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The effect of the $H_2/(H_2 + Ar)$ flow-rate ratio on hydrogenated amorphous carbon films grown using $Ar/H_2/C_7H_8$ plasma chemical vapor deposition

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ABSTRACT

To produce hydrogenated amorphous carbon (a-C:H) films with high mass density at a high deposition rate and low substrate bias voltage, we deposited these films on a Si substrate by plasma chemical vapor deposition, using toluene as a source compound and varying the gas flow-rate ratio of $H_2/(H_2 + Ar)$. By decreasing the gas flow-rate ratio from 55% to 11%, the hydrogen content in the films decreased, and the density of sp^3 carbon atoms in the films increased, whereas their surface roughness increased. At the gas flow-rate ratio of 11%, we produced a-C:H films with a high bulk density of 1830 kg/m^3 at a high deposition rate of 81.1 nm/min.

1. Introduction

Hydrogenated amorphous carbon (a-C:H) films have superb properties such as high mechanical hardness, low friction coefficient, biocompatibility, good wear resistance, high corrosion resistance, and chemical inertness; hence, they have been used in many applications such as biomedical implants, protective coatings, and wear-resistance coatings in automotive components [1–9]. The properties of these films depend much on their surface structure and internal bonding, comprising a mixture of two carbon hybridization configurations: diamond-like sp^3 and graphite-like sp^2 hybridization together with carbon–hydrogen bonds [10,11]. In general, a-C:H films are classified into (a) soft polymer-like a-C:H (PLCH) with a mass density of 1200–1600 kg/m^3 and a high hydrogen content of 40–60 at. % [12], and (b) hard diamond-like a-C:H (DLCH) with a mass density of 1600–2200 kg/m^3 and a hydrogen content of 20–40 at.% [13].

The deposition method affects the surface structure and internal bonding of the produced layers, and hence the properties of the deposited a-C:H [14]. Methods for depositing a-C:H include ion beam deposition [15], sputtering [16], pulsed laser deposition [17], and plasma chemical vapor deposition (plasma CVD) [18,19]. Among these methods, plasma CVD is widely used, owing to its low deposition temperature, high deposition rate, technological simplicity, and uniform coating on complex and irregular surfaces [20,21]. The deposition rate and characteristics of the deposited a-C:H films are closely related to the synergetic effects of plasma species. For example, there is a direct relationship between the deposition rate and carbon-containing neutral radicals. Moreover, the bombardment of ions on the growing surface of the a-C:H film plays a crucial role in controlling the sp^3-to-sp^2 ratio and the hydrogen content in the film. In turn, the generation rates of such carbon-containing neutral radicals and ions depend on the precursor composition [22].

Although a-C:H films have been used in many areas, several issues remain that limit their further application. One issue is the relatively low deposition rate, as a high deposition rate of 100 nm/min or more is often required for mass production [23]. Another issue is the high bias voltage needed to produce hard a-C:H films with smooth surfaces.

Many groups have formed flat a-C:H films by various methods and investigated their characteristics. For example, Mahmud et al. deposited a-C:H films on plate samples by hybrid magnetron and studied how the substrate temperature affected the surface and tribological performance [24]. Roca et al. showed the relationship between peak voltage and surface roughness of a-C:H films deposited by pulsed-DC plasma CVD [25]. Dai et al. deposited the film using pulsed unbalanced magnetron sputtering and reduced the surface roughness by step biasing [26]. Cho et al. studied the properties of a-C:H films deposited using microwave plasma CVD and RF plasma CVD, comparing the results of using various substrate bias voltages [27]. However, all these reports used high substrate bias voltages above 500 V. Using such a high bias voltage, and the resulting impingement of ions at high kinetic energy, often damages the magnetic and semiconductor materials and devices below the a-C:H film [28,29]. In a word, to use a-C:H films with

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damage-sensitive materials and devices, we must be able to deposit quality a-C:H films at high deposition rate by using low bias voltage.

In this study, to produce hydrogenated a-C:H films with high mass density at high deposition rate and low substrate bias voltage, we deposited the films on a Si substrate by plasma CVD, using toluene as a source compound and varying the gas flow-rate ratio of $H_2/(H_2 + Ar)$. We discuss how the ion bombardment affected the film structure based on the physical process of subplantation and the chemical process of dehydrogenation [13].

2. Experimental

2.1. The source compound

The source gas used in plasma CVD greatly affects the properties of a-C:H films. Although methane (CH_4) is the most popular choice, especially in electronic applications, this source compound gives low deposition rates, often a few nm/min, and high hydrogen content in the growing film. Consequently, to improve the deposition rate and properties of the a-C:H films, we used several types of hydrocarbons as source compounds, such as ethylene (C_2H_4), ethane (C_2H_6), propane (C_3H_8), butylene (C_4H_8), benzene (C_6H_6), and toluene (C_7H_8). The ionization rate coefficients of such hydrocarbons were obtained [30–32].

Kim et al. [33] and Vacher et al. [34] reported electron-impact ionization cross-sections of several hydrocarbons, some of which are shown in Fig. 1. All of these cross-sections reach their maximum values near the incident electron energy of 70 eV. Among the materials, toluene has the lowest ionization potential and the highest ionization cross-section. According to the ion-core model, the electron-impact dissociation cross-sections of the source molecule into neutral radicals should be similar in shape to the corresponding electron-impact ionization cross-sections. The flux or density of such neutral radicals toward the substrate mainly determines the deposition rate. Therefore, we expect that the ionization rate coefficient correlates with deposition rate.

The ionization rate coefficient k was obtained by the following equation [35]:

$$k(T_e) = (d_\sigma/d_\varepsilon)\langle v\rangle(\varepsilon_T + 2T_e)\exp(-\varepsilon_T/T_e) \tag{1}$$

For this evaluation, we used a Maxwellian electron energy distribution with an electron temperature T_e of 3 eV. ε_T is the threshold of ionization, namely the ionization potential. d_σ/d_ε is the slope of the ionization cross-section just above the threshold of ionization. $\langle v\rangle$ is the thermal speed, which can be calculated by the following equation:

$$\langle v\rangle = \sqrt{(8T_e/\pi m_e)}, \tag{2}$$

where m_e is the mass of an electron.

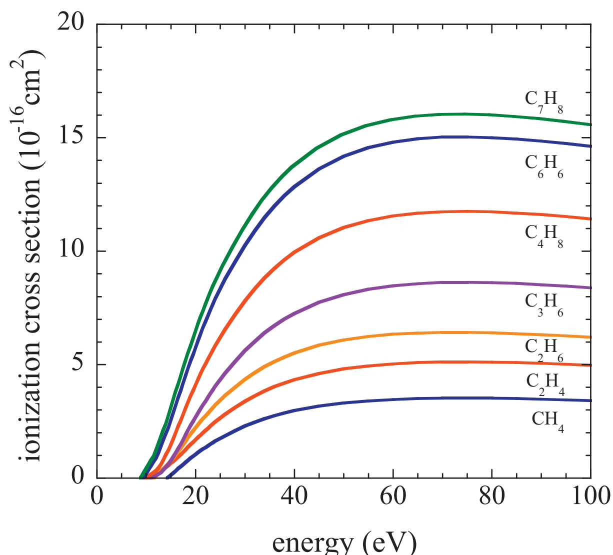

Fig. 1. Electron-impact ionization cross-sections of various hydrocarbons.

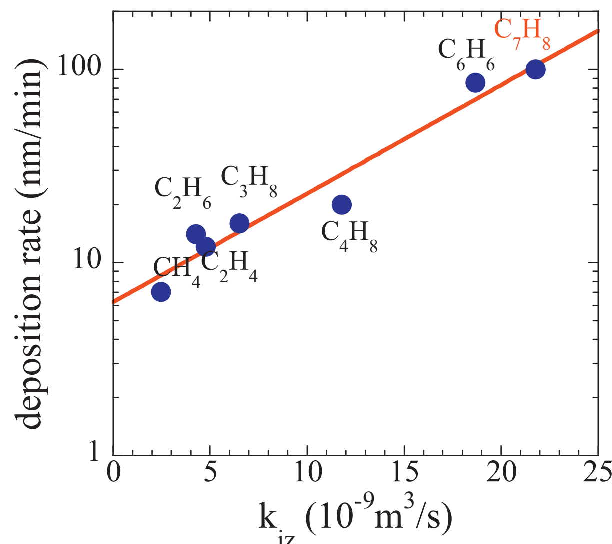

Fig. 2. Relationship between deposition rate and ionization rate coefficient.

Fig. 2 shows relationship between the deposition rate and k. The deposition rate grows exponentially with increasing k, and toluene has the highest k. Therefore, toluene is a good precursor to obtain a high deposition rate. In addition, the methyl group of toluene should improve the thermal stability of the a-C:H film, which can be enhanced by creating cross-linked structures [36,37]. Therefore, we chose to use toluene as the precursor in this study.

2.2. Film preparation

a-C:H films were deposited by using the H-assisted plasma CVD reactor shown in Fig. 3, which sustained a capacitively coupled main discharge and an inductively coupled discharge of the H atom source [38–41]. The main discharge was sustained between a mesh powered electrode of 85-mm diameter and a plane substrate electrode of 85-mm diameter at a distance of 33 mm, producing carbon-containing radicals as deposition precursors. The excitation frequency of the main discharge was 28 MHz, and the supplied voltage was 170 *V*. The discharge of the H atom source, which was sustained using a radio-frequency (RF) induction coil of 100-mm diameter placed 65 mm above the substrate electrode of the main discharge, generated a high flux of H atoms toward the substrate. This reactor is advantageous because it allows independent control of the generation rates of the carbon-containing radicals and H atoms. The H atom source was separated from the main discharge using a grounded mesh (30 meshes/in.) of 160-mm diameter placed 2 mm above the mesh-powered electrode of the main discharge. To control the kinetic energy of incident ions, an RF bias voltage of 400 kHz was applied to the substrate. The corresponding substrate bias voltage was set at −60 V to enhance the ion bombardment and to produce hard a-C:H films. The H atom source was not used during deposition.

Deposition used a gas mixture consisting of Ar, H_2, and vaporized toluene. Toluene was supplied at a constant flow rate of 5 sccm. The total flow rate of H_2 and Ar was 90 sccm. The gas flow-rate ratio, R, is defined as follows:

$$R = [H_2]/[H_2] + [Ar], \tag{3}$$

where $[H_2]$ and $[Ar]$ are the flow rates of hydrogen gas and argon gas, respectively. R was varied from 11% to 55%. Toluene was introduced

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