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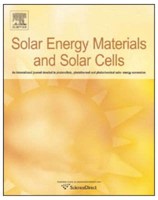

Tungsten doped indium oxide film: Ready for bifacial copper metallization of silicon heterojunction solar cell

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ABSTRACT

Tungsten doped indium oxide (IWO) film was deposited by reactive plasma deposition technology for a-Si:H/c-Si heterojunction (SHJ) solar cell. The average transmittance and absorption of IWO film from 350 to 1200 nm wavelength was 88.33% and 2.16% respectively. The hall mobility is 77.8 cm^2/Vs, with a corresponding carrier concentration of 2.86E20 cm^{-3} and resistivity of 2.80$E-04$ Ω cm. Based on high-performance IWO film, the 5 in. SHJ solar cell with efficiency value of 22.03% and power of 3.37 W was obtained by electroplated copper metallization technology. Compared with screen printed SHJ solar cells, the fingers of electroplated cells show finer width, higher aspect ratio and lower series resistance, resulting in increased fill factor and higher efficiency. The long term stability test of copper electroplated cells reveal that IWO film has excellent stability at the solar cell modules' operating temperature and can prevent copper diffusion effectively, which makes copper metallization of high efficiency heterojunction solar cell possible.

1. Introduction

Silicon heterojunction (SHJ) solar cell has attracted extensive attention due to its excellent passivation, high efficiency, low process temperature and better temperature coefficient, compared to conventional crystalline solar cell [1–3]. Panasonic has presented its bifacial SHJ solar cell with the world's highest cell efficiency of 24.7% [4], and this record has been increased to 25.6% for back contact SHJ solar cell last year [5].

Typically, screen printing low temperature silver paste is the most common technique for SHJ solar cell's metallization. However, this process suffers from low aspect ratio, high contact resistance, high resistivity of low temperature silver paste and excessive shading and high price of silver [6]. Therefore, recent progresses dedicated to metallization of SHJ solar cells are utilizing electroplated copper to replace expensive silver paste as the electrode material, which benefits from reduced optical and electrical losses and can cut the production cost dramatically [7–11]. Hernandez et al. has presented the remarkable results on copper electroplated SHJ solar cell with an efficiency value of 24.2% (aperture area) [12], which are the highest copper electroplated cell for now and show promising application.

Transparent conductive oxide (TCO) film can be seen as the crucial factor to achieve high efficiency and long term stable SHJ solar cell with a copper metallization scheme. Due to the bifacial-ready symmetric structure, the metal electrodes should be deposited on TCO layers directly, while the diffusion of copper into silicon and the reaction with silicon cause electrical performance degradation [13]. In this category, tin-doped indium oxide (ITO) film is usually used with its unique characteristics combining high transparency, low resistivity and excellent adhesion toward metal contact and substrate, but also more absorption at long wavelength band [14–16]. Compared with ITO film, IWO film demonstrates higher mobility, more stable at high temperature and higher transmittance at NIR wavelength region [16–18]. Therefore, IWO film could be a perfect candidate for diffusion barrier, concurrently with contact layer and anti-reflection coating.

In this paper, we deposit IWO film for a-Si:H/c-Si heterojunction solar cell by reactive plasma deposition technology and employ electroplated copper to replace the screen printed silver paste. IWO film displays excellent stability and effective prevention of copper diffusion. The copper electroplated SHJ solar cell shows excellent properties and means great potential to achieve even higher efficiency after proper optimization.

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2. Experimental details

2.1. Preparation of SHJ substrates

The n-type c-Si (100) wafers with resistivity of 1–3 Ω cm were used as the substrates. The wet-chemical process was applied to remove saw damage and create a random pyramid surface texture. Both intrinsic and doped a-Si:H layers on the front and rear side were deposited for the emitter and back surface field by plasma enhanced chemical vapor deposition (PECVD), respectively. Then, tungsten doped indium oxide films, with the thickness of 80 nm on the front side and 60 nm on the rear side, were deposited by using a reactive plasma deposition (RPD) system installed with a 1 wt% WO_3-doped In_2O_3 target. The deposition was performed in 20% O_2/Ar mixture at the working pressure of 0.35–0.40 Pa. The substrate holder was maintained at 150 °C during the deposition and the tray speed is 13.8 mm/s. The detailed researches about IWO films could be found in our previous papers [18,19]. Besides, IWO films were deposited on the glass at the same condition to test optical and electrical properties.

2.2. Metallization of SHJ solar cells

Following RPD, the samples were sorted into two groups. Group A was metalized by electroplating Cu/Sn stack layer. Considering electroplating copper on IWO film directly is non-selective, photoresist and photo mask were used for both sides. The unexposed photoresist could then be developed easily to form designed finger pattern, when placed under a UV exposure machine. Thus, selective electroplating was achieved. Finally, photoresist was stripped to form copper electroplated SHJ solar cell. Group B was metalized by screen printing silver grids on both sides and annealed at 200 °C for 30 min.

2.3. Measurement systems

The optical transmittance spectra of IWO film was examined by a Perkin-Elmer Lambda UV/vis/NIR spectrophotometer at a wavelength range from 300 to 2400 nm. Hall measurements for the electrical resistivity, carrier concentration and mobility determination were accomplished at room temperature in an Ecopia HMS-5300 system. Spectroscopic ellipsometer (J. A. Wollam Co., Inc. M-2000) was used to measure the thickness of IWO film to match the thickness proper as an antireflection layer for SHJ solar cell. The geometries of grids were measured by a 3D microscope (Keyence). Finally, SHJ solar cells were characterized by using current–voltage (*I–V*) measurements and Suns-Voc system.

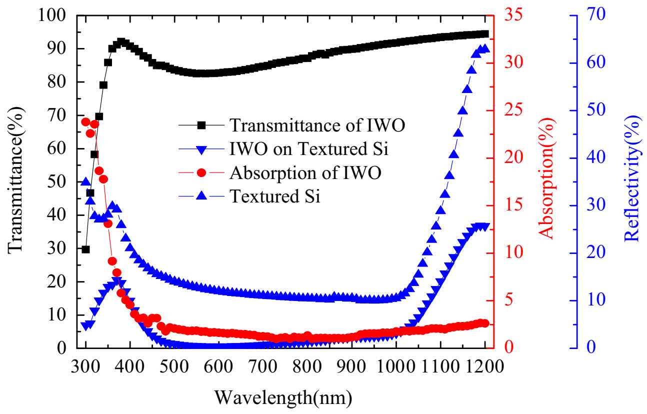


Fig. 1. Optical characteristics of IWO film.

Table 1
Optical and electrical properties of TCO films.

	Band gap (eV)	Mobility (cm^2/Vs)	Carrier concentration (cm^{-3})	Resistivity (Ω cm)	Refractive index @632.8 nm
IWO	3.82	77.80	2.86*E*20	2.80*E* – 04	1.99
ITO	3.89	38.24	7.59*E*20	2.14*E* – 04	1.97

3. Results and discussion

3.1. Optical and electrical characteristics of IWO film

The optical properties of IWO film's transmission, reflection and absorption are determined by its refraction index, extinction coefficient, band gap, which depend on its chemical composition and solid structure. According to Fig. 1, the average transmittance and absorption of IWO film from 350 to 1200 nm wavelength was 88.33% and 2.16% respectively, which indicate high transparency and low absorption. Considering the band gap of IWO film is 3.82 eV (seen in Table 1), the absorption at short wavelength remarkably increases due to the inter-band optical absorption [20], resulting in the rapid decrease of transmittance from 300 to 350 nm. IWO film was then deposited on textured silicon. Compared to textured silicon, the average reflectivity decreases obviously, from 11.56% to 1.92% at 450 to 1000 nm wavelength band, which means perfect light trapping.

Table 1 compares the optical and electrical properties of IWO film with those of ITO film when both were deposited by RPD system. According to Moss–Burstein effect, the band gap is shifted to higher values at greater carrier concentration. The shift arises because the Fermi energy lies in the conduction band and the filled states block thermal or optical excitation due to the Pauli principle. This explains the band gap of ITO film (3.89 eV) is higher than IWO film (3.82 eV). The resistivity of IWO film is 2.80*E* – 04 Ω cm, a little higher than ITO film, while Hall mobility of IWO film is 77.80 cm^2/Vs, exceeding two times higher than ITO film. The resistivity of TCO film is intrinsically limited for two reasons: carrier concentration and mobility. Carrier concentration and mobility cannot be independently increased for practical TCOs with relatively high carrier concentrations. At high carrier concentration, mobility is limited primarily by ionized impurity scattering. Higher doping concentration reduces mobility to a degree that the conductivity cannot increase, and the optical transmission is reduced at the NIR wavelength due to the free carrier absorption. By increasing the concentration of the dopant, the resistivity reduces until lower limit, and cannot decrease further, whereas the optical window becomes narrower. At low carrier concentration, the optical absorption at NIR region is improved, but the resistivity will increase fast. Considering the interrelation of these parameters, mobility is the key factor to make the compromise between optical property and electrical property. IWO film is such a suitable candidate as anti-reflection coating and conductive layer benefited by its higher mobility, which helps to increase conductivity without sacrificing transparency according to the Drude model.

3.2. IWO film-based copper electroplated SHJ solar cell

The total power loss (P_{loss}) of solar cell is limited for two parts: electrical loss and optical loss. Generally, negative correlation is seen between electrical loss and optical loss, and the key way to reduce this correlation is lower finger resistivity with higher aspect ratio. Consequently, the resistivity has a significant influence on the total power loss, especially when the resistivity gap between screen-printed low temperature silver paste ($8E-06\ \Omega$ cm) and electroplated copper finger ($2E-06\ \Omega$ cm) is relatively big for SHJ solar cell [21].

The total power loss is calculated in Fig. 2, in dependence on the finger height and width, respectively, for different resistivity. The simulation was performed with a contact resistance of $\rho_{\text{contact}}=3\ \text{m}\Omega\ \text{cm}^2$ on the IWO film with a sheet resistance of $R_{\text{sh-IWO}}=55\ \Omega$/sq. The simulated grid design has 84 fingers and 3 bus bars (1 mm each) on a 125 mm × 125 mm large solar cell.

The total power loss decreases as the finger resistivity decrease. At high resistivity, P_{loss} is dominated by electrical loss. The fingers with wider width and higher height are necessary to decrease the electrical loss. At low resistivity, the loss mechanism strongly depends on the finger width and height at first, and then dominated by the optical loss with the increasing finger width.

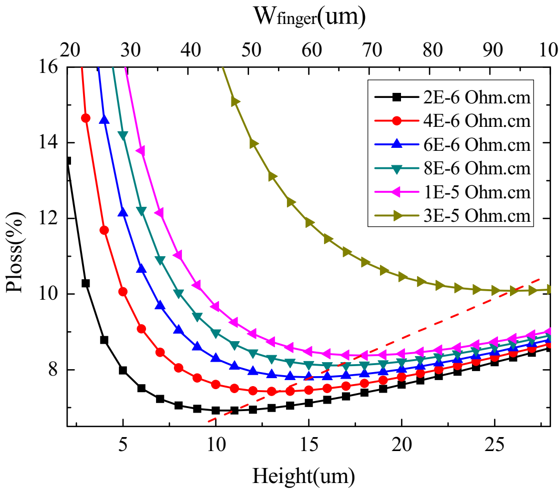


Fig. 2. Finger simulation of SHJ solar cell with different width, height and resistivity.

The lowest power loss for different resistivity (dotted line) was set. The optimized finger width of screen printed low temperature silver paste should not below 60 μm, while the copper electroplated finger width can reach 45 μm. For copper electroplated fingers, the resistivity is extremely low and the electrical loss is limited, which means optimal grid design can be applied for high efficiency. In addition, the total power loss curve is not symmetric, and the dependence of the total loss is higher at smaller finger heights. Thus, it is more favorable to plate too much copper than too litter. The high conductivity of electroplated finger is beneficial in two ways: the total loss is diminished and the amount of required process time for electroplating is shorter.

Combined with optical loss and electrical loss, both copper electroplated and screen printed SHJ solar cells were fabricated successfully in SIMIT's R&D line. Limited by the temperature mandatory of SHJ solar cells, the annealing temperature of silver paste is set at 200 °C for 30 min. Therefore, the low temperature silver paste after annealing is porous and has many voids in the size of hundreds nanometers, the contact resistance and the bulk resistivity is higher [21]. Fig. 3 represents surface morphologies of both screen printed and electroplated fingers. According to Fig. 3 (a) and (c), the edge of screen printed silver finger is unsmooth, and the finger surface is uneven due to the limitation of screen printing technology. In comparison, the edge of copper electroplated finger is sharp and without obvious extension. The copper electroplated finger shows a botryoidally morphology with surface roughness less than 2 μm, which is more smooth than screen printed silver finger. Considering the width of electroplated copper finger is about 53 μm, which is remarkably lower than screen printed silver finger, the shading loss of the electroplated finger is obviously deceased compared to screen printed finger, and can boost solar cell's current. Since the thickness of copper electroplated finger is about 25 μm, the aspect ratio can easily reach 0.5, which is higher than screen-printed silver grids (about 0.35).

Due to the small obtainable feature sizes, high aspect ratio and low bulk resistivity, electroplated copper grids can be realized with significantly reduced finger spacing and smaller optical

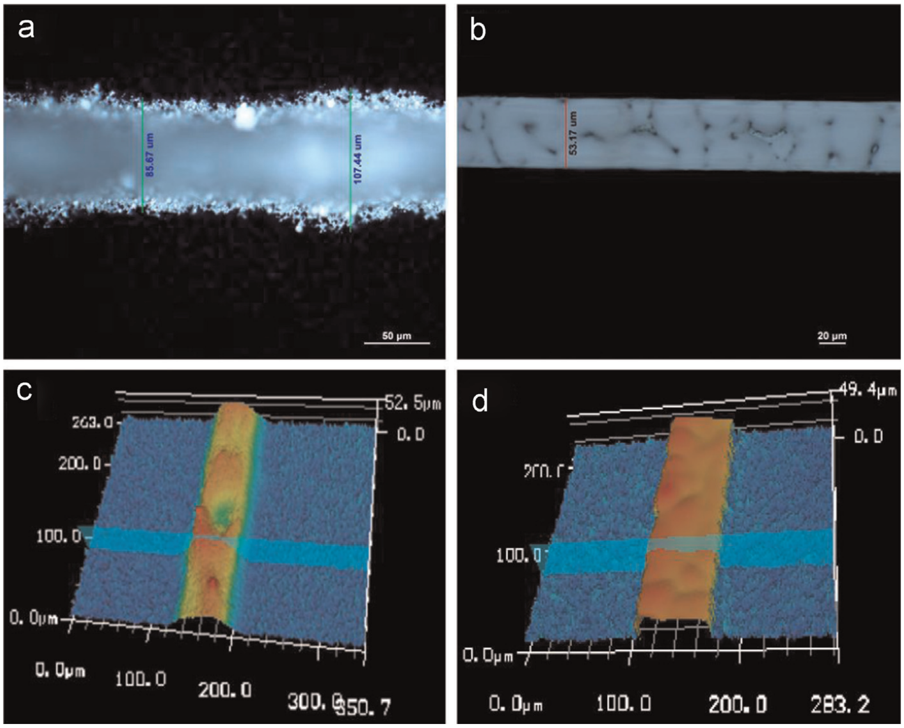


Fig. 3. SHJ solar cells (a) and (c) with screen printed finger, (b) and (d) with electroplated finger.

shading loss. In order to compare the influence of two metallization technologies, a special grids design for copper electroplated SHJ solar cell is applied: the designed finger width is 80 µm, making shading loss close to screen printed SHJ solar cell. According to Fig. 4, the Voc of both cells is about 730 mV, which means excellent passivation; the short-circuit current density is almost the same due to approximate shading loss. The only difference between the electroplated cell and screen printed cell is the formation of fingers. The lower bulk resistivity of fingers makes copper electroplated solar cell obtaining about 2% increase of fill factor, resulting in 0.47% efficiency gain.

The smaller the finger spacing, the higher the fill factor, but more shading loss, and the short-circuit current density will be lower. Thus, it is expected to be even higher efficiency with further optimization of the finger design. Fig. 5 shows the *I–V* characteristic under standard test condition. After simple optimization of the finger design, a Jsc gain of 0.76 mA/cm^2 is observed compared with the un-optimized cell presented in Fig. 4. An impressive efficiency of 22.03% and power of 3.37 W have been obtained based on 5 in. bifacial SHJ solar cell.

3.3. Long term stability of copper electroplated SHJ solar cells

Copper can diffuse into silicon easily and react with silicon to form deep level defects, which causes electrical performance degradation of the devices. Therefore, a barrier layer between copper and silicon is necessary and become the crucial factor affecting the device reliability. For copper metallization of SHJ solar cell, IWO film is not just as contact layer and anti-reflection coating, but a barrier layer to prevent copper diffusing into silicon. In our previous work [22], we investigated the GIXRD of the Cu/IWO/Si samples and leakage of Cu/IWO/Si/Al samples annealed at different temperatures. The results indicate that IWO film is an effective copper diffusion barrier until 800 °C, which means excellent stability when the solar cell modules' operating temperature below 100 °C.

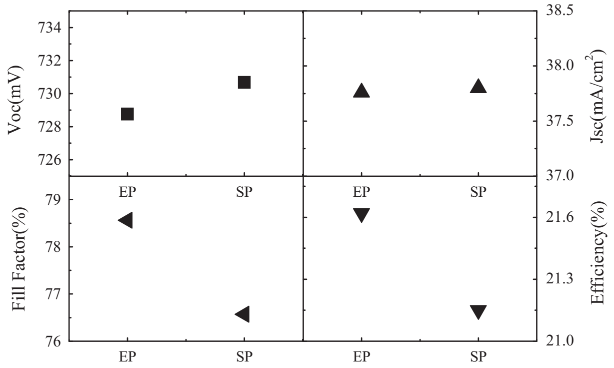
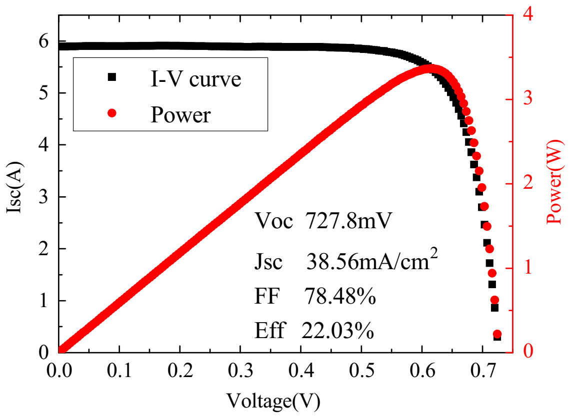


Fig. 4. Electrical properties of screen printed cell and copper electroplated cell.



Voc 727.8mV
Jsc 38.56mA/cm^2
FF 78.48%
Eff 22.03%

Fig. 5. *I–V* curve of copper electroplated SHJ solar cell under 1-sun illumination.

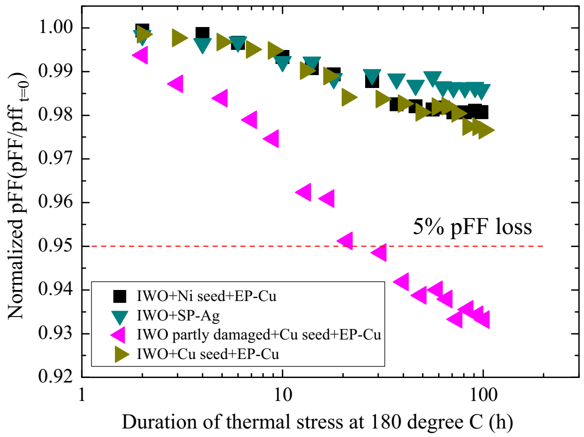


Fig. 6. Evolution of the normalized pFF of SHJ solar cells with different front metallization stacks.

Unfortunately, there is not an effective method to evaluate SHJ solar cells' degradation due to copper diffuse into the junction. Bartsch et al. and Kraft et al. had suggested a fast degradation method to characterize the long term stability of cells at elevated temperatures [23,24]. This method assumed that 5% loss of pFF was the critical boundary not to be crossed to quickly evaluate the long-term effects of copper electroplated silicon solar cells.

In this work, we measured pFF to characterize the evolution of SHJ solar cells after thermal treatment. Considering the passivation of SHJ solar cell, the treatment temperature was set at 180 °C. For each measurement, the cells were removed from the furnace and cooled down to room temperature. Fig. 6 exhibits the normalized pFF of three different kinds of SHJ solar cells for thermal stress in a furnace in N_2. Each kind of SHJ solar cell shows good long term stability, the pFF loss is less than 2.5% after 100 h duration of thermal stress, which means IWO film shows excellent property to prevent copper diffusion. However, some small difference still can be found: the IWO/Ag stack shows best stability, the normalized pFF loss is about 1.4%, smaller than IWO/Ni/Cu stack (1.8%) and IWO/Cu stack (2.3%). The results imply infinitesimal copper still diffuse through IWO and deteriorate the pFF. On the other hand, the degradation of the pFF is significantly accelerated when IWO film is partly damaged. It only takes 8 h when the pFF loss reach 2.5% and the failure time (5%) is less than 30 h. That's because the damaged IWO film provides the path for copper diffuse into junction, which affect the pFF obviously. Compare with Kraft and Bartsch's results, we can reasonably speculate that the operation time of SHJ solar cell with copper grids can achieve at least 30 years, which makes the application of modules possible.

4. Conclusion

In this study, tungsten doped indium oxide film was deposited by reactive plasma deposition technology as anti-reflection coating and conductive layer. The average transmittance and absorption of IWO film from 350 to 1200 nm wavelength was 88.33% and 2.16% respectively. The maximum hall mobility of IWO film was 77.8 cm^2/Vs, with a corresponding carrier concentration of 2.86*E*20 cm^{-3}. Then, copper metallization of SHJ solar cell were investigated. Compared to screen printed SHJ solar cell, the fingers of electroplated cell show finer width, higher aspect ratio and lower series resistance. An impressive efficiency of 22.03% and power of 3.37 W have been obtained based on 5 in. bifacial SHJ solar cell. Therefore, IWO film has excellent optical and electrical properties and stable enough to prevent copper diffusion effectively, which is ready for copper metallization of high efficiency SHJ solar cell.

Acknowledgments

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