Thin Solid Films 528 (2013) 86–92

Contents lists available at SciVerse ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

The effect of different radio-frequency powers on characteristics of amorphous boron carbon thin film alloys prepared by reactive radio-frequency plasma enhanced chemical vapor deposition

Tsuen-Sung Chen, Shao-En Chiou, Sham-Tsong Shiue *

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

ARTICLE INFO

Available online 7 November 2012

Keywords:
Chemical vapor deposition
Carbon
Amorphous boron carbon thin film alloys
Photovoltaic

ABSTRACT

The effects of different radio-frequency (rf) powers on the characteristics of amorphous boron carbon (BC) thin film alloys on *n*-type silicon (*n*-Si) wafers prepared by reactive radio-frequency plasma enhanced chemical vapor deposition (rf-PECVD) are investigated. The reactive rf-PECVD was the combination of rf-PECVD and sputtering. Five kinds of amorphous BC thin film alloys were prepared with rf powers of 100, 200, 300, 400, and 500 W. Experimental results show that when the rf power increases from 100 to 500 W, the deposition rate of amorphous BC thin film alloys slightly decreases from 1.14 to 1.00 nm/s that is resulted from the increase of the B/C ratio. The amorphous BC thin film alloy prepared at the rf power of 300 W has a maximum graphitization degree and sp^2 carbon bonds, so it has the lowest energy band gap and electrical resistivity. All the amorphous BC thin film alloys prepared with different rf powers are *p*-type. When the amorphous BC thin film alloy prepared at the rf power of 300 W, the amorphous BC/*n*-Si diode possesses the lowest series resistance of 279 Ω and an ideality factor of 4.9; after annealed at 623 K, the series resistance and ideality factor of this diode reduce to 98 Ω and 2.47, respectively. When the amorphous BC thin film alloys were prepared at the rf power of 300 W, the built-in voltages of the amorphous BC/*n*-Si devices are 0.45 and 0.88 V for the amorphous BC thin film alloys before and after annealed at 623 K, respectively. When an additional native oxide of SiO_2 layer was prepared on the *n*-type silicon substrate surface, the power conversion efficiency and fill factor of amorphous BC/SiO_2/*n*-Si devices are 1.04% and 88.3%, respectively. Hence, the amorphous BC thin film alloys prepared by reactive rf-PECVD have the potential applied to the fabrication of solar cells.

1. Introduction

Amorphous carbon (*a*-C) films have several advantages including low-cost, easy to produce massively, semiconductor characteristics, and tunable band gap, which can be prepared with various characteristics by changing the sp^3/sp^2 ratio [1,2]. Recently, *a*-C films were not only applied as protective layers or anti-reflective layers for solar cells, but also constructed as *n*-type carbon/*p*-type silicon or *p*-type carbon/*n*-type silicon heterojunction devices using doping method. Generally, the *p*-type amorphous carbon (*p*-C) films were prepared by doping boron [3–9] or metal elements [10–15] in *a*-C film using chemical vapor deposition (CVD) or physical vapor deposition (PVD) methods [4–9,16–23]. If the carbon materials with variable properties are demanded, CVD is better than PVD. However, the doping sources (such as: BH_3 [5], B_2H_6, and C_3H_9B [9,18] gases) for CVD are usually dangerous.

In this study, we will prepare the amorphous boron carbon (BC) thin film alloys using a reactive radio-frequency plasma enhanced chemical vapor deposition (reactive rf-PECVD) system. The purpose of this study is to prepare boron-doped amorphous carbon films. However, sometimes the B concentration in the films is much larger than 1%, so these films are called amorphous boron carbon thin film alloys [24]. The reactive rf-PECVD system was the combination of rf-PECVD and sputtering. A boron target was used as the dopant source, and a mixture of pure methane (CH_4) and argon (Ar) was selected as the precursor gas. The effect of different rf powers on the properties of amorphous BC thin film alloys will be investigated. The current density–voltage (*J*–*V*) and capacitance–voltage (*C*–*V*) characteristics of amorphous BC thin film alloys deposited on *n*-type silicon (*n*-Si) will be studied. Furthermore, the potential of amorphous BC thin film alloys prepared by reactive rf-PECVD to construct the carbon-based solar cell will be also discussed.

2. Experimental details

The experimental details proceeded as follows. First, 12.5×25×0.35 mm^3 *n*-type (100) Si wafers, 20×20×1 mm^3 stainless steel plates, and 12.5×25×1 mm^3 silica glass plates were cleaned in ultrasonic bath of acetone, ethanol, and deionized (DI) water, in that order,

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

0040-6090/$ – see front matter
http://dx.doi.org/10.1016/j.tsf.2012.09.091

to improve the adhesion of amorphous BC thin film alloys onto these substrates. The Si wafers were additionally etched by 10% HF to remove the oxide layer on the substrate surfaces. Second, the amorphous BC thin film alloys were separately deposited on *n*-type (100) Si wafers, stainless steel plates, and silica glass plates using a 13.56 MHz capacitively coupled reactive rf-PECVD system. Fig. 1 illustrated the schematic diagram of the reactive rf-PECVD system, which was the combination of rf-PECVD and sputtering. The reactive rf-PECVD system adopted 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 doped source used the boron target (99.99% pure, 76.2 mm in diameter). Before deposition, the reaction chamber was pumped, and the base pressure was less than 2.7×10^{-4} Pa (2.0×10^{-6} Torr). During deposition, the substrate temperature was 298 K (25 °C), and the working pressure was 6 Pa (45 mTorr). Methane (99.999%) and argon (99.990%) flux were injected into the deposition chamber, and maintained 2 and 10 standard cubic centimeters per minute (sccm), respectively. Five kinds of amorphous BC thin film alloys were prepared with rf powers being 100, 200, 300, 400, and 500 W. The deposition time was controlled such that amorphous BC thin film alloys with identical thickness of 100 nm were produced for all rf powers. Notably, during the deposition process, a self-bias voltage is generated between the top electrode (boron target) and bottom electrode (substrate holder). As the rf power increases from 100 to 500 W, the self-bias voltage increases linearly from 162 to 435 V. The carbon atom in the film is emanated from methane by rf-PECVD, while the boron in the film is originated from boron target by sputtering. Hence, this process is called reactive rf-PECVD.

The characteristics of amorphous BC thin film alloys were measured as follows. First, the thicknesses of amorphous BC thin film alloys were examined by FESEM (JEOL JSM-6700F). Each thickness was estimated from the average value of three data with the same deposition condition. Second, the microstructure and chemical composition of the amorphous BC thin film alloys were investigated using a Raman scattering spectroscopy (RSS, Horiba Jobin Yvon Triax 550), a Fourier transform infrared (FTIR) spectroscopy (Thermo-Nicolet NEXUS 470), and an X-ray photoelectron spectroscopy (XPS, Ulvac-PHI 1600). The RSS was measured in the back-scattering geometry with the 633 nm line of a He–Ne laser at room temperature in the spectral range from 1000 to 2000 cm^{-1}. The laser power and irradiation time on amorphous BC thin film alloys were 25 mW and 60 s/point, respectively. Each deconvoluted Raman data were estimated from the average value of five data with the same deposition condition. The FTIR can identify the nature of bonding (C–H stretching vibration modes) by absorbance spectrum at 298 K. All FTIR absorption spectra were detected in the range of 650–4000 cm^{-1} with 32 scans at a resolution of 1 cm^{-1}. The XPS measurements were executed with a monochromatic X-ray source of Mg K_α ($h\nu=$ 1253.6 eV). All carbon (C1s) and boron (B1s) core lines spectra were acquired when the X-ray incident angle was 54° to enhance the contribution of amorphous BC thin film alloys on these core line shapes. The measurements of microstructures were made on the amorphous BC thin film alloys located at the middle portion of the substrate. The chemical bonding states in the films were analyzed after the Ar^+ ions etching of the films surface for 2 min. Thirdly, the optical band gap of amorphous BC thin film alloys was measured by UV/VIS/IR spectrophotometer (Hitachi U3010) for wavelengths ranging from 200 to 1100 nm with a bare silica glass plate in the reference beam to eliminate the substrate contribution. Finally, the *J*–*V* behavior of amorphous BC/*n*-Si devices was analyzed using the current–voltage meter (Keithley 2400) and the *C*–*V* curve was analyzed using the precision LCR meter (Agilent 4284A) with test leads (Agilent 16048D). Before these measurements, the contacts on amorphous BC and *n*-Si sides were formed by sputtering with 100 nm gold and 500 nm aluminum, respectively. Notably, the optical band gaps of amorphous BC thin film alloys were measured using the samples with silica glass plate substrates. Nevertheless, the other properties were measured using the specimens with silicon wafer substrates. Moreover, the amorphous BC thin film alloys prepared at a certain rf power with the best *J*–*V* characteristic were further annealed at 573, 623, and 673 K for 30 min in the Ar atmosphere at a heating rate of 10 K/min, using a thermal annealing furnace (Lindberg/Blue M TF55030A-1). All the properties of amorphous BC thin film alloys after annealing were measured as those of amorphous BC thin film alloys before annealing.

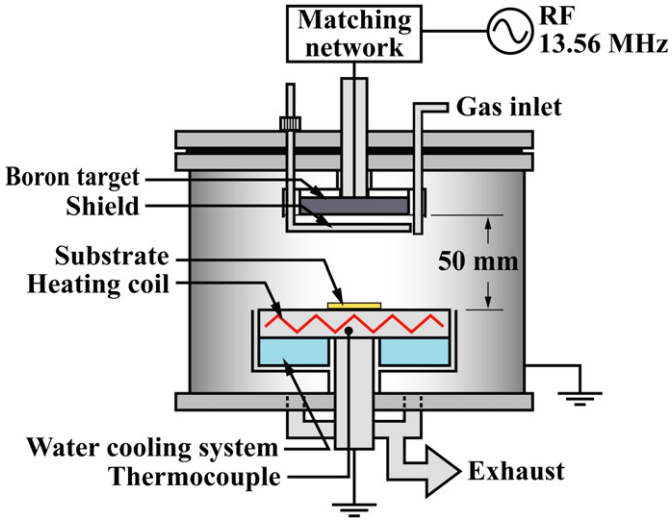

Fig. 1. The schematic diagram of the reactive rf-PECVD system.

3. Results and discussion

After the thicknesses of amorphous BC thin film alloys deposited at different rf powers were measured, the deposition rate of these carbon films can be obtained. Experimental results show that when the rf powers are 100, 200, 300, 400, and 500 W, the deposition rates are 1.14, 1.12, 1.11, 1.06, and 1.00 nm/s, respectively. This indicates that the deposition rate of amorphous BC thin film alloys decreases with increasing the rf power. Generally, the deposition rate of PECVD carbon films increases with increasing the rf power [25]. Nevertheless, Liu et al. [26] reported that the deposition rate is strongly influenced by the B/C ratio and it decreases with increasing the B/C ratio. In this work, the B/C ratio increases with increasing the rf powers (as shown below in the XPS result), and thus, the deposition rate of carbon films decreases with increasing the rf power.

Fig. 2(a) shows the typical Raman spectra (RS) measured from the amorphous BC thin film alloys deposited at different rf powers. The RS can be decomposed into two absorption peaks, a *D* band at about 1350 cm^{-1} and a *G* band at about 1580 cm^{-1}, using the Gaussian function. The *D* band is associated with the breathing mode of six-fold sp^2 rings and identified as the disorder-activated band. This mode is forbidden in perfect graphite and only becomes active in the presence of disorder [27–32]. The *G* band is associated with the bond stretching vibrations of all sp^2 sites [30–34]. Alternatively, Fig. 2(b) reveals the fitting results of RS for various rf powers. The RS fitting results include the *D* peak position (ω_D), the *G* peak position (ω_G), the full-width-at-half-maximum of *D* band ($FWHM_D$), the full-width-at-half-maximum of *G* band ($FWHM_G$), and the ratio of the integrated intensity of the *D* band to *G* band (I_D/I_G) for the amorphous BC thin film alloys that were prepared at different rf powers. Fig. 2(b) apparently reveals the $FWHM_G$ value increases from 212 to 239 cm^{-1} when the rf power increases from 100 to 500 W. Alternatively, the ω_D, ω_G, $FWHM_D$, and I_D/I_G values increase with increasing