The investigation of preparation by magnetron sputtering and application in amorphous silicon solar cells of pyramid-like textured ZnO:Al thin film

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Abstract. In this paper, the pyramid-like texture aluminum doped zinc oxide (ZnO:Al) thin films was prepared by adding negative bias voltage and controlling the sputtering parameters properly, and the lowest resistivity of 7.8×10^{-4}Ω·cm, light transmittance above 83% was achieved, respectively. Instead of the traditional tin oxide doped with fluorine (SnO_2:F), using the ZnO:Al film as a front electrode transparent conducting oxide (TCO) layer for hydrogenated amorphous silicon (a-Si:H) solar cells, the higher contact potential barrier of ZnO:Al /p-a-SiC:H have to be overcome. In this paper, we attempt to resolve the contact potential barrier by inserting a buffer layer of microcrystalline silicon (µc-Si:H) between ZnO:Al layer and p-SiC: H windows layer, and its efficiency increases from 7.6% for the SnO_2:F TCO to 8.3% for the ZnO:Al /µc-Si:H TCO.

1. Introduction
As a front electrode transparent conducting oxide (TCO) layer for hydrogenated amorphous silicon (a-Si:H) solar cells, the electrical properties of tin oxide doped with fluorine (SnO_2:F) can be degraded seriously at the hydrogen plasma atmosphere. Compared with SnO_2:F, the textured aluminum doped zinc oxide (ZnO:Al) thin-film not only has the equivalent electrical properties, but also has a lot of advantages, such as the high electrical properties stability under the hydrogen plasma environment, the effective light trapping action. Those are the potential advantages in improving the a-Si:H solar cell performance when using it as a front electrode, and it has attracted a great deal of attention[1-3]. However, there are still two problems as follows: (1) the preparing technology of pyramid-like textured ZnO:Al thin-film is not easy to grasp by magnetron sputtering; (2) the problem of higher contact potential barrier between ZnO:Al layer and p-SiC: H windows layer need to be overcome when used as front electrode in solar cells.

In this paper, the pyramid-like texture ZnO:Al films was prepared by adding negative bias voltage and controlling the sputtering parameters properly. In order to use the ZnO:Al thin film as a front electrode in solar cells well, we attempt to resolve the contact potential barrier by inserting a buffer layer of microcrystalline silicon (µc-Si:H) between ZnO:Al layer and p-SiC: H windows layer, namely ZnO:Al /µc-Si:H TCO/pin solar cell was fabricated.

2. Experiment
The ZnO:Al films were deposited on the quartz substrates by RF magnetron sputtering. A sintered ceramic ZnO:Al target with 90 mm in diameter and 5mm of thickness was used. Before each deposition, the sputtering chamber was pumped down to below 4.2×10^{-7}Pa, and then working pressure...
was maintained at 1 Pa with Ar/O\textsubscript{2} (30/3) ambient gas and with the sputtering power of 150 W. The sample was prepared at 120 °C for 60min with negative bias voltage showing in table 1.

**Table 1.** Parameters of magnetron sputtering.

| Bias voltage (V) | 0V  | 20V | 50V | 100V | 130V |
|------------------|-----|-----|-----|------|------|
| Samples No.      | A1  | A2  | A3  | A4   | A5   |

In order to study the light-scattering abilities of the textured surfaces for solar cell applications, two a-Si:H solar cells were deposited in an RF PECVD system. The each solar cell structure was as follows: the cell A with structure of glass/SnO\textsubscript{2}:F (0.7 µm) / p-SiC:H, p-a-Si:H (~30 nm) / i-a-Si:H (~0.4 µm) / n-a-Si:H (~35 nm) / Ag; the cell B with structure of glass/textured ZnO:Al (0.8 µm) / μc-Si:H (~90 nm) / p-SiC:H, p-a-Si:H (~30 nm) / i-a-Si:H (~0.4 µm) / n-a-Si:H (~35 nm) / Ag.

The resistivity of the sample was measured by four-probe method. A X-ray instrument (XRD-Rigaku D/ max 2500) was used to characterize crystallization orientation of sample, SEM (SEM-JSM 6700F) was used to observe surface morphology of the film. For the thin film light-transmission, A UV2Vis-NIR Spectrophotometer (Backman-Du 8B Spectrophotometer) whose wavelength is in the range of 400~900 nm was carried out. All the sample measurements were performed at room temperature. The solar cell illuminated current-voltage characteristics were measured using a solar simulator (Wacom WXS-140S-Super) at standard test conditions (AM 1.5, 100 mW/cm\textsuperscript{2}, 25 °C).

![Figure 1](image1.png)

**Figure 1.** The XRD patterns of samples A1, A2, A3, A4 and A5.

3. Results and Discussion
3.1. The influence of the bias on the structure of ZnO:Al films

The XRD patterns of samples with different bias are shown in Fig.1. As shown in Fig.1, the sample A1 has a preferred orientation with the c axis perpendicular to the substrate, which agreed with a large number of research results of the ZnO:Al films fabricated by magnetron sputtering. From the XRD pattern of the sample A2 whose bias is 20V in Fig.1(b), the peak intensities of (002) preferred orientation is somewhat increase. It is maybe that the larger bias increase particles energy, and the particles have enough energy to reach to the lowest energy place after reaching the substrate. The XRD pattern of sample A3 is given in Fig.1(c). It can be seen the value of (002) peak decrease and the preferred orientation is inhibited with the bias increasing to 50V. The XRD patterns of samples A4 and A5 are shown in Fig.1(d) and Fig.1(e), respectively. The value of (002) peak are getting smaller and smaller with bias increasing, and the peaks (100) and (101) appear when the bias is higher than 100V. These suggest that the growth of ZnO: Al thin film and crystal quality may be changed. The result can be interpreted as follows: the bigger of bias voltage is, the higher of particles` energy is. Therefore, there are large of particles reaching the substrate, and the growth of ZnO: Al thin film has the chance to change from the lowest energy (002) crystal plane to the higher energy (101) and (100) crystal plane.

![Figure 2](image)

Figure 2. The SEM patterns of samples A2, A3, A4 and A5. A represented columnar structure, B represented polygon structure, C represented pyramid-like structure.

3.2. The influence of the bias on the surface morphology of ZnO:Al films
The SEM pictures of samples A2, A3, A4 and A5 are shown in Figure 2 (a), (b), (c) and (d), respectively. It can be seen that surface morphology of A2 sample shows the mainly columnar structure with relative small grain size, containing some parts of the polygon structure. Samples A3 and A4 possess obvious pyramid-shaped surface structure with larger grain size, also including some parts of the polygon structure. While sample A5 shows the polygon surface structure with the largest grain size, containing some parts of the pyramid-like structure. There is a possible reason to explain the phenomena above. As negative bias increase, not only most of ions grow along the lowest surface energy (002) face, but also some higher energy ions can grow along other crystal face. According to the literature [4], ZnO: Al film grains exhibit an obvious columnar growth, when it appears the preferred orientation peak (002). When (100) peak of thin film is observed, the grain growth along rod or polygon structure, while the appearance of (101) peak suggests that the grain growth exhibits pyramid-like structure, and the film surfaces are roughness with a certain textured structure.

3.3. The influence of the bias on the optical and electrical properties of ZnO:Al films

Fig. 3 shows the UV transmission spectrum of samples A1, A4, A5. The visible light transmission rate was above 83%. Among all the samples, sample A4 has the lowest light transmittance, and sample A1 has the highest one. According to the literature [5], sample A4 is relatively thinner compared with the other two samples, and samples A1 and A5 have the same thickness. However, the light transmittance of sample A4 is the lowest, and the light transmittance of sample A5 is lower than sample A1. The reason for sample A4 and A5 with abnormal light transmittance phenomenon is that rough surfaces of samples A4 and A5 with like-pyramid structure morphology can enhance scattering effect of short-wavelength light, and light vertical transmittance decreases obviously, which can be proved by SEM images in figure 2 (c) and (d).

![Image of Optical transmission spectra of samples A1, A4, A5.](image1)

![Image of I-V curves for solar cell A and B.](image2)

Figure 3. Optical transmission spectra of spectrum of samples A1, A4 and A5.

Figure 4. The I-V curves for solar cell A and B.

The resistivity of sample A1, A2, A3, A4 and A5 was measured. For sample A1, the resistance is high which can not detect by four-probe method, and for A2, A3, A4 and A5, the resistance is 30 $\Omega \cdot cm$, 0.146 $\Omega \cdot cm$, 0.083 $\Omega \cdot cm$, and 0.00078 $\Omega \cdot cm$, respectively. From the electrical properties measurement, it is shown that the resistivity decreases with the increasing of the bias. This result may be relative to grain size, and it can be proved by SEM image in figure 2. The increase of the ZnO:Al grain size can decrease the mounts of grain boundary, and reduce the carries scattering effect, which can improve the electron mobility.

The synthetic analysis of electrical properties and the light trapping properties indicated that the sample A4 is an ideal transparent conductive film for amorphous silicon solar cells.

3.4. The application of textured ZnO:Al thin films on amorphous silicon solar cells

The resistivity of sample A1, A2, A3, A4 and A5 was measured. For sample A1, the resistance is high which can not detect by four-probe method, and for A2, A3, A4 and A5, the resistance is 30 $\Omega \cdot cm$, 0.146 $\Omega \cdot cm$, 0.083 $\Omega \cdot cm$, and 0.00078 $\Omega \cdot cm$, respectively. From the electrical properties measurement, it is shown that the resistivity decreases with the increasing of the bias. This result may be relative to grain size, and it can be proved by SEM image in figure 2. The increase of the ZnO:Al grain size can decrease the mounts of grain boundary, and reduce the carries scattering effect, which can improve the electron mobility.

The synthetic analysis of electrical properties and the light trapping properties indicated that the sample A4 is an ideal transparent conductive film for amorphous silicon solar cells.
For comparison, cell A using SnO$_2$:F and cell B with ZnO:Al films of sample A4 as transparent conductive electrodes is fabricated, respectively. As buffer layer a µc-Si:H layer is inserted between ZnO:Al layer and p-SiC:H layer for cell B. The I-V curves of the two type solar cells are shown in figure 4. It can be seen that efficiency increases from 7.6% for the SnO$_2$:F TCO to 8.3% for the ZnO:Al /µc-Si:H TCO. The results indicated that the ZnO:Al /µc-Si:H films with pyramid-shaped textured structure as front electrode can improve the cell performance compared with that of SnO$_2$:F. Meanwhile, µc-Si:H, as a buffer layer, can overcome the higher contact potential barrier of ZnO:Al /p-a-SiC:H.

4. Conclusions
The following results have been obtained: (1) the pyramid-like textured ZnO:Al films were prepared directly by magnetron sputtering through adding negative bias voltage and controlling the sputtering parameters properly. (2) when the pyramid-like textured ZnO:Al film was used as a front electrode transparent conducting oxide layer for a-Si:H solar cells, a µc-Si:H layer was inserted between ZnO:Al and p-a-SiC:H, and it is in favor to the improvement of solar cell performance.

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References
[1] Berginski M, Hüpkes J, Reetz W, Rech B and Wuttig M 2008 Thin Solid Films 516 5836
[2] Groenen R, Linden J L and van Lierop H R M 2001 Applied Surface Science 173 40
[3] Schropp R E I, Li H and Franken R H J 2009 Solar Energy Materials & Solar Cells 93 1129
[4] Hu Y H, Wang L F and Xu H J 2010 Proc. Int. Conf. on Advanced Optical Manufacturing and Testing Technologies 2010 (Dalian) vol. 7658 (Dalian: SPIE proc) p. 7658E-1
[5] Swanepoel R 1983 J. Phys. E: Sci. Instrum. 16 1214