying the morphology, optical and electrical properties of ZnO films. The surface roughness of the textured ZnO film is increasing with the increase of the hydrochloric acid concentration resulting in light scattering, which in turn favors light trapping to enhance the light absorption. The resistivity of ZnO films decreases from 5.84 x 10^{-2} Ω·cm to 1.10 x 10^{-3} Ω·cm as the hydrochloric acid concentration increases from untreated to 0.05 M. Present study demonstrates that the light scattering and resistivity of ZnO film can be significantly improved by introducing textured surfaces through chemical etching in the hydrochloric acid.

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