

新規アルミニウム添加酸化亜鉛系材料の開発と 太陽電池への応用

倉 持 豪 人^{*1}
 秋 池 良^{*1}
 飯 草 仁 志^{*1}
 玉 野 公 章^{*1}
 内 海 健 太 郎^{*1}
 渋谷 見 哲 夫^{*1}
 Porponth Sichanugrist^{*2}
 小長井 誠^{*2}

Development of Novel Aluminum - Doped Zinc Oxide Material and Its Application to Solar Cells

Hideto KURAMOCHI
 Ryo AKIIKE
 Hitoshi IIGUSA
 Kimiaki TAMANO
 Kentaro UTSUMI
 Tetsuo SHIBUTAMI
 Porponth SICHANUGRIST
 Makoto KONAGAI

This study addresses the electrical and optical properties, durability under high-humidity condition, and surface morphology of the novel aluminum-doped zinc oxide (AZO) films formed by DC magnetron sputtering. These novel AZO films showed higher transmittance in the near-infrared area and good durability under 85°C-85%RH condition. These novel films also had a higher haze value after wet chemical etching than normal AZO films. The haze value of the novel AZO films was higher than that of the normal AZO films; their values are 90% at 550 nm and 60% at 800 nm. Furthermore, the novel AZO films were applied in amorphous Si (a-Si) single-type solar cells as the front electrode. The short-circuit current of the solar cell using the novel AZO films was higher than that of the solar cell using the normal AZO films. As an optimization-based result, an efficiency as high as 10.2% was obtained, showing that the novel AZO films are a promising material for the front electrode of a-Si solar cells.

1. Introduction

Transparent conductive oxide (TCO) films are necessary as front electrode for most thin film solar

cells. They provide low electrical and optical losses, and fulfil in most cases additional optical function such as light scattering to improve the performance of these solar cells¹⁾. Additionally, the durability of TCO films is important for stabilizing the performance of such cells.

It is known that TCO films with a textured surface

* 1 東京研究所

* 2 東京工業大

can scatter light at the interface between TCO and Si layers². The degree of light scattering property can be represented by haze value, which should be increased to further enhance the light scattering property. It is well known that the haze value of TCO films is strongly affected by their surface morphology³.

Typically, fluorine-doped tin oxide (FTO) films⁴ and aluminum-doped zinc oxide (AZO) films⁵ formed by magnetron sputtering, gallium-doped zinc oxide (GZO) films⁶ formed by magnetron sputtering or boron-doped zinc oxide (BZO) films⁷ formed by low-pressure chemical vapour deposition (LPCVD) are used as thin-film Si solar cells. Conductive zinc oxide films such as AZO films and BZO films have attracted attention as front TCO films because it is easy to modify their surface morphology by selecting their deposition technique and conditions, and by using post-treatment conditions⁸⁻¹⁰. Furthermore, AZO, GZO or BZO films are high stability against hydrogen plasma as compared with FTO films¹¹. However, the stability of AZO, GZO or BZO film properties under 85°C -85%RH condition is inferior to that of FTO film properties¹².

Some deposition techniques for preparing conductive zinc oxide films have been reported. Among the various deposition techniques, the main process is sputtering using ceramic targets because it has an advantage of the reliable control of film properties and film thickness.

Berginski et al.¹³ have reported the effect of substrate temperature during RF magnetron sputtering deposition, the aluminum content of AZO targets, and film surface morphology after wet etching. According to their report, the substrate temperature in sputtering should be over 300 °C for a high haze value of approximately 5% at 1000 nm. However, a substrate temperature of more than 300 °C is very high because it is difficult to select the materials for the sputtering system. Therefore, it is necessary to satisfy the high haze value at a substrate temperature below 200°C .

Jorj and coworkers^{14,15} have prepared an AZO film by RF sputtering using a ZnO target doped with 0.5 or 1.0 wt% Al₂O₃. The AZO film with a HCl etching time of 50 s has a high haze value of approximately 60% at 550 nm. Furthermore, a higher haze value of approximately 70% has been obtained with additional HF etching.

In contrast, it is known that it is difficult to achieve a good balance between high transmittance and

high durability for AZO films^{16,17}. A film with a lower aluminum doping level has good transmittance, but its durability is poor.

In this work, we have developed novel AZO films, named AZO-X and AZO-HX films, formed by DC magnetron sputtering. After film deposition, wet chemical etching using HCl was employed to modify the surface morphology of the films. As the results, we have achieved such films formed on a flat substrate with a higher haze value than AZO film for excellent light scattering. And then we have applied these films to the front electrodes of amorphous Si solar cells and achieved high cell performance.

2. Experimental Procedure

[1] Preparation of TCO films

The AZO films were deposited on the glass substrate (Corning EAGLE XG) by DC magnetron sputtering using AZO targets. The alumina content was 1.0 or 2.0 wt%. The novel AZO films were also deposited by DC magnetron sputtering using the novel AZO targets. These targets are ZnO targets doped with Al and other elements.

The deposition was carried out at a substrate temperature of 200°C , a discharge power density of 3.7 W/cm², and an argon deposition pressure of 0.4 Pa. The base pressure just before sputtering was about 1.0×10^5 Pa.

The thickness, resistivity, and optical transmittance of the films were measured using a surface profiler, a Hall effect measurement system at room temperature, and a spectrophotometer in air, respectively. The rate of the resistivity change of these films was evaluated under 85°C -85%RH condition. By wet chemical etching using diluted HCl (0.5%), the surface morphology of the films was modulated into a textured surface structure.

After wet chemical etching, the surface morphology, film thickness, and roughness of these films were evaluated using scanning electron microscopy (SEM), surface profilometry, and atomic force microscopy (AFM), respectively. The total and diffuse transmittances of the textured films were measured with a spectrophotometer in air. The haze value is defined as the ratio of diffuse transmittance to total transmittance.

[2] Preparation of amorphous Si solar cell

p-i-n-type amorphous Si:H single-junction thin-film solar cells were fabricated using the etched films as the front TCO films. The structure of these solar cells was glass substrate/textured TCO films/p-i-n type amorphous Si:H/B-doped ZnO/Ag/Al. The test cells had an area of 0.09 cm². The photocurrent density - voltage (J-V) characteristics of the fabricated cells were measured at 25 °C under 1 sun (AM 1.5, 100 mW/cm²) solar simulator radiation. The spectral response of these cells was evaluated using quantum efficiency (QE) measurement.

3. Result and Discussion

[1] Resistances, transmittances, and durabilities of the formed AZO films

The transmittance spectra of formed AZO films are shown in Fig. 1. The transmittance in the near-infrared areas was decreased with increasing alumina contents. Fig. 2 shows the durability test result of AZO films under 85°C - 85%RH condition. The rate of resistivity change was increased with decreasing alumina contents. That phenomenon means that the durability was inferior.

Thus, it is difficult to achieve a good balance between transmittance in the near-infrared areas and durability. However, our developed material, novel AZO (AZO-X) film, achieved a good balance between transmittance in the near-infrared areas and durability.

Minami and coworkers¹⁸⁻²¹⁾ have reported that improving the crystallinity of as-deposited polycrystalline AZO films is important for improving the resistivity stability, and that their resistivity increase with exposure time in a high-humidity environment

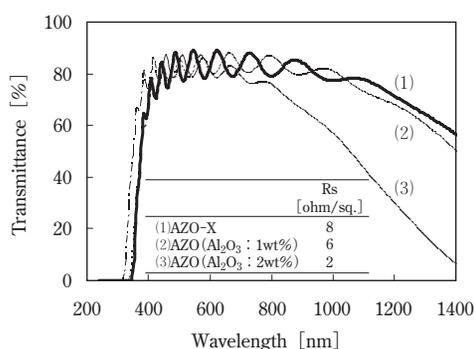


Fig. 1 Transmittance spectra of formed AZO films. (Film thickness : 1000nm)

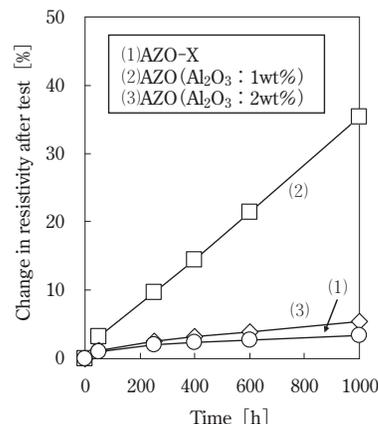


Fig. 2 Durability for formed AZO films. (Film thickness : 1000nm)

is attributable to grain boundary scattering, on the basis of experimental and theoretical considerations²²⁾ concerning the relationship between carrier concentration and Hall mobility. Thus, the durability-enhancing effect of AZO-X film is thought to be due to the crystallinity improvement of as-deposited films achieved by doping with Al and other elements.

[2] Resistances, transmittances, and durabilities of the texture-etched AZO films

The resistances and transmittances of the texture-etched AZO films and FTO film (CVD) are shown in Table 1 and Fig. 3. With increasing alumina content, the sheet resistance decreased, and the transmittance in near-infrared areas also decreased. In this case, increasing alumina content leads to a higher carrier concentration and the carrier concentration of the films affects sheet resistance and transmittance²³⁾. That is, increasing carrier concentration results in a lower sheet resistance and a lower transmittance in near-infrared areas. The novel texture-etched AZO films, named AZO-X and AZO-HX films, have resistances and transmittances that are approximately the same as those of the AZO (Al₂O₃ : 1 wt%) film and FTO film (CVD).

Table 1 Resistivity of texture-etched AZO films.

	Film thickness [nm]	Rs [ohm/ sq.]
(1)AZO (Al ₂ O ₃ : 1wt%)	700	9
(2)AZO (Al ₂ O ₃ : 2wt%)	700	4
(3)AZO-X	700	11
(4)AZO-HX	700	11
(5)SnO ₂ : F(CVD)	1000	10

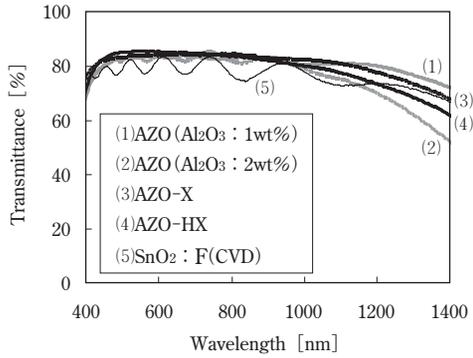


Fig. 3 Transmittance of texture-etched AZO films.

Fig. 4 shows the relationship between the transmittance at 1000nm and the durability test result of the textured films under 85°C -85%RH condition at 1000h. After wet chemical etching, the novel texture-etched AZO films, named AZO-X and AZO-HX films, achieved good balance between transmittance in near-infrared areas and durability. The durability of these films was comparable to that of the FTO film (CVD).

As described above, the novel texture-etched AZO films showed the excellent properties of transmittance and durability after wet chemical etching.

[3] Surface morphology of the textured AZO films

The surface of the fabricated AZO films was modulated into a textured surface structure by wet chemical etching using diluted HCl.

Fig. 5 shows the surface morphology of the various films measured by SEM. The rms roughness of each film is shown in Fig. 5. The surface morphology of the novel AZO films showed a larger crater than the other films. Furthermore, the rms roughness of the AZO-HX film increased up to 172 nm. Figure 6 shows the haze value spectra of the various films. The haze value of

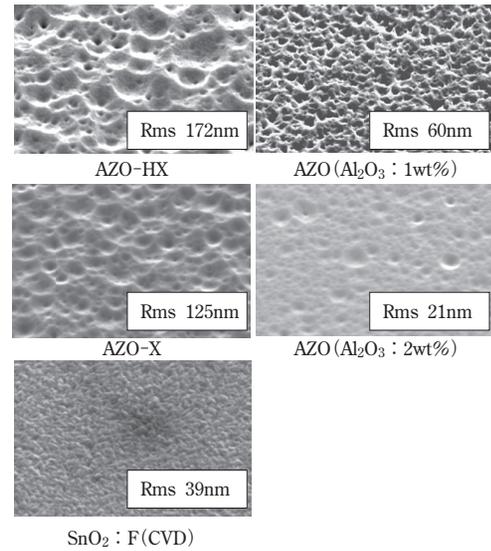


Fig. 5 SEM image of texture-etched AZO films.

the novel AZO films were higher than that of the other films; their values of the AZO-HX film are 90% at 550 nm and 60% at 800 nm. As shown in Fig. 5, the high rms contributed to the high haze value.

[4] Performance of amorphous Si solar cell

The novel films have been applied as the front electrode of a-Si single-type solar cells. Fig. 7 shows the relationship between the haze value at 800 nm and the typical parameters of a-Si single cells. As can be seen in this figure, the open-circuit voltages (V_{oc}) were approximately the same for all the cells, and the short-circuit current (J_{sc}) increased with increasing haze value, as expected. There is a positive correlation between J_{sc} and the haze value at 800 nm. Masumo et al. reported that the short-circuit current of the cells peaks at approximately 40% haze value at 800 nm²⁴⁾. However, that result was based on a tandem-type solar

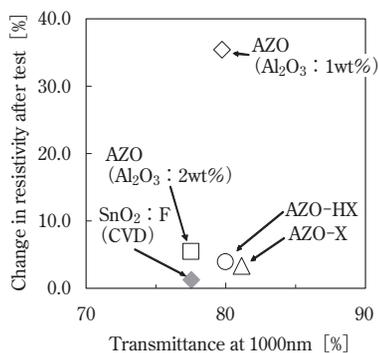


Fig. 4 Relationship between the transmittance at 1000nm and the durability test result.

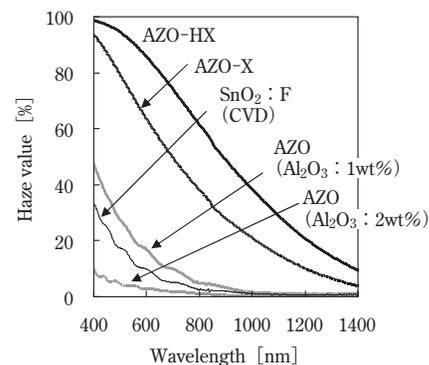


Fig. 6 Haze value spectra of texture-etched AZO films.

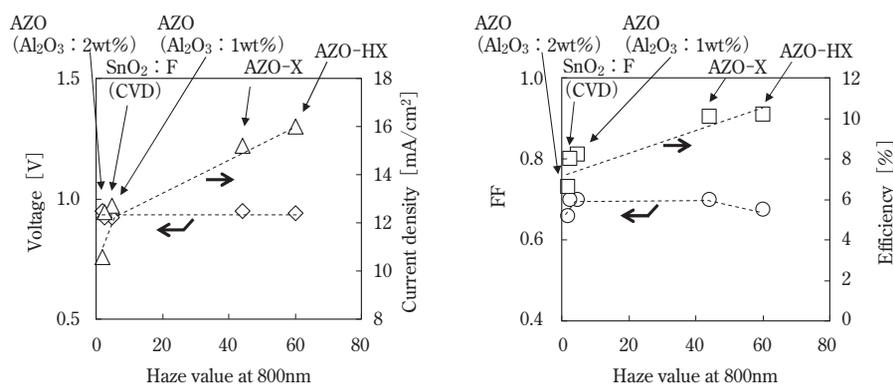


Fig. 7 Relationship between the haze value at 800nm and the typical parameter of a-Si single cells.

cell that required the current balance of each cell.

In contrast, as shown in Fig. 7, our results showed that J_{sc} could be increased even when the haze value at 800 nm increased up to 60% when AZO-HX was applied as the front electrode.

Fig. 7 shows these efficiencies of a-Si single cells. A high efficiency of 10.2% was achieved in the AZO-HX film. A higher efficiency with better FF can be achieved by optimizing the nature of contact between the AZO-HX film and the p-layer of the cell.

4. Conclusions

We have developed the novel AZO films for solar cell. The novel AZO films achieved good balance between transmittance in near-infrared areas and durability under 85 °C -85%RH condition. After wet chemical etching, the surface of the novel AZO films showed a larger crater than the other films. The haze value of the novel AZO films were higher than that of the other films fabricated with an additional wet etching process.

Furthermore, the novel AZO films were applied in amorphous Si single-type solar cells as the front electrode. The short-circuit current of the solar cell using the novel AZO films were higher than that of the solar cell using the other films.

Finally, as an optimization-based result, an efficiency as high as 10.2% was obtained, showing that the novel AZO films are a promising material for the front electrode of a-Si solar cells.

These features of the novel AZO films are suitable for the application to other-type solar cells.

References

- 1) A. V. Shah, J. Meier, F. Meillaud, J. Guillet, D. Fischer, C. Droz, X. Niquille, S. Faye, and M. Vanecek, *J. Non-Cryst. Solids*, 338-340, 639 (2004)
- 2) J. Muller, B. Rech, J. Springer, and M. Vanecek, *Sol. Energy Mater. Sol. Cells*, 77, 917 (2004)
- 3) L. Yang and L. F. Chen, *MRS Proc.*, 336, 669 (1994)
- 4) K. Sato, Y. Gotoh, Y. Hayashi, K. Adachi, and H. Nishimura, *Rep. Res. Lab. Asahi Glass Co., Ltd.*, 40, 233 (1990)
- 5) O. Kluth, B. Rech, L. Houben, S. Wieder, G. Schope, C. Beneking, H. Wagner, A. Löffl, and H. W. Schock, *Thin Solid Films*, 351, 247 (1999)
- 6) M. Miyazaki, K. Sato, A. Mitsui, and H. Nishimura, *J. Non-Cryst. Solids*, 218, 323 (1997)
- 7) S. Fay, S. Dubail, U. Kroll, J. Meier, Y. Ziegler, and A. Shah, *Proc. 16th EU-PVSEC*, p. 361 (2000)
- 8) K. Tabuchi, W. W. Wenas, A. Yamada, M. Konagai, and K. Takahashi, *Jpn. J. Appl. Phys.*, 32, 3764 (1993)
- 9) Y. Nasuno, M. Kondo, and A. Matsuda, *Jpn. J. Appl. Phys.*, 40, L303 (2001)
- 10) J. Bailat, D. Domine, R. Schluchter, J. Steinhauser, S. Fay, F. Freitas, C. Bucher, L. Feitknecht, X. Niquille, T. Tschärner, A. Shsh, and C. Ballif, *Proc. 4th World Conf. Photovoltaic Energy Conversion*, p. 1533 (2006)
- 11) H. C. Weller, R. H. Mauch, and G. H. Bauer, *Proc. 22nd IEEE PVSC*, p. 1290 (1991)
- 12) F. J. Pern, R. Noufi, X. Li, C. DeHart, and B. To, *Proc. 33rd IEEE PVSC*, Print ISBN: 978-1-4244-1640-0 (2008)

- 13) M. Berginski, J. Hupkes, M. Schulte, G. Schope, H. Stiebig, B. Rech, and M. Wuttig, *J. Appl. Phys.*, 101, 074903 (2007)
- 14) J. I. Owen, J. Hupkes, E. Bunte, S. E. Pust, and A. Gordijn, *25th European Photovoltaic Solar Energy Conf.*, p. 2951 (2010)
- 15) J. I. Owen, J. Hupkes, H. Zhu, E. Bunte, and S. E. Pust, *Phys. Status Solidi A*, 208, 109 (2011)
- 16) H. Kuramochi, H. Iigusa, R. Akiike, K. Matsumaru, K. Utsumi, and T. Shibutami, *TOSOH Res. Technol. Rev.*, 54, 35 (2010)
- 17) H. Kuramochi, R. Akiike, H. Iigusa, K. Utsumi, T. Shibutami, P. Sichanugrist, and M. Konagai, *37th IEEE PVSC*, p. 3023 (2011)
- 18) T. Minami, *Thin Solid Films*, 516, 5822 (2008)
- 19) T. Minami, *Ceramics*, 42, 26 (2007)
- 20) T. Minami, T. Miyata, Y. Ohtani, and T. Kuboi, *Phys. Status Solidi Rapid Res. Lett.*, 1, R31 (2007)
- 21) T. Miyata, Y. Ohtani, T. Kuboi, and T. Minami, *Thin Solid Films*, 516, 1354 (2008)
- 22) J. Y. W. Seto, *J. Appl. Phys.*, 46, 5247 (1975)
- 23) I. Hamberg and C. G. Granqvist, *J. Appl. Phys.*, 60, R123 (1986)
- 24) K. Masumo, M. Kambe, K. Chonan, A. Takahashi, and E. Shidoji, *37th IEEE PVSC*, p. 795 (2011)