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The effect of different radio-frequency powers on characteristics of carbon-titanium nanocomposite thin films prepared by reactive sputtering

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ABSTRACT

The effect of radio-frequency (rf) powers on the characteristics of carbon-titanium nanocomposite thin films (C-Ti films) prepared by reactive sputtering is investigated. The C-Ti films were prepared on n-type silicon (n-Si) wafers by reactive sputtering, which was the combination of rf plasma enhanced chemical vapor deposition (rf-PECVD) and sputtering. Pure methane was used as the precursor gas to form the amorphous carbon (*a*-C) film by rf-PECVD, and argon was used as the sputtering gas to bombard the titanium target surface to dope titanium in *a*-C films by sputtering. Seven kinds of C-Ti films were prepared with the rf power being 50, 100, 150, 200, 250, 300, and 350 W, and all the thickness of C-Ti films were fixed at 100 nm at various rf powers. The measured results indicate that the carbon-hydrogen bonds in C-Ti films decrease with increasing the rf power from 50 to 350 W, but the degree of graphitization of C-Ti films increases. The Ti/C ratio of C-Ti films increases from 0.3 to 116% with increasing the rf power from 50 to 350 W, and the $sp^2/(sp^2 + sp^3)$ carbon ratio of C-Ti films also increases from 14.7 to 44%. On the other hand, the C-Ti films are amorphous at the rf power from 50 to 250 W, but nano-crystalline titanium carbide grains are encapsulated in *a*-C matrix at the rf powers of 300 and 350 W. Furthermore, the optical band gap of C-Ti films decreases from 2.6 to 0 eV with increasing the rf power from 50 to 350 W, and the electrical resistivity of C-Ti films decreases from 2.1×10^3 to 5×10^{-6} Ω·m. This implies that the C-Ti film changes from semiconductor to conductor with increasing the rf power from 50 to 350 W. The current density-voltage results show that the C-Ti/n-Si device prepared at various rf powers exhibits the rectifying behavior. The C-Ti/n-Si device prepared at the rf power of 300 W has a best ideality factor of 2.1. The C-Ti/*n*-Si device has the potential to be applied in the electronic/optoelectronic fields.

1. Introduction

Amorphous carbon (*a*-C) films are taken much attention, and their characteristics can be varied by adding other elements [1]. Among of them, the carbon titanium nanocomposite thin films (C-Ti film) have remarkable mechanical [2–4], electrical [4], and optical [5] properties; therefore, they were applied as protective coatings [6], electrical contacts [7], and solar absorber coatings [8]. In the literature, Coronel et al. [9] studied the effect of C content on the microstructure of hydrogen-free physical vapor deposited titanium carbide films using Ti and C targets. Fouad et al. [10] investigated the effect of different Argon/methane (Ar/CH_4) gas mixtures on characteristics of titanium carbide prepared by reactive sputtering. Caschera et al. [11] examined effects of composition on mechanical behavior of diamond-like carbon (DLC) coatings modified with Ti prepared by plasma enhanced chemical vapor deposition (PECVD) using titanium isopropoxide ($C_{12}H_{28}O_4Ti$) with different CH_4 flow rates. El Mel et al. [12] studied the surface composition modification of titanium carbide and carbon nanocomposite films prepared by reactive sputtering under in situ Ar ion bombardment. Grigore et al. [13] investigated structural characterization and electrochemical behavior of titanium carbon thin films using DC magnetron co-sputtering deposition process with Ti and C targets. Zhang et al. [14] examined the effect of substrate bias voltages on titanium carbide/*a*-C nanocomposite films deposited by filtered cathodic vacuum arc using Ti target and acetylene (C_2H_2). Oláh et al. [15] investigated the structural, chemical, and mechanical properties of titanium carbide/*a*-C deposited thin films prepared by DC magnetron co-sputtering system using Ti and C targets with varying the power of Ti target. Xu et al. [16] studied the effect of different synthetic times on the surface morphology, composition, and structure of titanium carbide containing DLC nanocomposite coatings prepared by cathodic arc evaporation using Ti target with different C_2H_2 flow rates. Nguyen et al. [17] investigated the structure of hydrogen insertion in titanium carbide based thin films prepared by hybrid physical vapor deposition

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(PVD) and PECVD using Ti target and benzene. Daniel et al. [18] studied the effect of the substrate to target position on the properties of titanium carbide/C coatings prepared by hybrid PVD and PECVD using Ti target and C_2H_2. Rubshtein et al. [19] examined the composition, structure, and surface properties of the titanium-carbon coatings prepared by PVD using Ti and C targets with different arc pulse frequencies.

As mentioned above, the preparation of C-Ti films mostly adopts co-sputtering of Ti and C targets in argon [9,13,15,19] or reactive sputtering (also known as hybrid PVD and PECVD) of Ti target with hydrocarbon and Ar gases [10,12,14,17,18]. The reactive sputtering, combination of sputtering and PECVD, has the advantages of PVD and PECVD; hence, the method for preparing C-Ti films not only reduces the risk of using organometallic gases but also easily adjusts C-Ti films with variable properties. The characteristics of C-Ti films were affected by the process parameters (such as: hydrocarbon/Ar ratios, radio-frequency (rf) powers, and working pressures) of reactive sputtering. Nevertheless, no work on the characteristics of C-Ti films prepared by reactive sputtering with different rf powers was found. Thus, in this study, the effect of different rf powers on microstructure, chemical composition, and optical and electrical properties of C-Ti films prepared by reactive sputtering is investigated. Additionally, the current density-voltage (*J-V*) and capacitance–voltage (*C-V*) characteristics of C-Ti films deposited on *n*-type silicon (*n*-Si) are also studied.

2. Experimental details

The following experiment was performed. The *n*-Si (100) substrates ($20 \times 20 \times 0.35\ mm^3$) and sodium (Na) glass plates ($25 \times 20 \times 2\ mm^3$) were cleaned, and the cleaning procedure had been described in the previous work [20].

The C-Ti films were separately deposited on *n*-Si substrates and Na glass plates by reactive sputtering. The detailed description of reactive sputtering was also reported in the previous paper [20]. Remarkably, the dopant source, precursor gas, and sputtering gas of this study use the Ti target (99.99% pure, 76.2 mm in diameter), CH_4 (99.999%), and Ar (99.99%), respectively. The substrate temperature, working pressure, and CH_4/Ar ratio were controlled at 298 K (25 °C), 4 Pa, and 1/5, respectively. Seven kinds of C-Ti films were prepared with the rf power being 50, 100, 150, 200, 250, 300, and 350 W. All the thicknesses of C-Ti films prepared at different rf powers are fixed at 100 nm by controlling the deposition time from 1 to 2 min.

The characteristics of C-Ti films were measured as follows. The thicknesses of C-Ti film were obtained using a field emission scanning electron microscope (FESEM). And then, the microstructure and chemical composition of the C-Ti films were investigated using Fourier transform infrared (FTIR) spectroscopy, Raman scattering spectroscopy (RSS), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), and field emission transmission electron microscope (FETEM). On the other hand, the optical property of C-Ti films was investigated using UV/VIS/IR spectrophotometer. The detailed description of FESEM, FTIR, RSS, and UV/VIS/IR spectrophotometer can be seen in the previous work [1]. Besides, the XPS (ULVAC-PHI PHI 5000 Versaprobe II) measurement was executed with a monochromatic X-ray source of Al Kα ($h\nu = 1486.6$ eV). All spectra of carbon core (C1s) and titanium core (Ti3p, Ti3s, $Ti2p_{3/2}$, $Ti2p_{1/2}$, and Ti2s) lines were acquired when the X-ray incident angle was 54° to enhance the contribution of C-Ti films on these core line shapes. The XRD (BRUKER D8 Discover) measurement was performed using Cu Kα radiation ($\lambda = 1.54$ Å) in grazing incident diffraction mode, and the incident angle is 0.5°. The C-Ti films were discerned by 2θ angles ranging from 10 and 90° to acquire diffraction peaks. Data from the Joint Committee on Powder Diffraction Standards (JCPDS) database were used to identify the microstructure of C-Ti films from the diffraction peaks. The FETEM (JEOL JEM-2100F) operated at an accelerating voltage of 200 kV. Before FETEM measurement, the sample for FETEM was prepared by focused ion beam (FIB, JEOL JIB-4601F) system. A platinum (Pt) layer (200 nm thickness) covered the surface of C-Ti films can decrease process-induced damage using FIB. The cross section and diffraction pattern of C-Ti films deposited on the *n*-Si substrate were measured from the FETEM images and selected-area electron diffraction pattern, respectively. Notably, all of the microstructure and chemical composition measurements were made on the C-Ti films located at the middle portion of the *n*-Si wafer substrate. Based on the accuracy of measured results, the electrical resistivity of C-Ti films was measured using either the series method or four-point probe (FPP) method. The details of series method and FPP method had been described in the references [1,21], respectively.

The *J-V* and *C-V* behaviors of C-Ti/*n*-Si devices were analyzed using the source meter (Keithley 2400) and the precision LCR meter (Agilent 4284A) with test leads (Agilent 16048D), respectively. The detailed description of these measurements had also been described in the previous work [20].

3. Results and discussion

3.1. Thicknesses of C-Ti films

The thicknesses of C-Ti films prepared with different rf powers were estimated using FESEM. FESEM results reveal that all the thicknesses of C-Ti films prepared at various rf powers are about 100 nm with an error less than 5%, implying that the thicknesses of C-Ti films are well controlled at fixed value.

3.2. Microstructure and chemical composition of C-Ti films

Fig. 1 displays the FTIR absorption spectra of C-Ti films deposited with different rf powers, and that is ranging from 2750 to 3150 cm^{-1} to identify the nature of C-H bonds in stretching mode. The C-H bonds in the film mainly consist of sp^3-CH_x bonds (ranging from 2820 to 2970 cm^{-1}) and sp^2-CH_x bonds (ranging from 2970 to 3100 cm^{-1}) [22–25]. Fig. 1 shows that as the C-Ti film were prepared at the rf powers of 50 W, the sp^3-CH_x bonds include the sp^3-CH_2 symmetric bond

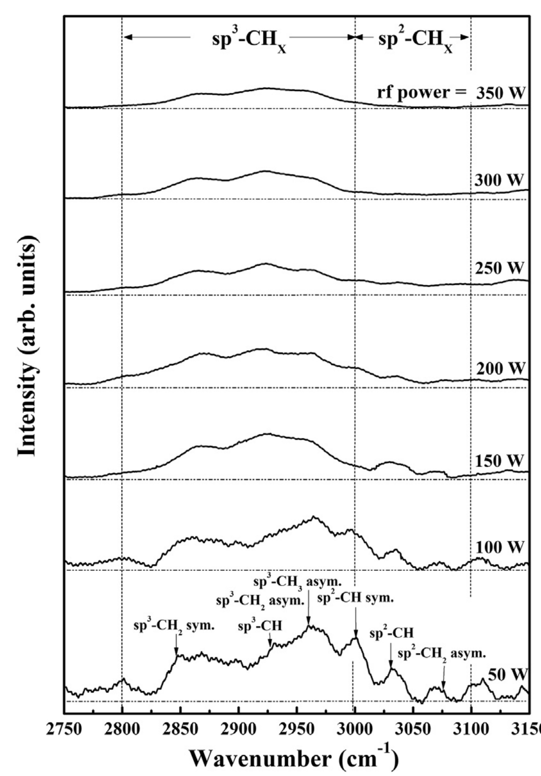

Fig. 1. FTIR absorption spectra of C-Ti films deposited with different rf powers.