

Article



Aluminum–Titanium Alloy Back Contact Reducing Production Cost of Silicon Thin-Film Solar Cells

Hsin-Yu Wu¹, Chia-Hsun Hsu², Shui-Yang Lien^{2,*} and Yeu-Long Jiang¹

- ¹ Graduate Institute of Optoelectronic Engineering and Department of Electrical Engineering, National Chung Hsing University, Taichung 40227, Taiwan; xinmarchentic@gmail.com (H.-Y.W.); yljiang@nchu.edu.tw (Y.-L.J.)
- ² Department of Materials Science and Engineering, Da-Yeh University, Changhua 51591, Taiwan; cstcaptive@gmail.com
- * Correspondence: syl@mail.dyu.edu.tw; Tel.: +886-404-851-1888 (ext. 1760)

Academic Editor: Senthilarasu Sundaram Received: 12 August 2016; Accepted: 16 November 2016; Published: 22 November 2016

Abstract: In this study, metal films are fabricated by using an in-line reactive direct current magnetron sputtering system. The aluminum–titanium (AlTi) back contacts are prepared by changing the pressure from 10 mTorr to 25 mTorr. The optical, electrical and structural properties of the metal back contacts are investigated. The solar cells with the AlTi had lower contact resistance than those with the silver (Ag) back contact, resulting in a higher fill factor. The AlTi contact can achieve a solar cell conversion efficiency as high as that obtained from the Ag contact. These findings encourage the potential adoption of AlTi films as an alternative back contact to silver for silicon thin-film solar cells.

Keywords: silicon thin-film solar cells; aluminum-titanium (AlTi) alloy; contact resistance

1. Introduction

Silicon thin-film solar cells have received much attention, and appear to be promising alternatives to crystalline silicon solar cells, which are dominant in photovoltaic power generation. The main benefits of silicon thin-film solar cells over crystalline silicon solar cells are cost-effective fabrication, compatibility with various flexible substrates, reliable large-area module encapsulation, low temperature coefficient, very low weight per unit power and aesthetic design for building integrated photovoltaic applications [1–3]. To achieve silicon thin-film solar cells with high short circuit currents and conversion efficiencies, the incident light has to be efficiently scattered and diffracted. Conventional solar cells normally achieve light trapping with three methods, a textured front surface, a highly reflective rear reflector and an antireflection coating [4-6]. Silver (Ag) is the conventional metal for back reflectors, but its drawbacks are high price, low adhesion and agglomeration behavior [7–9]. Therefore, researchers are searching for a cheaper alternative. Aluminum (Al) is a good candidate owing to its low price and good adhesion [10], but it has lower reflectance and conductivity than Ag. Metallic impurities such as titanium (Ti), chromium and vanadium can be added to the Al films to improve the thermal stability, conductivity and ohmic contact [11–14]. For this purpose, aluminum–titanium (AlTi) film, which is 1/100 of the cost of Ag, is proposed as a back contact for p-i-n silicon thin-film solar cells. The AlTi thin films are prepared by a direct current (DC) magnetron sputter system. The effects of sputtering pressure on the optical and electrical properties of AlTi films are investigated. Finally, the performance of the solar cells with the AlTi back contact is compared to the device with the traditional Ag contact.

2. Experimental Details

The AlTi and Ag films were prepared on glass substrates by an in-line reactive DC magnetron sputtering system (LJ UHV Technology Co., Ltd., Hsinchu, Taiwan). The composition of the AlTi target was 99 wt% Al and 1 wt% Ti. The base pressure of the deposition chamber was 5×10^{-7} Torr; the DC power was 200 W; the argon (Ar) gas flow rate was 20 sccm, and the substrate was at room temperature. The dependence of the sputtering pressure changing from 10 mTorr to 25 mTorr on the properties of the sputtered AlTi films was investigated. The structure of the a-Si:H thin-film solar cell was glass/fluorine-doped tin dioxide (SnO₂:F)/p-a-Si:H/i-a-Si:H/n-a-Si:H/(gallium, Al)-doped zinc oxide (GAZO)/metal back contact. The GAZO was deposited by radiofrequency (RF) magnetron sputtering with a thickness of 80 nm. The p-, i- and n-a-Si:H layers, with a total thickness of 288 nm, were deposited by a plasma-enhanced chemical vapor deposition. The contact resistance between back contact and GAZO was measured using the transmission line model (TLM) method [15–17]. The optical reflectance of the films was measured with an ultraviolet-visible spectrophotometer (UV-VIS, Hong-Ming Technology Co., Ltd., Taipei, Taiwan). The refractive index was determined by a spectroscopy ellipsometry. The electrical resistivity was measured using a four-point probe method. The cross-section microstructure of the solar cells was examined by a scanning electron microscopy (SEM, JEOL Ltd., Tokyo, Japan). Finally, the current-voltage (I-V) characteristics and external quantum efficiency (EQE) of the devices were measured by a solar simulator under AM1.5G (100 mW/cm^2) conditions.

3. Results and Discussion

Figure 1a shows the optical reflectance of the AlTi films prepared at different pressures. The reflectance of the AlTi films decreases as the pressure increases from 10 mTorr to 25 mTorr. The average reflectance at wavelengths of 400–800 nm at 10 mTorr is 89.8%, which is about 7% lower than that of the Ag film. The reflectance in the short wavelengths should have insignificant effects on the solar cell performance, since the light will be nearly absorbed before reaching the rear contact. For long wavelengths (650–800 nm), the AlTi films have a reflectance of around 85%–88%, while the Ag film has a reflectance of around 97%. The lower reflectance of the AlTi films at higher pressure can be explained by more collision among sputtered atoms and argon ions, lowering the density of the sputtered films [18]. This is also reflected by the measurement of the refractive index, as shown in Figure 1b. The AlTi film at 10 mTorr has the highest refractive index value, indicating that it has the densest film structure.



Figure 1. (a) Optical reflection and (b) refractive index of aluminum–titanium (AlTi) films prepared with different pressures.

Figure 2 shows the resistivity of AlTi films prepared with different pressures. It can be seen that the resistivity of the AlTi films increases from $7.94 \times 10^{-6} \Omega$ -cm to $11.8 \times 10^{-6} \Omega$ -cm with the pressure

increasing from 10 mTorr to 25 mTorr. The AlTi film with a pressure of 10 mTorr has a minimum electrical resistivity, and this can also be linked to its dense structure. In comparison, the resistivity of the Ag film is $4.13 \times 10^{-6} \Omega$ -cm. Overall, the AlTi and Ag films have low resistivity at a level of $10^{-6} \Omega$ -cm, so their bulk resistance should make an insignificant contribution to the total device series resistance.



Figure 2. Resistivity of AlTi films prepared at different pressures.

The contact quality between the metal and semiconductor device is important when considering an electrode material. In this work, the back electrode is covered on the GAZO, so the contact resistance R_c between these two layers is determined by using the TLM method with the following equation [19]:

$$R_{\rm t} = 2R_{\rm c} + \frac{R_{\rm SH} \cdot d}{W} \tag{1}$$

where R_t denotes the total resistance between any two contacts (of width *W*) separated by a distance *d*, and R_{SH} is the sheet resistance of the GAZO film. R_c can be obtained from the *y*-axis interception. Figure 3 shows R_c as a function of the sputtering pressure, where R_c increases with the increasing pressure. The minimum R_c at 10 mTorr is $3.0 \times 10^{-3} \Omega$, which is lower than that $(7.84 \times 10^{-3} \Omega)$ using Ag/GAZO. The contact resistance can be associated with the work function (Φ) of the metal films and the adhesion at the contact interface. As the metal films are responsible for collecting electrons in a device, they require a work function close to or smaller than the electron affinity of the GAZO films [19]. The Ag ($\Phi = 4.26 \text{ eV}$) and AlTi ($\Phi = 4.28 \text{ eV}$) films are all available with work functions lower than GAZO ($\Phi = 4.45 \text{ eV}$) to achieve the *n*-type ohmic contact. Consequently, the adhesion factor, rather than the work function, might be the reason for the lower contact resistance of the AlTi film compared to the Ag film.



Figure 3. Contact resistance for metal/GAZO interface as a function of sputtering pressure.

Figure 4 shows the *I-V* curves of the solar cells with AlTi back contacts prepared at different pressures. Table 1 summarizes the photovoltaic parameters of the solar cells such as open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}), fill factor (*FF*) and conversion efficiency (η). The V_{oc} values do not change significantly for all the AlTi and Ag films. J_{sc} and *FF* both decrease with the

increasing pressure, due to the reduced reflectance and increased resistivity, respectively. The cell with the AlTi deposited at 10 mTorr has the highest conversion efficiency of 8.15% with $V_{oc} = 0.84$ V, $J_{sc} = 13.7$ mA/cm² and FF = 0.71. This conversion efficiency value is even higher than that of the cell with the Ag film, owing to the greater *FF* compensating for the lower J_{sc} .



Figure 4. I-V curves of p-i-n solar cells with AlTi back contacts prepared at different pressures.

Pressure (mTorr)	$V_{\rm oc}$ (V)	$J_{\rm sc}$ (mA/cm ²)	FF	η (%)	$R_{\rm oc}\left(\Omega\right)$
Ag	0.84	13.93	0.68	8.03	106.0
10	0.84	13.70	0.71	8.15	74.0
15	0.84	13.31	0.71	7.99	82.3
20	0.84	13.05	0.71	7.82	88.4
25	0.84	12.68	0.69	7.38	99.1

Table 1. Performance of p-i-n solar cells prepared at different pressures. FF: fill factor.

Figure 5 shows the EQE curves of the p-i-n silicon thin-film solar cells with AlTi back contacts prepared at different pressures. The EQE values are similar in the short-wavelength region (400–550 nm) in all cases, as the short-wavelength light is nearly completely absorbed before reaching the back contact. The EQE in the long-wavelength region decreases with the increasing deposition pressure. The cell with the Ag back contact has the highest long-wavelength EQE response, due to the higher reflectance. Comparing the best AlTi film (at 10 mTorr) to the Ag film, the lower EQE of the AlTi back contact only leads to a 1.6% loss in J_{sc} . Therefore, in combination with the IV result, the present study shows that the reduction in the contact resistance is more helpful than the improvement in the back surface reflectance for increasing the solar cell efficiency. The AlTi back contacts demonstrate high potential for application in thin-film solar cells.



Figure 5. External quantum efficiency (EQE) curves of p-i-n solar cells with Ag and AlTi films prepared at different pressures.

Figure 6 illustrates the cross-section SEM image of the solar cells with the AlTi back contact. The textured SnO₂:F, in order to scatter light to increase the light traveling path in the absorber, is observed. The thicknesses of the rough SnO₂:F thick film and a-Si:H device are 800 nm and 280 nm, respectively. The interfaces in the solar cells closely follow the surface profile of the SnO₂:F layer. The thin, crystalline GAZO layer with a thickness of about 80 nm is clearly seen on the a-Si:H, and the AlTi film is covered at the top. Sputtering the back contact could lead to voids or cracks at the valleys or mountains of the textured surface, but those are not observable at the interface. This result confirms that good adhesion and coverage of the AlTi film lead to good contact properties between AlTi and GAZO films.



Figure 6. Cross-section scanning electron microscopy (SEM) image of p-i-n silicon thin-film solar cell with AlTi back contact.

4. Conclusions

In this study, low-cost AlTi films as the back contact of p-i-n silicon thin-film solar cells are prepared. The films achieved a high average reflectance of 90% in the wavelength range of 400–800 nm, and a low resistivity of $7.9 \times 10^{-6} \Omega$ -cm could be obtained. The optimal AlTi back contact has a short-circuit current density of 13.7 mA/cm^2 , which is slightly lower than the 13.93 mA/cm^2 obtained from the Ag back contact. However, the AlTi back contact has a fill factor of 0.71, which is higher than the 0.68 for the Ag back contact. Thus, the AlTi back contact performs as well as the Ag back contact. In conclusion, AlTi metal alloys are a promising alternative to Ag metal as a back contact for silicon thin-film solar cells. The AlTi back contact can achieve low cost and high efficiency. Future work will examine the use of AlTi for high-efficiency Si-based tandem solar cells.

Acknowledgments: This work is sponsored by the Ministry of Science and Technology of the Republic of China under contract No. 105-2632-E-212-001- and 104-2221-E-212-002-MY3.

Author Contributions: Hsin-Yu Wu and Shui-Yang Lien designed the experiments; Hsin-Yu Wu performed the experiments and measurements; Hsin-Yu Wu, Chia-Hsun Hsu, Shui-Yang Lien and Yeu-Long Jiang analyzed the results; Hsin-Yu Wu and Chia-Hsun Hsu wrote the paper.

Conflicts of Interest: The authors declare no conflict of interest.

References

- Liu, H.; Huang, Q.; Hou, G.; Jiao, B.; Wang, G.; Zhang, W.; Zhang, D.; Zhao, Y.; Zhang, X. Cost-effective hollow honeycomb textured back reflector for flexible thin film solar cells. *Sol. Energy Mater. Sol. Cells* 2016, 155, 128–133. [CrossRef]
- Cashmore, J.S.; Apolloni, M.; Braga, A.; Caglar, O.; Cervetto, V.; Fenner, Y.; Goldbach-Aschemann, S.; Goury, C.; Hötzel, J.E.; Iwahashi, T.; et al. Improved conversion efficiencies of thin-film silicon tandem (MICROMORPHTM) photovoltaic modules. *Sol. Energy Mater. Sol. Cells* 2016, 144, 84–95. [CrossRef]

- Jung, K.H.; Yun, S.J.; Lee, S.H.; Lee, Y.J.; Lee, K.S.; Lim, J.W.; Kim, K.B.; Kim, M.; Schropp, R.E.I. Double-layered Ag–Al back reflector on stainless steel substrate for a-Si:H thin film solar cells. *Sol. Energy Mater. Sol. Cells* 2016, 145, 368–374.
- 4. Green, M.A. Silicon solar cells: Evolution, high-efficiency design and efficiency enhancements. *Semicond. Sci. Technol.* **1993**, *8*, 1–12. [CrossRef]
- 5. Cho, J.S.; Yoo, J.; Park, J.H.; Shin, K.; Yoon, K.H. Fabrication of dc sputtered Ag/Al:Si bilayers with improved optical reflectance. *Thin Solid Film* **2013**, *529*, 45–49. [CrossRef]
- Palanchoke, U.; Kurz, H.; Noriega, R.; Arabi, S.; Jovanov, V.; Magnus, P.; Aftab, H.; Salleo, A.; Stiebig, H.; Knipp, D. Tuning the plasmonic absorption of metal reflectors by zinc oxide nano particles: Application in thin film solar cells. *Nano Energy* 2014, *6*, 167–172. [CrossRef]
- 7. Kim, M.; Kim, K.B.; Lee, D.; Lee, S.N.; Lee, J.M. Effects of rapid thermal annealing for E-beam evaporated Ag films on stainless steel substrates. *Surf. Coat. Technol.* **2015**, *278*, 18–24. [CrossRef]
- 8. Kawamura, M.; Zhang, Z.; Kiyono, R.; Abe, Y. Thermal stability and electrical properties of Ag–Ti films and Ti/Ag/Ti films prepared by sputtering. *Vacuum* **2013**, *87*, 222–226. [CrossRef]
- 9. Sugawara, K.; Kawamura, M.; Abe, Y.; Sasaki, K. Comparison of the agglomeration behavior of Ag(Al) films and Ag(Au) films. *Microelectron. Eng.* **2007**, *84*, 2476–2480. [CrossRef]
- Wang, G.H.; Shi, C.Y.; Zhao, L.; Yan, B.J.; Wang, G.; Chen, J.W.; Li, Z.C.; Diao, H.W.; Wang, W.J. Improved aluminum-doped ZnO/metal back reflector for p-i-n amorphous silicon germanium thin film solar cells. *Thin Solid Films* 2013, 534, 591–593. [CrossRef]
- 11. Mondolfo, L.F. Aluminium Alloys: Structure and Properties; Butterworths: London, UK, 1976.
- 12. Auchet, J.; Bretonet, J.L. Experimental measurement of resistivity of aluminium based liquid alloys. *Rev. Int. Hautes Temper. Refract.* **1990**, *26*, 181–192.
- Johnson, B.J.; Capano, M.A. The effect of titanium on Al–Ti contacts to p-type 4H-SiC. *Solid-State Electron*. 2003, 47, 1437–1441. [CrossRef]
- 14. Dobos, L.; Pécz, B.; Tóth, L.; Horváth, Z.J.; Horváth, Z.E.; Tóth, A.L.; Poisson, M.A. Annealed Ti/Cr/Al contacts on n-GaN. *Vacuum* **2014**, *100*, 46–49. [CrossRef]
- 15. Schroder, D.K. Semiconductor Material and Device Characterization, 2nd ed.; Wiley: New York, NY, USA, 1998.
- 16. Foresi, J.S.; Moustakas, T.D. Metal contacts to gallium nitride. *Appl. Phys. Lett.* **1993**, *62*, 2859–2861. [CrossRef]
- 17. Sawdai, D.; Pavlidis, D.; Cui, D. Enhanced transmission line model structures for accurate resistance evaluation of small-size contacts and for more reliable fabrication. *IEEE Trans. Electron Device* **1999**, *46*, 1302–1311. [CrossRef]
- Hsu, F.H.; Wang, N.F.; Tsai, Y.Z.; Chuang, M.C.; Cheng, Y.S.; Houng, M.P. Study of working pressure on the optoelectrical properties of Al–Y codoped ZnO thin-film deposited using DC magnetron sputtering for solar cell applications. *Appl. Surf. Sci.* 2013, 280, 104–108. [CrossRef]
- 19. Brillson, L.J.; Lu, Y. ZnO Schottky barriers and Ohmic contacts. J. Appl. Phys. 2011, 109. [CrossRef]



© 2016 by the authors; licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC-BY) license (http://creativecommons.org/licenses/by/4.0/).