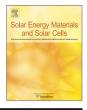


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# The effect of the native silicon dioxide interfacial layer on photovoltaic characteristics of gold/*p*-type amorphous boron carbon thin film alloy/silicon dioxide/*n*-type silicon/aluminum solar cells



#### Tsuen-Sung Chen, Yu-Chun Hsueh, Shao-En Chiou, Sham-Tsong Shiue\*

Department of Materials Science and Engineering, National Chung Hsing University, 250 Kuo Kuang Road, Taichung 402, Taiwan

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#### ABSTRACT

The effect of the thin native silicon dioxide (SiO<sub>2</sub>) interfacial layer on the photovoltaic characteristics of gold/*p*-type amorphous boron carbon thin film alloy/silicon dioxide/*n*-type silicon/aluminum (Au/*a*-BC/SiO<sub>2</sub>/*n*-Si/Al) solar cells is investigated. *a*-BC thin film alloy was deposited on *n*-Si substrate with an SiO<sub>2</sub> layer using a reactive sputtering system. The front and back surfaces of this *a*-BC/SiO<sub>2</sub>/*n*-Si/Al solar cell were covered with Au and Al electrodes, respectively. *a*-BC thin film alloys and Au/*a*-BC/SiO<sub>2</sub>/*n*-Si/Al solar cells were annealed at 623 K in an atmosphere of argon. Raman spectra and X-ray photoelectron spectroscopy results show that the *a*-BC thin film alloy has a *D* band and a *G* band and the boron/carbon ratio is 12.4%. The optical band gap and electrical resistivity of the *a*-BC/SiO<sub>2</sub>/*n*-Si/Al solar cell exhibits a short-circuit current density, open-circuit voltage, fill factor, and power conversion efficiency of 165 A/m<sup>2</sup>, 0.22 V, 0.904, and 3.3%, respectively. Remarkably, the Au/*a*-BC/SiO<sub>2</sub>/*n*-Si/Al solar cell has a fill factor of 0.934 at an illumination intensity of 200 W/m<sup>2</sup>, which exceeds any value obtained to date. The thin SiO<sub>2</sub> layer improves the photovoltaic characteristics of Au/*a*-BC/SiO<sub>2</sub>/*n*-Si/Al solar cells, and the reasons for this improvement are discussed herein.

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#### 1. Introduction

Recently, the vast potential of photovoltaic solar cells has been widely recognized owing to the shortage of fossil fuels and environmental concerns [1]. Many materials have been considered for making solar cells, but the current cost of solar cells that use those materials is too high to allow their use in daily life. Hence, finding new materials for generating clean and cheap solar energies are very important [2]. Amorphous carbon (*a*-C) films have many advantages, including their low-cost, ease of mass-production, semiconducting characteristics, and a tunable band gap. They can be prepared with various characteristics by changing the sp<sup>2</sup>/sp<sup>3</sup> ratio [3]. Recently, a-C films have been used not only as protective layers or anti-reflective layers [4–6], but also in *n*-type carbon/*p*-type silicon [7–9] or *p*-type carbon/n-type silicon [8,10–13] heterojunctions for solar cells. p-Type amorphous carbon (p-C) films are generally prepared by doping boron [8,10,11,14–16] or metal elements [2,17,18] in *a*-C films using chemical vapor deposition (CVD) [9-11,15,16] or physical vapor deposition (PVD) [2,7,8]. When various versions of the material with variable properties are formed, CVD is better than PVD. However, the sources of dopants in CVD, such as BH<sub>3</sub> [15],  $B_2H_6$ , and  $C_3H_9B$  [11,16] gases, are usually dangerous because they are toxic or explosive.

Reactive sputtering combines sputtering and plasma-enhanced chemical vapor deposition (PECVD); the method is not dangerous, and has all of the advantages of CVD [19]. Therefore, this method was used in this study to fabricate amorphous boron carbon (a-BC) thin film alloy. The deposition of a semiconductor on silicon with a native silicon dioxide (SiO<sub>2</sub>) layer reportedly improves the photovoltaic characteristics of solar cells in which it is used [2,19–21]. Hence, the effect of a native SiO<sub>2</sub> layer on the photovoltaic characteristics of a-BC/SiO<sub>2</sub>/ *n*-Si solar cells is investigated. In this study, a boron target was utilized as the dopant source, and the precursor gas was a mixture of pure methane  $(CH_4)$  and argon (Ar). The *a*-BC thin film alloys were separately deposited on *n*-type silicon (*n*-Si) with and without a native SiO<sub>2</sub> layer. Gold (Au) and aluminum (Al) metals were used to form the front and back electrodes of solar cells, respectively. The photovoltaic characteristics of Au/a-BC/n-Si/Al and Au/a-BC/SiO<sub>2</sub>/n-Si/Al solar cells were investigated, and the effect of the SiO<sub>2</sub> layer on the photovoltaic characteristics of Au/a-BC/SiO<sub>2</sub>/n-Si/Al solar cells was discussed.

<sup>\*</sup> Corresponding author. Tel.: +886 4 22857211; fax: +886 4 22857017. *E-mail address:* stshiue@dragon.nchu.edu.tw (S.-T. Shiue).

#### 2. Experimental details

The following experiment was performed.  $20 \times 20 \times 0.35$  mm<sup>3</sup> *n*-Si (100) wafers were cleaned at 348 K (75  $^{\circ}$ C) in hot sulfuric acid for 20 min, and  $12.5 \times 25 \times 1 \text{ mm}^3$  silica glass plates and  $20 \times 10^{-3}$  $20 \times 2 \text{ mm}^3$  stainless steel plates were cleaned in an ultrasonic bath of acetone for 20 min. Then, all of the *n*-Si wafers, silica glass plates, and stainless steel plates were cleaned in an ultrasonic bath of ethanol for 20 min and washed using de-ionized water, in that order, to improve the adhesion of *a*-BC thin film allovs to these substrates. The *n*-Si wafers were also etched by 10% hydrofluoric acid for 3 min to remove the oxide laver from the substrate surfaces and then 500 nm of Al was deposited on one side of a silicon substrate by sputtering. Some of the Si substrates were placed in the ambient environment for three weeks to form a native SiO<sub>2</sub> layer [22]. The *a*-BC thin film alloys were separately deposited on *n*-Si substrates, *n*-Si substrates with native SiO<sub>2</sub>, silica glass plates, and stainless steel plates using a 13.56 MHz radio-frequency reactive sputtering system. Fig. 1 schematically depicts the reactive sputtering system with a cylindrical stainless steel reaction chamber with two parallel planar electrodes. The top electrode was the target holder and the bottom electrode was the planar substrate holder. The distance between the target and the substrate was 50 mm. The dopant source was the boron target (99.99% pure and 76.2 mm in diameter). Before deposition, the reaction chamber was pumped to a base pressure of less than  $2.7 \times 10^{-4}$  Pa (2.0  $\times$  $10^{-6}$  Torr). During deposition, the substrate temperature was 298 K (25 °C); the rf power was 300 W, and the working pressure was 6 Pa ( $45 \times 10^{-3}$  Torr). CH<sub>4</sub> (99.999%) and Ar (99.99%) gases were injected into the deposition chamber at 2 and 10 standard cubic centimeters per minute (sccm), respectively. The deposition time was set to 30 s to yield *a*-BC thin film alloys with a thickness of 40 nm. The above process conditions were determined by trial and error to yield a solar cell device with favorable photovoltaic characteristics. Notably, a self-bias voltage of 312 V was generated between the top electrode (boron target) and the bottom electrode (substrate holder) during the deposition process. The carbon atoms were incoporated into the film from methane, while the boron atoms were incoroporated into the film from the boron target.

The characteristics of *a*-BC thin film alloys were measured as follows. Before the measurement, the *a*-BC thin film alloys were annealed at 623 K (350 °C) for 30 min in the Ar atmosphere using a thermal annealing furnace (Lindberg/Blue M TF55030A-1). The cross sections of the *a*-BC thin film alloys that were deposited on the *n*-Si substrate without and with the SiO<sub>2</sub> layer were examined using a field emission transmission electron microscope (FETEM, JEOL JEM-2100F). The surface of the *a*-BC thin film alloy was covered with a protective platinum (Pt) layer with a thickness of 200 nm, and a focused ion beam (FIB, JEOL JIB-4601F) system was

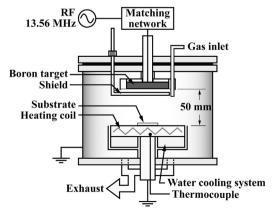


Fig. 1. The schematic of the reactive sputtering system.

then used to prepare the sample for FETEM. The thicknesses of the SiO<sub>2</sub> layer and the a-BC thin film alloy were measured from the FETEM images, and an average of three measurements of each was taken for each sample. The microstructure and chemical composition of the *a*-BC thin film alloys were investigated by Raman scattering spectroscopy (RSS, Horiba Jobin Yvon Triax 550), Fourier transform infrared (FTIR) spectroscopy (Thermo-Nicolet NEXUS 470), and X-ray photoelectron spectroscopy (XPS, Ulvac-PHI 1600). The Raman spectra (RS) were measured in back-scattering geometry using the 633 nm line of an He-Ne laser at room temperature in the spectral range from 1100 to  $1800 \text{ cm}^{-1}$ . The laser power was 25 mW, and a damper was used to attenuate the laser power. When the irradiation time of the *a*-BC thin film allovs by the laser was set to 10 s/point, the surface morphologies of the a-BC thin film alloys, determined using an optical microscope, were not significantly damaged. The deconvoluted Raman data were estimated as average values from nine measurements made on each sample. The FTIR absorption spectra were obtained in the range of  $2750-3150 \text{ cm}^{-1}$  with 32 scans at a resolution of 1 cm<sup>-1</sup>. After  $Ar^+$  ions were used to etch the surfaces of *a*-BC thin film alloys for 2 min, XPS measurements were made using a monochromatic X-ray source of Mg K<sub> $\alpha$ </sub> (hv = 1253.6 eV). Carbon and boron core line spectra were acquired when the X-ray incident angle was 54°. Notably, the RSS, FTIR, and XPS measurements were made on the *a*-BC thin film alloys in the middle of the *n*-type silicon wafer substrate. The optical band gap of the *a*-BC thin film alloys was measured using a UV/VIS/IR spectrophotometer (Hitachi U3010) at wavelengths from 200 to 1100 nm with a bare silica glass plate in the path of the reference beam to eliminate the contribution of the substrate. The electrical resistances of a-BC thin film alloys were measured using a current-voltage meter (Keithley 2400). Notably, the optical band gaps and resistances of *a*-BC thin film allovs were measured using the samples with silica glass plate substrates and stainless steel plates, respectively.

Finally, the photovoltaic characteristics of solar cells were measured as follows. Before the measurements were made, the contacts on *a*-BC sides of the *a*-BC/*n*-Si/Al and *a*-BC/SiO<sub>2</sub>/*n*-Si/Al solar cells were formed by sputtering with 100 nm Au. The Au contact had a  $10 \times 10 \text{ mm}^2$  channel to enable the light directly to illuminate the *a*-BC thin film alloys. The Au/*a*-BC/*n*-Si/Al and Au/*a*-BC/SiO<sub>2</sub>/*n*-Si/Al solar cells were also annealed at 623 K for 30 min in the Ar atmosphere. Fig. 2 schematically depicts the Au/*a*-BC/SiO<sub>2</sub>/*n*-Si/Al solar cell. The current densities versus voltage (*J*-*V*) characteristics of the Au/*a*-BC/*n*-Si/Al and Au/*a*-BC/SiO<sub>2</sub>/*n*-Si/Al solar cells were analyzed using the current–voltage meter (Keithley 2400). The photovoltaic characteristics were measured at room temperature using a xenon lamp as the radiation source. The intensity of illumination was attenuated to a specified value by inserting a neutral density filter.

#### 3. Results and discussion

#### 3.1. Properties of a-BC thin film alloys

Fig. 3a shows the cross-section of the a-BC/SiO<sub>2</sub>/n-Si structure after annealing, which was examined by FETEM. This figure reveals that an SiO<sub>2</sub> layer is between the a-BC and n-Si layers. Notably, the Pt layer in Fig. 3a was produced to undergo FIB cutting, and covered the surface of the a-BC thin film alloy. This figure also shows that the thickness of the a-BC thin film alloy is approximately 30 nm, with an error of less than 5%. Fig. 3b displays the enlarged cross-section of the a-BC/SiO<sub>2</sub>/n-Si structure, and indicates that the thickness of the SiO<sub>2</sub> layer is approximately 3 nm with an error of less than 5%. Fig. 3b displays the enlarged cross-section of the a-BC/SiO<sub>2</sub>/n-Si structure, and indicates that the thickness of the SiO<sub>2</sub> layer is approximately 3 nm with an error of less than 20%. The thickness of the native SiO<sub>2</sub> layer on an Si substrate surface is reported in the range of 1.2–3 nm [22], and so,

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