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Modify the Schottky contact between fluorine-doped tin oxide front electrode and p-a-SiC:H by carbon dioxide plasma treatment

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ABSTRACT

Carbon dioxide plasma (COP) treatment of a fluorine-doped tin oxide (SnO_2:F, FTO) front electrode was used for the fabrication of p–i–n hydrogenated amorphous silicon (a-Si:H) solar cells. The oxygen and carbon monoxide radicals in COP play important roles of de-doping and doping effects on the surface of FTO, respectively. Through changing the COP treatment time, the de-doping and doping effects could alter the number of oxygen vacancies for both the bulk and the surface of FTO, resulting in an increase in the work function (W_F) and a decrease in the Schottky barrier at the p-a-SiC:H/FTO interface. Due to an increase in the W_F from 4.16 eV to 4.34 eV after 95 s treatment, the open circuit voltage (V_{oc}) of the a-Si:H solar cells increased from 915 mV to 965 mV and the fill factor (*FF*) increased from 67.7% to 74.4%. Although the short-circuit current density (J_{sc}) decreased from 11.76 mA/cm^2 to 10.36 mA/cm^2 after 95 s COP treatment due to the weakness of Burstein–Moss (BM) shift and the recombination at FTO surface, the conversion efficiency of the a-Si:H solar cell was enhanced by 12.24% after 45 s COP treatment, accompanied by improving the V_{oc} and *FF* with almost constant J_{sc}.

1. Introduction

Fluorine-doped tin oxide films (SnO_2:F, FTO), called the transparent conductive oxide (TCO) material are most commonly used as transparent electrodes in thin film solar modules based on hydrogenated amorphous silicon (a-Si:H) absorber materials (Myong, 2014; Turan et al., 2014). In order to minimize light absorption in doped p-type layer, the implementation of boron-doped hydrogenated amorphous silicon carbide film (p-a-SiC:H) as a window layer has been a significant advance in a-Si:H solar cell production (Han et al., 2015; Jeong et al., 2010; Myong et al., 2005). This material exhibits a slightly wider bandgap than p-type a-Si:H. However the Schottky barrier existed at the p-a-SiC:H/FTO interface, limited the performance of the a-Si:H solar cells (Smole et al., 1996; Poortmans and Arkhipov, 2007).

To improve the open-circuit voltages (V_{oc}) and fill factors (*FF*) of a-Si:H solar cells, a contact layer between p/TCO interface, such as boron-doped hydrogenated microcrystalline silicon (p-μc-Si:H) has been introduced to decrease the Schottky barrier, often forming an Ohmic contact (Koval et al., 2002; Kim et al., 2012). However, the Sn^{4+} species in the FTO could be destabilized and reduced to its metallic state (Sn^0) by exposing to the high-flux hydrogen plasma (Choi et al., 2013). This occurs upon the deposition of p-μc-Si:H or p-nc-SiC:H with the high-flux hydrogen plasma via radio-frequency plasma-enhanced chemical vapor deposition (RF-PECVD) (Moralesmasis et al., 2014). Thus, the degradation in optical transmittance of FTO contributes to the low short-circuit current densities (J_{sc}) and V_{oc} of a-Si:H solar cells (Moralesmasis et al., 2014; Hegedus, 2002). To solve this problem, TiO_2 and ZnO thin films were generally introduced as protective layers to provide high durability to the FTO against high-flux hydrogen plasma (Kambe et al., 2006; Franken et al., 2006; Park et al., 2013; Chantarat et al., 2012; Fujibayashi et al., 2006). In addition, Jeehwan et al. proposed high-work-function metallic nanodots used as interfacial buffers at the p-a-SiC:H/FTO interface to minimize the Schottky barrier and then provide an ohmic contact to the p-a-SiC:H (Jeehwan et al., 2010).

Carbon dioxide plasma (COP) treatment of TCOs has been reported decades ago, they found that a buffer layer was formed at interface and the incorporation of oxygen into the TCO which

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result in lower recombination and improved cell efficiency (Bauer et al., 1993; Kubon et al., 1994; Wanka et al., 1996). The COP properties and the chemisorbed mechanism on the FTO surface need further investigation. We herein propose carbon dioxide plasma (COP) treatment of the FTO front electrode with short time to modify the Schottky barrier at the p-a-Si:C/FTO interface, followed by detailed investigations into the use of RF-PECVD for the preparation of a-Si:H solar cells. In contrast to the use of protective layers or buffers on the FTO front electrode, it is expected that the COP treatment will be a simple and effective method for the manufacture of thin-film solar cells in PECVD technology, which will ultimately result in the performance improvement of solar cells.

2. Experimental details

The FTO (Asahi U type) front electrode was treated under a condition of CO_2 plasma by RF-PECVD operated at a radio frequency of 13.56 MHz, 175 °C, 10 sccm and 40 Pa, 0.5 W/cm^2. For the detection of excited species in the CO_2 plasma, an optical emission spectrometer (OES, Emicon HR system, France) was employed. Van-der-Pauw HL5550PC Hall Measurement System was performed to investigate the electricity properties of FTO after COP treatment. X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) were carried out by Escalab 250Xi to investigate the chemical composition and the Fermi level of the FTO surface. The FTO surface energy was calculated by JC-2000CD contact angle measurement. Photoluminescence measurements were performed using Hitachi M-850 fluorescence spectrometer.

The p–i–n type single junction a-Si:H solar cells were deposited on COP treated FTO front electrode. The structure of single junction a-Si:H solar cell is FTO/p-a-SiC:H/i-a-Si:H(200 nm)/n-a-Si:H/Al. The solar cells were characterized using light *J–V* characteristics under 1-sun (AM1.5, 100 mW/cm^2) simulator radiation (WXS-156S-L2) at 300 K with an effective cell area of 0.25 cm^2, and the short-circuit current densities (J_{sc}) were calculated from external quantum efficiency (EQE) measurement (QEX10, PV Measurement).

3. Results and discussion

3.1. The properties of CO_2 plasma

Table 1 shows the performance of a-Si:H solar cells with or without COP treatment, the V_{oc} and *FF* have been improved from 915 mV to 990 mV and 67.7–69.7% respectively after COP treatment. The conversion efficiency of the a-Si:H solar cell was enhanced by 12.24% by this method. In order to know well the COP treatment impact on the FTO front electrode, the COP properties have been investigated firstly.

Fig. 1(a) shows the optical emission spectroscopy (OES) of CO_2 glow discharge. In the CO_2 plasma, five radical species (O_2^+, O_2, O_3, CO^+, and CO) play an important role on the surface of FTO (Reyes et al., 2008; Martinez et al., 2010). Relational species in the spectra of Fig. 1(a) are reported in Table 2. These radicals O_2^+, O_2, O_3, CO^+, and CO in their ground and excited states, are generated by electron impact as follows:

Table 1
The performance of a-Si:H solar cells with or without COP treatment.

Sample	V_{oc} (mV)	J_{sc} (mA/cm^2)	FF (%)	η (%)
Untreated	915	11.76	67.7	7.27
Treated (45 s)	990	11.80	69.7	8.16

$$CO_2 + e \rightarrow CO_2^*(^1B_2) + e \quad (1)$$

$$CO_2 + e \rightarrow CO_2^+(A^2\Pi) + 2e \quad (2)$$

$$CO_2 + e \rightarrow CO(a'^3\Sigma) + O + e \quad (3)$$

$$CO_2 + e \rightarrow CO(a'^3\Sigma) + O^+ + 2e \quad (4)$$

$$CO_2 + e \rightarrow CO^+(A^2\Pi) + O + 2e \quad (5)$$

$$CO_2 + e \rightarrow C + O_2^+(A^2\Pi_u) + 2e \quad (6)$$

$$CO_2 + e \rightarrow C + O_2(b^1\Sigma_g^+) + 2e \quad (7)$$

However, a recombination reaction has the possibility of occurring with (6) as an intermediate reaction to produce highly energetic intermediate species and ions:

$$C + C \rightarrow C_2 \quad (8)$$

The inset of Fig. 1(a) shows that the oxygen and carbon monoxide radicals have a similar intensity which has not been stabilized with the glow discharge time, it appeared a linear increment during glow (Fig. 1(b)). These two radicals might have competitive relationship in the treatment process because of comparable quantities. And the quantity of CO^+ increased significantly with the glow discharge time and that might affect the surface of FTO at a long treatment time.

3.2. The possible mechanism of CO_2 plasma treatment on the FTO front electrode

To investigate the behavior of the oxygen and carbon monoxide radicals, high-resolution Sn $3d_{5/2}$ and O 1*s* core-level spectra of FTO were obtained by XPS. The binding energy (E_B) peak located at approximately 486.7 eV was calibrated using Sn^{4+} (Sn $3d_{5/2}$), and the positions of the E_B peaks corresponding to the other six components, namely Sn^{2+} (486.0 eV), Sn^0 (484.5 eV), O–Sn^{4+} (530.3 eV), O–Sn^{2+} (529.7 eV), chemisorbed oxygen species O^{-chem} (531.4 eV) and chemisorbed hydroxyl ion OH^{-chem} (531.7 eV), were calculated accordingly (Fig. 2) (Kawabe et al., 2001; 2000; Szuber et al., 2001). Table 3 shows the ratio of relative element concentration of the FTO surface with different COP treatment time from XPS spectra. A continuous reduction in Sn^{4+}/Sn^{2+} intensity ratio from 4.6 to 2.5 was observed with increasing the COP treatment time from 0 s to 45 s, and ultimately to 95 s, confirming that COP treatment can reduce the oxygen content in the SnO_2 bulk lattice. As summarized in Table 3, the intensity ratios of SnO_2 lattice (O^{latt}) to the chemisorbed oxygen and hydroxyl ion (O^{chem}), decreased from 1.3 to 0.9 when the FTO was COP-treated for 45 s, and then increased to 1.8 when the COP treatment time reached 95 s. Clearly, a lower O^{latt} to O^{chem} ratio (0.9) indicates a greater amount of chemisorbed O^{-chem} and OH^{-chem} species (Gercher and Cox, 1995). In contrast, the higher O^{latt}-to-O^{chem} ratio (1.8) was observed when the COP treatment time was extended to 95 s. It indicates that the OH^{-chem} species is desorbed from the FTO surface after 95 s. The Sn^0 to Sn ratio in FTO has the similar tendency with the O^{latt}-to-O^{chem} ratio after COP treatment might due to the change of the chemisorbed oxygen. And the little quantity of Sn^0 was not considered in this work (see Fig. 2).

In order to confirm the behavior of chemisorbed oxygen, the surface energy has been calculated by Owens–Wendt model (Owens and Wendt, 1969) with water and ethylene glycol as the test liquids (Kozbial et al., 2014). Fig. 3 shows the surface energy of FTO with different COP treatment time. Surface energy values of treated and untreated FTO surface, as a sum of polar and