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Effects of radio-frequency powers on the properties of carbon coatings on optical fibers prepared by thermal chemical vapor deposition enhanced with inductively coupled plasma

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ABSTRACT

This study investigates the effects of different radio-frequency (rf) powers on the characteristics of carbon coatings on optical fibers that are prepared by thermal chemical vapor deposition (thermal CVD) enhanced with inductively coupled plasma (ICP). Methane and nitrogen were used as the precursor gases, and rf-powers of ICP were set to 0, 50, 100, 200, 300, and 400 W. The deposition temperature, working pressure, and deposition time in the thermal CVD process were set to 1248 K, 4 kPa, and 2 h, respectively. Experimental results indicate that the deposition rate of carbon coatings increases as the rf-power increases from 0 to 200 W, but decreases as the rf-power exceeds 200 W. The mean crystallite size and ordered degree of carbon coatings decrease with increasing the deposition rate. Moreover, when the rf-power increases, the carbon coatings have more sp^2 carbon atoms and shift to graphite-like. With the assistance of ICP, carbon coatings can be deposited by thermal CVD at a low working pressure (about 4 kPa). Furthermore, the deposition rate and film properties can be adjusted by the rf-power.

1. Introduction

Carbon films have many excellent properties including wide band gap, infrared transparency, high hardness, inertness to chemical attack, and high water resistance [1], so they have been extensively studied. Carbon films can be deposited using various methods, such as radio-frequency plasma enhanced chemical vapor deposition (rf-PECVD) [2], thermal chemical vapor deposition (thermal CVD) [3,4], microwave plasma chemical vapor deposition [5], sputtering deposition [6], filtered cathodic vacuum arc deposition [7], and ion beam deposition [8]. When carbon films are prepared by rf-PECVD, hydrocarbons are mostly used as the precursor gases. The precursor gas is decomposed and reacted in the plasma to create carbon species, and then, the carbon species are deposited on the substrate to form the carbon films. Hence, the characteristics of carbon coatings prepared by rf-PECVD are affected by the rf-power [9]. Alternatively, other carbon films called pyrolytic carbon films can be formed by decomposing hydrocarbons in a heating reactor and depositing them on the graphite particles [10] or optical fibers [3] using thermal CVD, and they were employed as the graphite anode in lithium ion secondary batteries [10], or hermetic optical fiber coating [3].

When carbon films are prepared by thermal CVD, their properties will be also affected by many factors, such as the substrate, precursor gas, deposition temperature, working pressure, and mass flow rate of inlet gas [3,10,11]. Recently, we have adopted methane (CH_4) as the precursor gas to study the effect of deposition temperature [4], substrate size [12], nitrogen (N_2) addition [13], and ammonia addition [14] on the properties of carbon films prepared by thermal CVD. The experimental results showed that if the carbon coatings were prepared by thermal CVD, the deposition rate of carbon coatings decreases with decreasing the working pressure, and thus, thermal CVD usually executed at the working pressure of about 50–100 kPa. It can be expected that the deposition rate of carbon films prepared by thermal CVD at low pressures can be changed with the assistance of plasma. Moreover, the properties of carbon coatings prepared by thermal CVD with and without the assistance of plasma would be quite different. However, we have found no evidence of previous works to deposit carbon coatings using thermal CVD that is enhanced with inductively coupled plasma (ICP). Hence,

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this study will fabricate carbon coatings on optical fibers using thermal CVD enhanced with ICP, and the effects of different rf-powers of ICP on the characteristics of carbon coatings will be investigated.

2. Experimental details

The experiment proceeded as follows. First, the optical fiber (also called silica glass fiber) (diameter = 0.125 mm, length = 120 mm) was cleaned in ultrasonic baths of acetone and de-ionized water, in that order, to improve the adhesion of carbon coatings onto these substrates. Second, the carbon coatings were deposited on silica glass fibers using the thermal CVD enhanced with ICP as shown in Fig. 1. The thermal CVD 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. The deposition zone length of the reaction chamber was 60 mm, 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. The ICP was placed before the thermal CVD system, which was constructed by winding six-turn hollow copper coils (called RFI coils) around the quartz tube. A 13.56 MHz rf was applied on the RFI coils to create the plasma inside the quartz tube. To avoid overheat in the coils, the hollow copper coils were cooled by circulated water with a temperature of 293 K. 99.999% CH_4 and 99.995% N_2 were used as the precursor gases, and the flow rates of CH_4 and N_2 were 16 and 4 sccm (standard cubic centimeter per minute, cm^3/min), respectively. Six kinds of carbon coatings were prepared with rf-powers of ICP being 0, 50, 100, 200, 300, and 400 W. The working pressure was maintained at 4 kPa by a mechanical pump. The temperature rose from room temperature to deposition temperature at a rate of 18 K/min. The deposition temperature and deposition time were set to 1248 K and 2 h, respectively. After the deposition process was finished, the temperature was quickly reduced to room temperature at a rate of 250 K/min by cooling in air with a fan. Third, the thicknesses of the carbon coatings were obtained by measuring the cross sections of the glass fiber located at the middle portion of the length using a field emission scanning electron microscope (FESEM, JEOL JSM-6700F). Finally, the microstructure of the carbon films was investigated by Raman scattering spectrometer (RSS, JOBIN YVON Triax 550) and X-ray photoelectron spectroscopy (XPS, ULVAC-PHI PHI 1600 VersaProbe). The RSS were measured 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}. Alternatively, the XPS used Mg K_α radiation (Photo energy = 1253.6 eV) as an excitation source was utilized to measure the binding energy spectra of carbon coatings. All carbon core lines (*C1s*) spectra were acquired when the X-ray incident angle was 54° to enhance the contribution of carbon coatings on this core line shape. The measurements of microstructures were made on the carbon coatings located at the middle portion of the substrate.

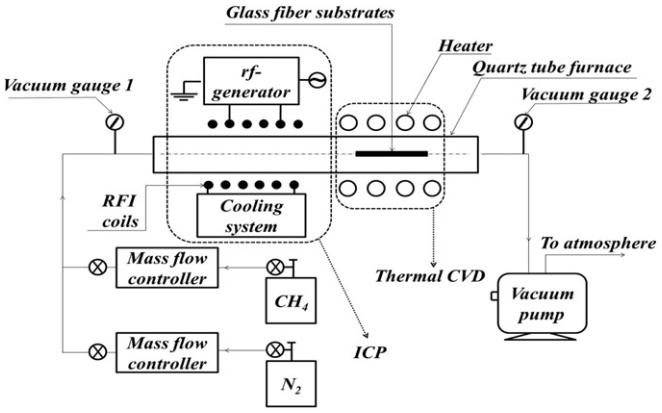

Fig. 1. Schematic of thermal CVD system with inductively coupled plasma (ICP).

3. Results

3.1. Deposition rate

The thickness t_f of carbon coatings are obtained by measuring cross sections of silica glass fibers, and the measured results show that the thickness t_f of the carbon coatings are 20, 61, 100, 140, 120, and 76 nm for the rf-powers of 0, 50, 100, 200, 300, and 400 W, respectively. The deposition rate r_f of the carbon coatings can be calculated from the coating thickness and deposition time, and thus, the deposition rates of carbon coatings are 10, 31, 50, 70, 60, and 38 nm/h for the rf-powers being 0, 50, 100, 200, 300, and 400 W, respectively. This result indicates that the deposition rate of carbon coatings increases with the rf-power in the beginning, and then decreases.

Legrand et al. [15] reported that the stable species in the CH_4 and N_2 plasma may include (a) electrons – e; (b) hydrocarbons – CH_4, C_2H_6, C_2H_4, C_2H_2, C_3H_8, and C_4H_{10}; (c) radicals – CH, CH_2, C, C_2H_5, C_2H_3, and C_2H; (d) hydrogen and nitrogen – H_2, H, N_2, N, N_2^*, and N^*; and (e) nitrogen containing species (stable product and radicals) – HCN, CN, H_2CN, and NH. Vassallo et al. [16] further proposed that the hydrocarbon radicals, CN, H_2, H, N_2, N, and N_2^* species in the low temperature plasma increase with increasing the rf-power. Our experimental results showed that the carbon film was deposited on the quartz tube around the ICP, and the thickness of these deposited carbon films increases with increasing the rf-power. Hence, we can predict that some of the species in the plasma were deposited on the quartz tube around the ICP, and thus, the thickness of the deposited carbon films increases with increasing the rf-power.

In the thermal CVD process, a hot-wall reactor is used to deposit carbon materials on silica glass fibers. In this process, substrates are heated in a deposition reactor and the species come from ICP are flowed through the reactor and heated up. After heated up in the deposition reactor, the species come from ICP undergo reactions in the gas phase. Simultaneously, complex heterogeneous reactions occur at the surface of the silica glass substrate [17]. Yokomichi et al. [18] reported that CN radicals are not deposited as the substrate temperature was over 823 K. The deposition temperature of this study is 1248 K, so the CN radicals may not helpful for the deposition of carbon films during thermal CVD process. Pan et al. [19] found that the existence of HCN is favored at high temperature process. Tsang et al. [20] further reported that the stability of HCN species will preclude most of the cycling of carbon during the CVD process, which is resulting in low deposition rate. Hence, when the rf-power increases from 0 to 200 W, the amount of hydrocarbon radicals come from ICP increases. The hydrocarbon radicals are responsible for the formation of carbon films in thermal CVD process [21], and thus, the deposition rate of carbon films on the optical fibers also increases. Nevertheless, when the rf-power increases from 200 to 400 W, more CN species were produced [16]. In this case, the CN species come from ICP are not favorable for the formation of carbon films in thermal CVD process [18]. Moreover, the CN species are helpful for the gas phase formation of HCN species in thermal CVD process [19], which may suppress the deposition rate of carbon films [20]. Consequently, this would cause the decrease of deposition rate of carbon films on the optical fibers.