Thin Solid Films 556 (2014) 544–551

Contents lists available at ScienceDirect

Thin Solid Films

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

Characteristics of carbon films prepared by thermal chemical vapor deposition using camphor

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ARTICLE INFO

Article history:
Received 18 May 2013
Received in revised form 10 December 2013
Accepted 15 January 2014
Available online 23 January 2014

Keywords:
Thermal chemical vapor deposition
Carbon film
Camphor
Microstructure

ABSTRACT

The properties of carbon films prepared by thermal chemical vapor deposition (thermal CVD) using camphor are investigated. As the deposition temperature increases from 1098 to 1198 K, the deposition rate follows the Arrhenius law with activation energy of 59.8 kJ/mol. The possible reaction paths and intermediate species of this thermal CVD process are also considered. The product gases CH_3, CH_4, and C_2H_2 can be speculated as the main species for pyrolytic carbon deposition. The crystallinity and ordering degree of carbon films decrease with increasing the deposition temperature. Nevertheless, the sp^2 carbon sites increase with increasing the deposition temperature, and results in the decrease of electrical resistivity and the increase of water contact angle. When the camphor weight changes from 0.06 to 0.50 g, the CVD reaction is controlled by a process of half order. Moreover, as the camphor weight increases from 0.30 to 0.50 g, the surfaces of carbon films are partially covered with spherical particles, the water contact angle substantially increases. Finally, the results of this work are compared to those of using CH_4 and C_2H_2 as the precursor gases.

1. Introduction

Carbon films have many excellent properties including wide band gap, good electrical conductivity, infrared transparency, high hardness, inertness to chemical attack, and high water-repellency [1–3], so they have been intensively studied. Absolutely, carbon films are of interest to many industries and are used in various areas, such as photovoltaic devices [4], graphite anodes in lithium ion secondary batteries [5,6], anti-reflection coatings [7], wear and tribological coatings [8], biomedical products [9], and hermetic coatings [10–13]. Pyrolytic carbon is a kind of carbon materials that has been developed for a long time. Although, pyrolytic carbon can be used by itself as free-standing structures such as crucibles or rocket nozzles, its major use is in the form of coatings on substrates such as metals, ceramics, molded graphite, carbon foam, and carbon fibers [3]. For example, pyrolytic carbon films have been formed by decomposing hydrocarbons in a heating reactor and depositing them on optical fibers [10–13] or graphite particles [5,6] using thermal chemical vapor deposition (CVD). When pyrolytic carbon films are prepared by thermal CVD, their properties are affected by many factors, such as the precursor gas, deposition temperature, working pressure, mass flow rate, and substrate size [13–17].

Camphor ($C_{10}H_{16}O$) is a nature carbon source, which is non-toxic, harmless to human body, low cost, and abundantly found. Camphor also has saturated carbon–hydrogen bonds including methyl groups, pentagon carbon rings, and aromatic carbon rings [18–21]. Additionally, lower H/C ratio in case of camphoric gas has another advantage in producing lower hydrogen contents in the film compared to methane gas [18]. Accordingly, camphor was extensively adopted as the precursor gas to synthesize carbon nanotubes [22,23], glassy carbons [24], amorphous carbon films [25–27], and graphenes [28,29]. On the other hand, many thermal CVD processes for carbon deposition by pyrolysis using hydrocarbons have been carefully investigated, showing reaction paths and intermediate species [30–33]. Nevertheless, we found no evidence of previous works to study the influences of deposition temperatures on the properties of pyrolytic carbon films prepared by thermal CVD using camphor, and the reaction paths and intermediate species of thermal CVD process had not yet been addressed in detail. Hence, this study prepared pyrolytic carbon films by thermal CVD using camphor as the precursor, and the effects of deposition temperatures on the properties of carbon films were investigated. Furthermore, the possible reaction paths and intermediate species of thermal CVD process and the connections between the properties of carbon films and thermal CVD process were also considered. Alternatively, the effects of camphor weights on the properties of carbon films were discussed. Finally, the results of this work are compared to those of using CH_4 [13] and C_2H_2 [34] as the precursor gases.

2. Experimental details

The experiment proceeded as follows. The silica glass plates (width = 12.5 mm, length = 12.5 mm, and thickness = 1 mm) were subsequently cleaned in ultrasonic baths of acetone and de-ionized water to improve the adhesion of carbon films onto the substrates. Then, the carbon films were deposited on silica glass

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http://dx.doi.org/10.1016/j.tsf.2014.01.035

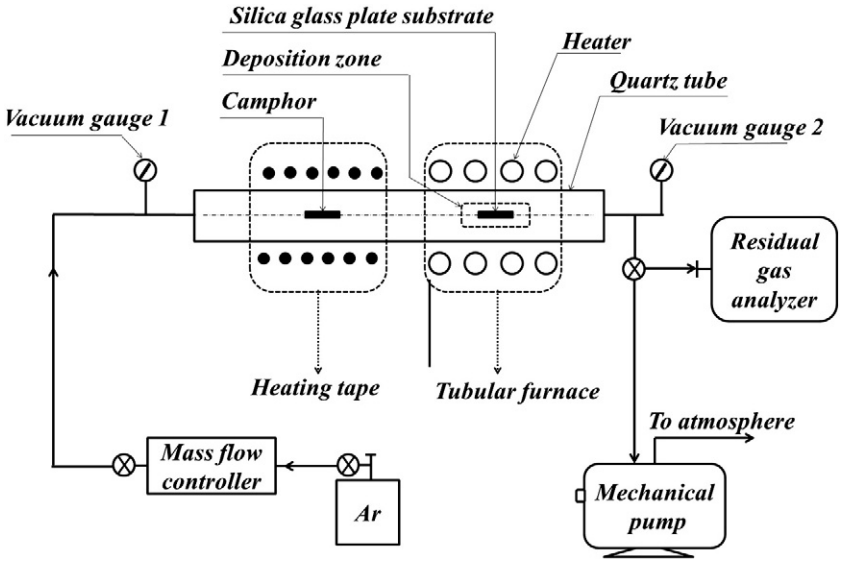

Fig. 1. Schematic of thermal CVD system.

plates using thermal CVD system. Fig. 1 demonstrates the schematic of thermal CVD system. This system adopted a quartz tube as the reaction chamber, which has a length of 900 mm, an internal diameter of 25 mm, and a wall thickness of 1.5 mm. A heating tape was wound around the quartz tube at a distance of 200 mm in front of the deposition zone of tubular furnace (Lindberg TF55030A-1). 0.13 g camphor powders were heated to become vapor by heating tape at a temperature of 473 K, and 30 sccm (standard cubic centimeter per minute) argon (*Ar*) was used to carry the camphor vapor to flow into the deposition zone. The deposition zone was 60 mm in length, and the substrate was placed in the reaction chamber so that the middle portion of the substrate's length coincides with that of the deposition zone. To investigate the effects of deposition temperatures on the properties of carbon films, five kinds of pyrolytic carbon films were prepared at the deposition temperatures of 1098, 1123, 1148, 1173, and 1198 K. The deposition temperature of the deposition zone was risen from room temperature at a rate of 18 K/min, and its accuracy was $\pm$ 2 K. The working pressure was maintained at 65 $\pm$ 25 kPa, and the deposition time was set to 390 s. Notably, a residual gas analyzer (RGA, Extorr-XT200M) was used to measure the molar fractions of residual gases as the temperature of deposition zone of tubular furnace is at room temperature (298 K) and various deposition temperatures (1098, 1123, 1148, 1173, and 1198 K). After the deposition process was finished, the temperature of the deposition zone was quickly reduced to room temperature at a rate of 250 K/min by cooling in air with a fan. Simultaneously, the residual product gases were exhausted by mechanical pump. The thicknesses of the carbon films were obtained by measuring the cross sections of silica glass plates located at the middle portion of the deposition zone using a field emission scanning electron microscope (FESEM, JEOL JSM-6700F). The operating voltage of the FESEM was 3 kV. The structural and chemical characteristics of carbon films were investigated by X-ray diffractometer (XRD, Bruker MXP-III), Raman scattering spectrometer (JOBIN YVON Triax 550), and X-ray photoelectron spectroscopy (XPS, ULVAC-PHI PHI 1600 VersaProbe). The XRD was measured using *Cu* K_α radiation ($\lambda = 0.154$ nm) in grazing incident diffraction mode, and the incident angle is 0.5°. Diffraction peaks from the carbon films were discerned by 2θ angles ranging between 10 and 40°. Data from the Joint Committee on Powder Diffraction Standard (JCPDS) database (Number: 75-1621) were used to identify the microstructure of the carbon films from the diffraction peaks. Each XRD datum was obtained from the average value of three data measured on the same specimen position. The Raman spectra were performed in back-scattering geometry with the 632.8 nm line of a He–Ne laser at room temperature in the spectral range of 1000–2000 cm^{-1}. The photoelectron spectra of carbon films were acquired with *Mg* K_α radiation (photon energy = 1253.6 eV). All carbon core line (*C* 1*s*) spectra were acquired at the X-ray incident angle of 54°. All the measurements of microstructures were made on the carbon films located at the middle portion of the substrate. Furthermore, the electrical properties of the carbon films were obtained using the source meter (Keithley 2400) with four point probe. A direct current of 1 mA was applied to the carbon film, and the output voltage was then measured. The sheet resistance was obtained from the relationship between output voltage and input current. With the application of the correction factors and film thickness, the electrical resistivity of carbon films can be obtained from its sheet resistance. The water contact angle of carbon films was measured using water contact angle meter (FTA 200). To verify the effects of camphor weights on the properties of carbon films, an extra experiment was executed as follows. The camphor weights were set to 0.06, 0.13, 0.30, and 0.50 g; the deposition temperature was fixed at 1173 K, and other process parameters were not changed.

3. Results

3.1. Film thickness and residual gases

Fig. 2 shows the FESEM images of cross sections of the carbon films that are deposited on silica glass plates at different deposition temperatures. The FESEM results show that the thicknesses t_p of carbon films are 227, 280, 314, 370, and 410 nm for the deposition temperatures being 1098, 1123, 1148, 1173, and 1198 K, respectively. The carbon films are uniformly deposited on silica glass plates, and the standard deviation of the measured values of the film thickness was within 5%. Fig. 2 also illustrates that the carbon films demonstrate a laminar structure. Pyrolytic carbon films prepared by thermal CVD usually exhibit a laminar structure [35]. Notably, as the deposition time was set to 390 s, the 0.13 g camphor powder was heated to become vapor completely. Assume that the 0.13 g camphor powder was exhausted at the time of t_e, and thus, t_e is smaller than 390 s. The deposition rate r_f of the carbon films can be calculated from the film thickness and t_e. Accordingly, the dependence of the deposition rate on the deposition temperature follows the Arrhenius law:

$$r_f = k_0 \exp(-E_a/RT), \tag{1}$$