

Influence of Surface Texture by NH_4Cl Aqueous Solution on the Electrical and Optical Properties of Al-Doped Zinc Oxide Films

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(Received on 4 June, 2008)

Aluminum-doped zinc oxide (AZO) films were prepared on glass substrate by mid-frequency direct current reactive magnetron sputtering (MF-DC-MS). The influence of surface texture by NH_4Cl aqueous solution on the surface morphology, electrical and optical properties of the AZO films was systematically investigated by scanning electron microscope, four-point probe and ultraviolet-visible-near infrared spectrophotometer, respectively. The results indicate that textured AZO film obtains a better texture surface for light trapping. The reflectivity for textured AZO film decreases drastically in visible light region and the electrical resistivity increases, which can be explained by the textured surface morphology of AZO film. The results above prove that NH_4Cl aqueous solution is an appropriate candidate for AZO wet etching because of its easy control and relatively low cost.

Keywords: NH_4Cl aqueous solution; Surface texture; AZO film; MF-DC-MS

1. INTRODUCTION

Transparent conductive ZnO film due to its wide band gap of 3.37 eV and large exciton binding energy of 60 meV has been widely studied for its practical application as flat panel displays, transparent electrodes and window materials in solar cells [1–4]. Compared with other transparent electrode materials such as SnO_2 : F, In_2O_3 : Sn, AZO film is a good candidate application as transparent and conductive contacts in solar cells [2–5]. AZO film has been prepared by many methods including chemical methods (chemical vapor deposition, sol-gel, spray pyrolysis, etc) and physical methods (sputtering, pulsed laser deposition and reactive evaporation, etc.) [6, 7]. Due to the high deposition rate, high stability and low cost for large-area films, magnetron sputtering technique, especially MF-DC-MS has been widely used to prepare AZO films recently. As a conductive contact in solar cells, an appropriate textured surface morphology for AZO film is essential to perform an effective light trapping and further increase the efficiency of silicon film solar cells. So a controllable and uniform etching process is indispensable if non-conductive substrate is used. ZnO is easily etched in all acids and alkalis [8, 9]. Most of etching process of AZO thin films use diluted hydrochloric acid [1, 10]. Although AZO film can obtain a good texture surface by diluted hydrochloric acid, the etching process and surface morphology are difficult to control due to the high etching rate even if the solution concentration is drastically reduced [9]. So far, there has been no report on the systematic investigation of the influence of wet etching of NH_4Cl aqueous solution on the surface texture, electrical and optical properties of AZO thin films by MF-DC-MS. In this paper, transparent conductive AZO thin films were prepared on glass substrate by MF-DC-MS. The dependence of surface morphology, electrical and optical properties of AZO films on the surface texture by NH_4Cl aqueous solution was systematically investigated by scanning electron microscope, four-point

probe and ultraviolet-visible-near infrared spectrophotometer. The results suggest that NH_4Cl aqueous solution indeed have a positive effect on the surface texture, electrical and optical properties of AZO thin films.

2. EXPERIMENTAL DETAILS

AZO transparent conductive thin films were prepared on glass substrate under O_2/Ar atmosphere by MF-DC-MS. A 220 mm × 80 mm × 5 mm rectangular Zn-Al metal alloy target with aluminum content of 3.0 wt.% was used as sputtering target. Before sample preparation, glass substrate was cleaned in an ultrasonic bath by using acetone, alcohol and de-ionized water for 10 minutes sequentially. In order to avoid the effect of impurities and gas in chamber, the sputtering chamber was initially evacuated to a base pressure below 4×10^{-4} Pa and then pre-sputtering of 5 minutes was carried out at an argon gas pressure of 1.0 Pa in order to clean the target surface. The total pressure and the O_2/Ar ratio during sputtering were maintained at 0.5 Pa and 1.2/18, respectively. The substrate temperature (T_s) is varied from 210⁰C to 290⁰C and the deposition lasts 3 hours. The surface texture for as-dep AZO films was performed by NH_4Cl aqueous solution with a 5% concentration for 5 min, 10 min and 20 min, respectively. Crystalline structure of AZO film was characterized by X-ray diffractometer (Philips PANalytical X'pert) with $\text{CuK}\alpha$ radiation. The surface morphology and electrical resistivity were measured by SEM and traditional four-point probe, respectively. The reflectivity was measured by ultraviolet-visible-near infrared spectrophotometer (Shimadzu UV-3150). All the measurements above were done at room temperature.

3. EXPERIMENT RESULTS

3.1. Structural properties

XRD patterns of AZO films deposited at different T_s are shown in Fig. 1. As seen from Fig. 1, all the films ex-

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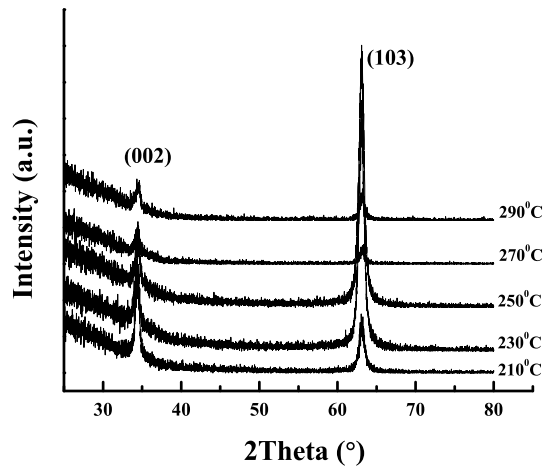


FIG. 1: XRD patterns of AZO films deposited at different T_s

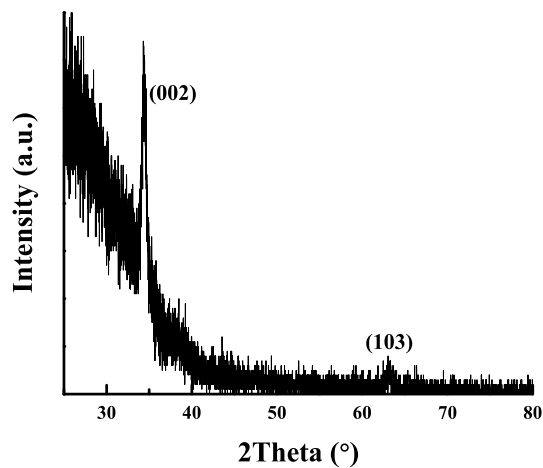
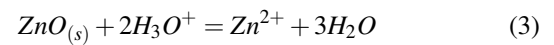
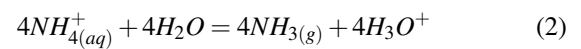
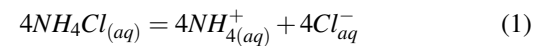


FIG. 2: XRD pattern of AZO film prepared at 250°C for only one hour

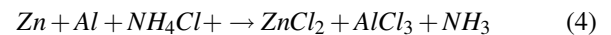
hibit two characteristic diffraction peaks due to (002) and (103) diffractions of ZnO. But polycrystalline AZO films have no obvious c-axis preferential orientation. The experimental result is different from that reported in some previous works where AZO films showed a strong c-axis preferential orientation [5, 11, 12]. In order to explain the result, AZO film was prepared at 250°C for only one hour and other deposition parameters kept constant. Fig. 2 shows the XRD pattern of the film. From Fig. 2, this AZO film exhibits a strong c-axis preferential orientation. So it might be presumed that AZO film grows while is annealed at the same time during 3 hour deposition. Long-time annealing process induces a change of crystalline structure and the growth mode from vertical growth to lateral growth along (103) orientation. But the shift mechanism of a growth orientation is not understood yet.

3.2. Surface texture

As a front contact in silicon thin film solar cells, AZO film should be highly conductive and transparent in the visible light region. Furthermore, in order to realize an effective light trapping inside silicon layers, an appropriate surface topography is necessary [13]. Nowadays, among the etching process of AZO film, using diluted hydrochloric acid is dominated [1, 10, 14]. Although AZO film can obtain a good texture surface by diluted hydrochloric acid, the etching process and surface morphology are difficult to control due to the high etching rate. So far, there is still no report about using the NH_4Cl aqueous solution to etch the surface of AZO films. The reactive mechanism of ZnO with NH_4Cl aqueous solution can be described by the following equations [9]



where aq, g and s mean the aqueous and gaseous and solid state, respectively. The reactive mechanism of AZO might be described by the following equation besides the above three equations



In terms with equation (1,2,3), it can be concluded that a linear relationship exists between etching rate and concentration of NH_4Cl . Interstitial Zn, interstitial Al and grain boundary always exists in as-dep AZO film. It might be extrapolated that NH_4Cl could react with interstitial Zn, interstitial Al and Al stacked at the grain boundary from equation (4). So the etching reaction might firstly take place at interstitial position and grain boundary where the etching reaction might be much faster than lattice sites.

Figure 3 shows the surface morphology of AZO films etched for 4 min by NH_4Cl aqueous solution, where the AZO films were prepared at T_s of 210°C and 270°C, respectively. As it can be seen from Fig. 3, T_s has a big influence on the surface morphology of textured AZO. The textured AZO film prepared at 210°C shows a much rougher face including many granular holes, while that prepared at 270°C shows a flat surface. Fig. 4 shows the surface morphology of non-etched AZO films prepared at T_s of 210°C and 270°C, respectively. From Fig. 4, AZO film prepared at 210°C shows a sparser and more defective surface than that prepared at 270°C. It can be concluded that the sparser and defective structure helps to enhance the etching rate. Hence, an appropriate T_s should be chosen to obtain a good and controllable surface texture for AZO film.

In order to investigate the influence of etching time on the surface texture of AZO film, the AZO films prepared at 250°C were chosen and were etched by NH_4Cl aqueous solution for different time. Fig. 5 shows the SEM images of etched AZO

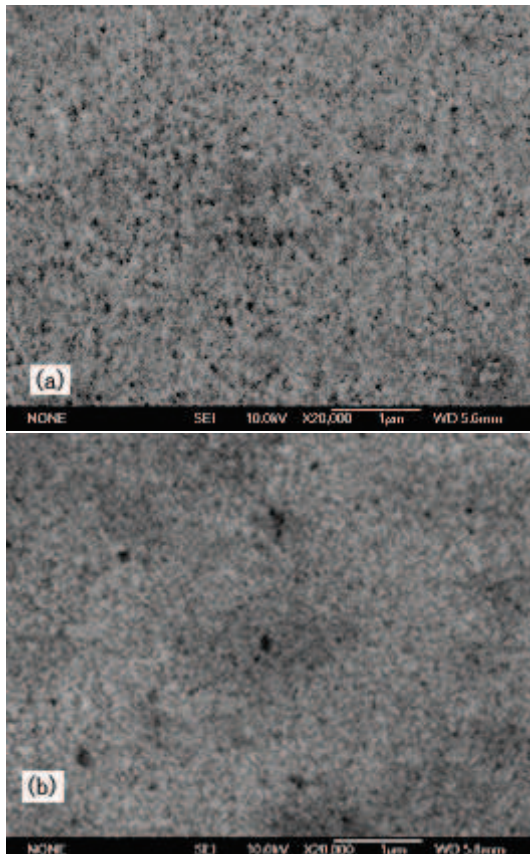


FIG. 3: Surface morphology of AZO films etched for 4 minutes by NH_4Cl aqueous solution, where the AZO films were prepared at T_s of 210°C and 270°C , respectively. (a) 210°C (b) 270°C

films for 0, 4 min, 10 min and 20 min, respectively. The surface of as-dep AZO film exhibits a homogeneous granular structure, which is not effective for light trapping. From Fig. 5b, the feature size decreases and the etching operation first occurs in some parts of the film where may be the dislocation and boundary after 4-min etching. The result is in good agreement with that reported in some previous work that the etching operation occurring at the dislocation and boundary was preferable [9, 15].

Seen from Fig. 5c, the film surface becomes rougher and out-of-flatness after 10-minute etching treatment. Some small flat crater-like structure distributes regularly over the surface. From Fig. 5d, some big flat crater-like structures are formed on the surface after 20-min etching. But it is noticeable that a big crack across the film surface is formed. It can be attributed to the long-time etching that makes the etching rate along boundary or large defect stacking place faster than that in the grain. As a result, the film surface becomes rougher and rougher and even the noticeable crack is formed over the surface with the etching time increased up to 20 minutes. Compared with the surface texture of AZO films etched by diluted hydrochloric acid [1, 10, 14], the surface texture of AZO films by NH_4Cl aqueous solution is satisfactory and easily con-

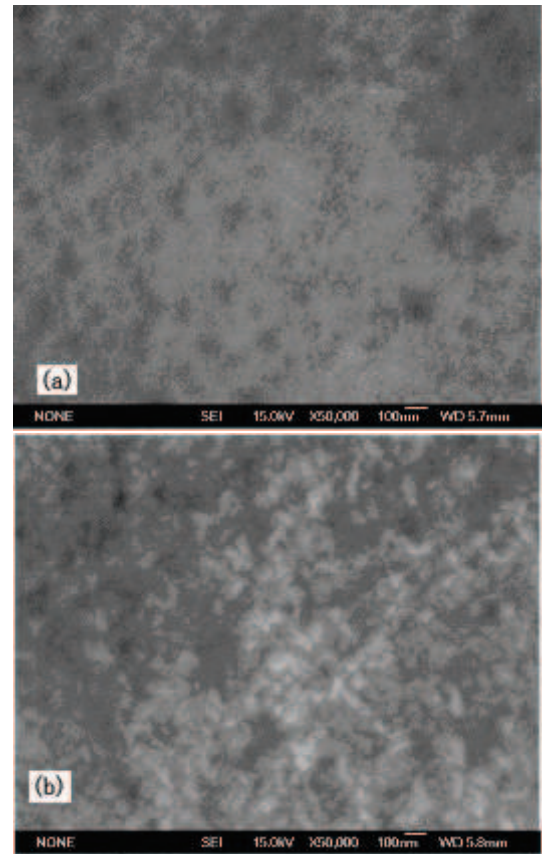


FIG. 4: Surface morphology of non-etched AZO films prepared at T_s of 210°C and 270°C , respectively. (a) 210°C (b) 270°C

trolled due to small etching rate even if the etching process still needs to be further improve.

3.3. Electrical properties

Figure 6 illustrates the electrical resistivity of AZO films as a function of etching time. After being etched for 20 minutes, the resistivity increases from $3.3 \times 10^{-3} \Omega \bullet \text{cm}$ to $9.3 \times 10^{-3} \Omega \bullet \text{cm}$. This might arise from the decreased film thickness and the rough surface with the etching time increasing. In addition, the increasing defects around the surface or the grain boundary resulting from the etching treatment may lead to higher resistivity.

3.4. Optical properties

Fig. 7 shows the optical reflectivity of AZO films prepared at 250°C . The average optical reflectivity in the visible light region is nearly 14.82%. The reflective spectrum exhibits clearly oscillations due to multiple beam interference due to coherent reflections in the AZO film surface. The interference feature indicates the good quality and high transparency of the

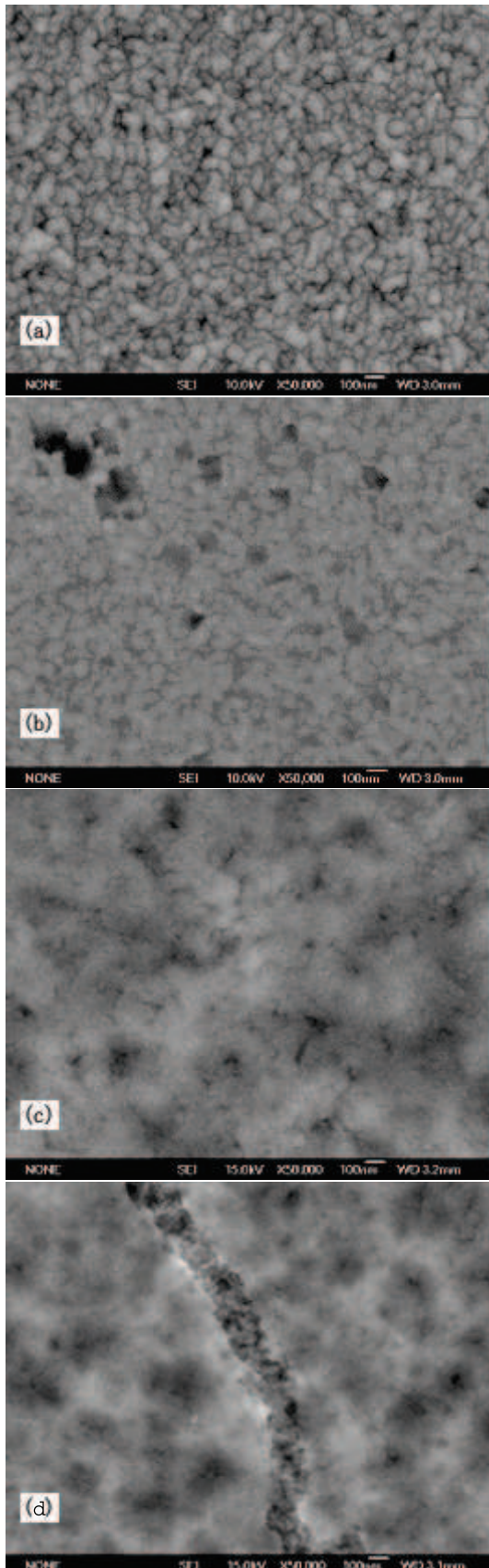


FIG. 5: SEM images of etched AZO films for 0, 4 min, 10 min and 20 min, respectively. (a) 0, (b) 4 min, (c) 10 min, (d) 20 min

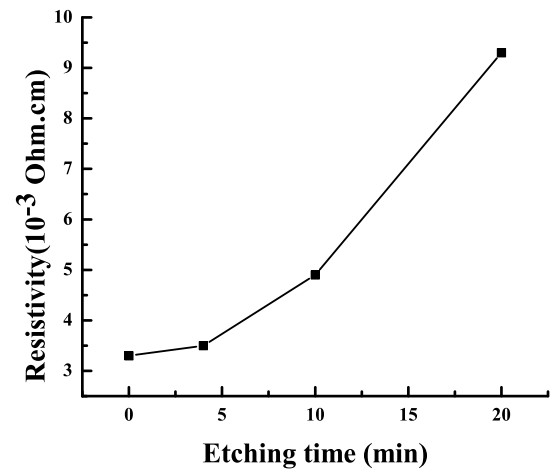


FIG. 6: Electrical resistivity of AZO films as a function of etching time

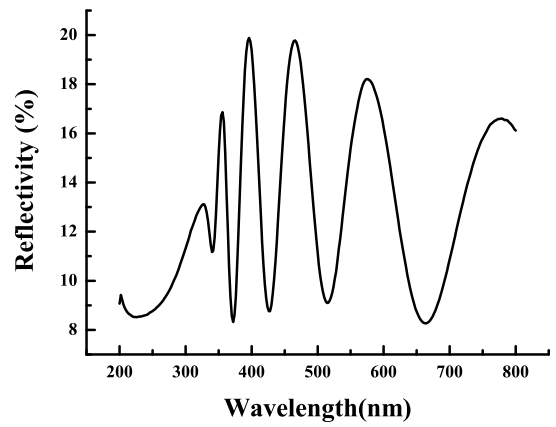


FIG. 7: Optical reflectivity of AZO films prepared at 250⁰C

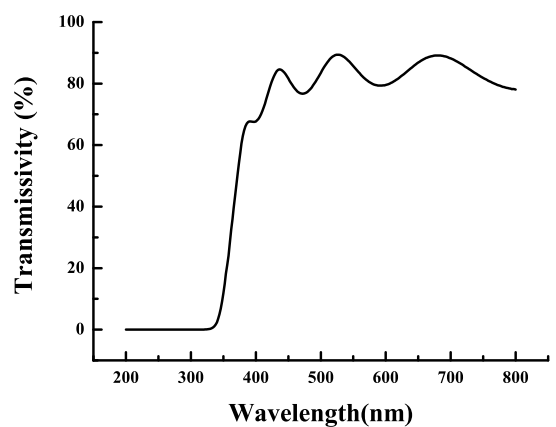


FIG. 8: Optical transmissivity of AZO films prepared at 250⁰C

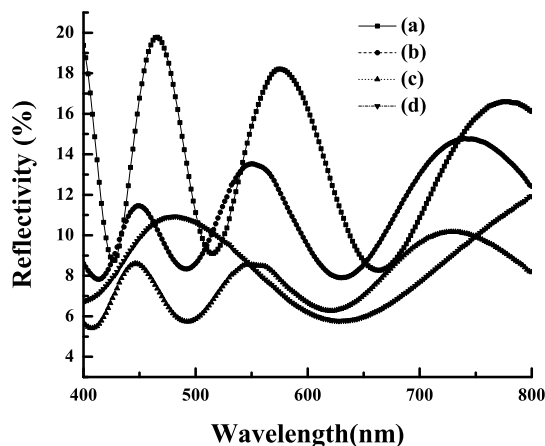


FIG. 9: Optical reflectivity of AZO film etched by NH_4Cl aqueous solution for 0, 4 min, 10 min and 20 min, respectively. (a) 0, (b) 4 min, (c) 10 min, (d) 20 min

AZO film in the visible light region. The same feature is also observed in Fig. 8 and Fig. 9. Fig. 8 illustrates the optical transmissivity of AZO films prepared at 250°C . The average optical transmissivity in the visible light region is more than 85% indicating the high transparency. The optical reflectivity of AZO film etched by NH_4Cl aqueous solution for different time is shown in Fig. 9. As seen in Fig. 9, the optical reflectivity in the visible light region is sharply reduced from 14.82% to 7.86%. It indicates that the obtained surface texture of AZO is effective for light trapping. The result is coincident with the surface texture of AZO films discussed. Besides, the distance between the maxima becomes larger for longer etching times,

meaning a decreasing of film thickness. The decreasing reflectivity with etching time is mainly due to the rougher texture surface instead of due to the losses from diffuse reflection and the decreasing of film thickness.

4. CONCLUSION

In conclusion, AZO films were prepared on glass substrate at different T_s by MF-DC-MS. The influence of surface texture by NH_4Cl aqueous solution on the surface morphology, electrical resistivity and optical reflectivity of AZO films has been investigated systematically by scanning electron microscope, four point probe and ultraviolet-visible-near infrared spectrophotometer. The results indicate that the etching firstly takes place at the interstitial position and grain boundary. To realize good and controllable surface texture, an appropriate substrate temperature should be chosen. The textured AZO films show a drastic decrease in reflectivity in the visible light region and an increase in resistivity. The result is coincident with the textured surface morphology of AZO films. The results also prove that NH_4Cl aqueous solution is an appropriate candidate for AZO wet etching because of its easy control and relatively low cost.

Acknowledgments

The authors would like to thank Professor Sun Hongwei and Senior engineer Song Tianfu for their help in SEM measurements and Dr. Jia Jianfeng for his help in XRD measurements. The work is supported by National Basic Research Program of China (973) with granted No. 2006CB202601.

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