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Diamond-like carbon deposited by plasma technique as a function of methane flow rate

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ABSTRACT

Diamond-like carbon (a-C:H) prepared by plasma enhanced chemical vapor deposition (PECVD) as a function of methane gas flow rate is reported. Films deposited at zero flow rate, i.e., without the use of vacuum pumps during the deposition, are also investigated. For that purpose, the reactor chamber was baked and pumped down to about 10^{-8} Torr to reduce contamination released from the reactor walls. The films were analyzed by visible, infrared and Raman spectroscopes. It was observed that the deposition rate, hydrogen concentration and optical gap depend on the methane gas flow rate. A maximum for deposition rate found at methane flow was much smaller than the flow usually adopted in conventional procedures.

1. Introduction

Diamond-like carbon (DLC) has been used in a number of application such as hard coating for tools, cold cathode electron emitters, micro-electro-mechanical systems (MEMS), car parts and protective coating in hard disk drives. These applications are mainly associated with the high hardness and low friction coefficient of DLC [1–4]. A number of different techniques have been explored for the development of these films [4–12]. One of the most used techniques is the plasma enhanced chemical vapor deposition (PECVD). In this technique, usually methane gas (CH_4) is introduced into the reactor chamber at a continuous flow rate, under vacuum condition or even in atmospheric pressure [12]. Plasma is then generated between the anode and cathode electrodes. As a result, polymeric-like carbon film is formed on the anode and DLC on the cathode. A continuous supply of methane gas is required to guarantee that the atmosphere be constant along the deposition. This procedure results in the waste of a considerable amount of methane gas to the atmosphere. In this work we investigated diamond-like carbon prepared by PECVD in a wide range of methane gas flow rates, including films prepared at zero flow rate. The main objective is to investigate deposition conditions that represent significant reduction on the use of methane gas for economic purpose as well as to prevent the release of contaminating gas to the environment. The films were investigated by visible, infrared and Raman spectroscopes.

2. Experimental

The films were deposited in an ultra-high-vacuum system to reduce desorption of contaminating gases from the walls of the reactor chamber. In addition, the reactor chamber was baked for more than 10 h at a temperature of about 120 °C and pumped down to about 10^{-8} Torr. Films were then deposited by PECVD (using a 13.56 MHz Dressler RF power supply at −120 V bias voltage) on the

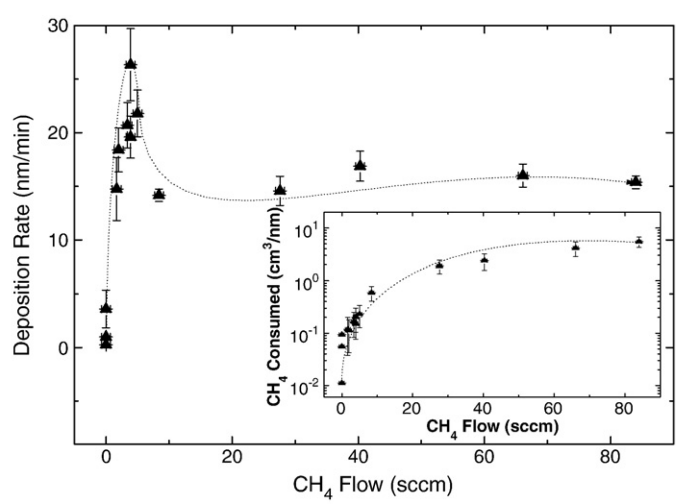

Fig. 1. Deposition rate of diamond-like carbon films deposited by PECVD as a function of methane flow. The inset shows the consumption of methane in the same flow range. The parameter "consumption" stands for volume of feed gas (including the gas used to form the film and the gas pumped out) spent to prepare a film per unit of film thickness.

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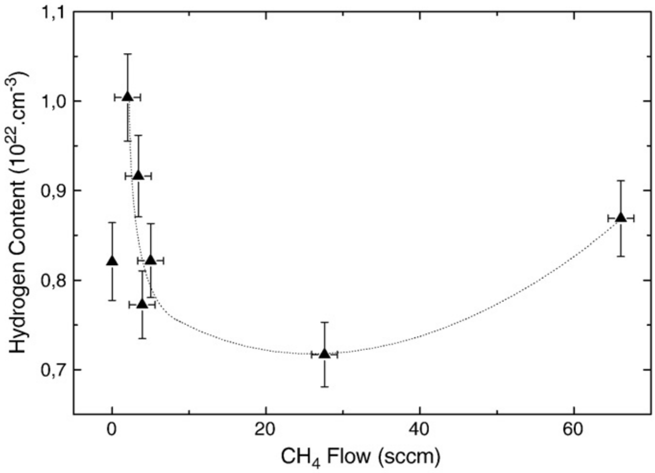

Fig. 2. Bonded hydrogen concentration of a-C:H films, using the integrated area of the C-H stretching mode (a wavelength range of 2800–3000 cm^{-1}), as a function of methane flow rate.

cathode electrode as a function of methane (99.999% pure) gas flow rate in the range of 0 to 80 sccm. This range includes uncommon methane flow rate (very low and very high flows), not adopted in conventional laboratory systems. A gate valve, placed between the reactor chamber and the vacuum turbomolecular pump, was used to reduce the pumping speed in order to keep the deposition pressure constant at 4×10^{-2} Torr as the methane flow was varied. For the deposition at zero flow, the chamber was closed and methane gas was introduced until the desired pressure was reached. Using this procedure, hydrogenated amorphous carbon (a-C:H) films with diamond-like structure were obtained. All films were deposited on crystalline <111> silicon (for deposition rate, Fourier transform infrared spectroscopy (FTIR) and Raman spectroscopy measurements) and corning 7059 glass (for optical measurements). The films' thickness was in the range of 90–600 nm, determined by a Dektak 150 perfilometer. Tauc's band gap was determined using the absorption coefficient extract with the PUMA software [13] inputted with transmittance data acquired from visible and infrared Lambda 9 photospectrometer. Hydrogen concentration was estimated through infrared measurement, extracted from a Nicolet FTIR spectrometer, using the C-H stretching mode in the frequency range of 2800–3100 cm^{-1} according to the procedure described elsewhere [14,15]. Micro-Raman scattering spectroscopy was carried in air at room temperature in an Acton Research SpectraPro 500i analyzer, using the 488 nm Ar^{+} laser line with 10 nW emission power.

3. Results

The deposition rate of the DLC films (Fig. 1) changes significantly in the methane flow rate range as investigated. A maximum is found at a relatively low flow, 4 sccm, with a deposition rate of about 50% higher than in normal condition (a range of 10–40 sccm). The hydrogen concentration, on the other hand, increases monotonically (except for the film prepared at zero flow rate) in the range investigated (Fig. 2), indicating some changes in the atmosphere composition due to the reduction of the pumping speed. In fact, this is somehow expected, since the methane gas is consumed during deposition. As a result, the atmosphere becomes richer in hydrogen (produced in plasma dissociation of methane).

Fig. 2 shows the concentration of hydrogen as a function of the methane flow rate. It is observed that the concentration increases as the methane flow decreases. This effect must be related to the increase in the partial pressure of H_2 in the atmosphere, promoted by the reduction of the pumping speed. The hydrogen concentration of the film prepared at zero flow rate does not follow the same trend of the other films. However, this sample has a particular characteristic. During the deposition, the partial pressure of methane is reduced and the partial pressure of H_2 increases, affecting the properties of the film.

The Tauc's band gap increases slightly as the methane gas flow rate decreases (Fig. 3A). One would expect that the band gap should increase, since the hydrogen concentration increases. However, the structure of the films must have changed in this methane flow range. The index of refraction, on the other hand, increases in the same range (Fig. 3B).

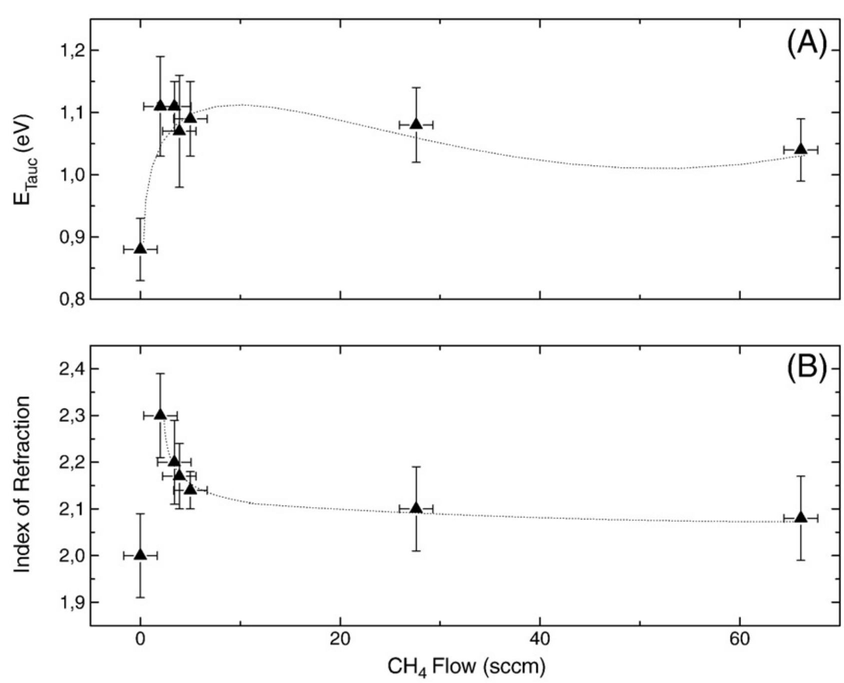

Fig. 3. (A) Tauc's band gap and (B) index of refraction of diamond-like carbon as a function of methane gas flow rate.