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Theoretical analysis of ion kinetic energies and DLC film deposition by $CH_4 + Ar$ (He) dielectric barrier discharge plasmas*

Liu Yan-Hong(刘艳红)[a)†], Zhang Jia-Liang(张家良)[a)],
Ma Teng-Cai(马腾才)[a)], Li Jian(李　建)[a)], and Liu Dong-Ping(刘东平)[b)]

[a)] *State Key Laboratory of Materials Modification by Laser, Ion and Electron Beams, Dalian University of Technology, Dalian* 116024, *China*
[b)] *Department of Mathematic and Physics, Dalian Nationality University, Dalian* 116600, *China*

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The kinetic energy of ions in dielectric barrier discharge plasmas are analysed theoretically using the model of binary collisions between ions and gas molecules. Langevin equation for ions in other gases, Blanc law for ions in mixed gases, and the two-temperature model for ions at higher reduced field are used to determine the ion mobility. The kinetic energies of ions in $CH_4 + Ar$(He) dielectric barrier discharge plasma at a fixed total gas pressure and various Ar (He) concentrations are calculated. It is found that with increasing Ar (He) concentration in $CH_4 + Ar$ (He) from 20% to 83%, the CH_4^+ kinetic energy increases from 69.6 (43.9) to 92.1 (128.5) eV, while the Ar^+ (He^+) kinetic energy decreases from 97 (145.2) to 78.8 (75.5) eV. The increase of CH_4^+ kinetic energy is responsible for the increase of hardness of diamond-like carbon films deposited by $CH_4 + Ar$ (He) dielectric barrier discharge without bias voltage over substrates.

Keywords: ion energy, dielectric barrier discharge, diamond-like carbon deposition
PACC: 7750, 6180J, 6855

1. Introduction

Dielectric barrier discharge (DBD), one of the most important atmospheric cold plasmas, has been widely used in ozone synthesis, surface modification, pollution control, CO_2 lasers, excimer lamps, flat plasma-display panels, and layer coatings.[1−3] In general, DBD plasma at an elevated pressure is characteristic of a series of micro-discharges.[4] However, DBD also exhibits diffuse mode at atmosphere pressure or at middle gas pressure of several hundreds of pascal (Pa). The diffuse mode of DBD at atmosphere pressure is called atmosphere pressure glow discharge (APGD), and has attracted wide attention due to its application suitable for continuous processing on a production line. APGD exhibits different configurations determined by the properties of feeding gas. The analysis of Massines *et al*[5] suggested that, the N_2 APGD is Townsend discharge in which the metastables stay in the gas and create electrons through cathode secondary emission, while He APGD is a glow discharge in which electrons and ions trapped in the positive column lead to the memory from one discharge to the following one. APGD is strongly influenced by the presence of impurities, gas additives, and residual metastables, electrons, or ions. In fact, APGD only exists in a few rare gases (He, Ne and N_2). This is a drawback for the industrial applications.[6,7]

The diffuse DBD at the gas pressure of several hundreds of Pa can be obtained much more easily.[1] It has been generally thought that, with decreasing gas pressure, an increase in the filamentary diameter leads to transition from the filamentary structure to the more diffuse appearance of the glow discharge. Using this kind of diffuse DBD plasma, dense diamond-like carbon (DLC) films have been deposited.[8,9] Different from typical ECR plasma or rf plasma, no voltage is biased across the substrates, through which the ion can gain enough energy for the deposition of dense a-C∶H films. In fact, it is widely accepted that the impinging of energetic ions is the prerequisite for the deposition of dense a-C∶H films.[10]

A theoretical model for ion energy in DBD plasma has been established based on the ion drift-diffusion model and the assumption that ions and neutral gas

*Project supported by the National Natural Science Foundation of China (Grant No 10405005).
†E-mail: dbd01@dlut.edu.cn

particles have the same temperature, and then the energies of CH_4^+ and Ar^+ in $CH_4 + Ar$ DBD can be calculated.[11] In this paper, the theoretical model for ion energy analysis is further discussed by considering that the velocity distribution function of ions is much different from that of the neutral gas particles when the reduced field E/n (the ratio of electric field strength to the gas number density) is not vanishingly small. Dependences of the energies of CH_4^+ and Ar^+ (He^+) ions in $CH_4 + Ar$ (He) DBD on the Ar (He) concentration are analysed. The deposition of DLC films by $CH_4 + Ar$ (He) DBD at different concentrations of Ar (He) is also studied experimentally. The results show that ions in DBD plasma have enough energy for deposition of dense a-C : H films, and that adding Ar or He to CH_4 has great effects on the ion energy and properties of the DLC film obtained.

2. Experimental details

The a-C : H films were deposited on Si substrates using $CH_4 + Ar$ (He) DBD plasmas at the gas pressure of several hundreds of Pa. Details of the set-up can be found in Ref.[12]. Two mass-flow controllers were used to adjust CH_4 and Ar (He) flows. The total gas flow was fixed at 5 sccm, the total pressure was set at 100 Pa, and Ar (He) volume concentration in the mixed gas of CH_4 + Ar (He) was changed from 17% to 83%. The DBD power supply was 28 kV at 1.4 kHz. No bias-voltage was applied to the substrate during the deposition process.

The breakdown voltages of $CH_4 + Ar$ (He) with various Ar (He) concentrations were measured. The atom force microphotograph (AFM) (taken with Digital Instrument Nanoscope 3100) was used to evaluate the film nano-hardness via the nano-indentation at a loading force of 175 μN. Scanning electron microscope (SEM) (taken with PHILIPS LX-30) was used to measure the film thickness in the specimen cross-section, and the growth rates were obtained.

3. Experimental results

The dependence of hardness of the DLC films on the Ar (He) concentration is shown in Fig.1. With increasing Ar or He concentration from 17% to 83%, the hardness of DLC films increases and reaches a maximum at Ar concentration of 67% or He concentration of 76%, then decreases drastically at higher Ar or He concentration. This trend is similar to that in Refs.[13, 14]. Their results show that the hardness of DLC films deposited from CH_4+ Ar (He) RF plasma reaches a maximum at Ar (He) concentration of about 50% (30%). The hardness of DLC films is related directly to the kinetic energy of the impinging ions during the process of deposition; the kinetic energy of ions in $CH_4 + Ar$ (He) DBD plasma will be discussed in next sections.

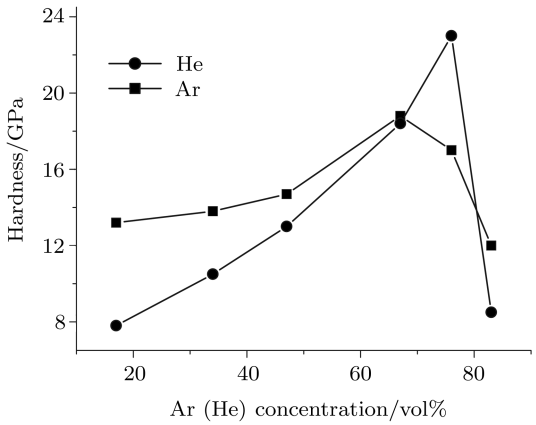


Fig.1. Hardness as a function of Ar or He concentration for DLC films deposited in $CH_4 + Ar$ or $CH_4 + He$ DBD plasma. Discharge conditions: total gas pressure = 100 Pa, discharge gap = 10 mm, power supply, 28 kV and 1.1 kHz.

Figure 2 shows the growth rate of DLC films deposited from $CH_4 + Ar$ (or He) DBD as a function of Ar (He) concentration. For the reaction gas of $CH_4 + Ar$, the growth rate reduces approximately linearly with increasing Ar concentration up to 67% and then shows an abrupt decrease as the Ar concentration is further increased. While for $CH_4 + He$, the growth rate decreases approximately linearly all along with increasing He concentration. Anyway, adding the inert gases into CH_4 leads to the decrease of CH_4 composition ratio; this is the direct origin for the decrease of growth rate. The conversion efficiency in Fig.3 is defined as the growth rate divided by the precursor gas flow, which evaluates the rate of precursor molecules transferred from the gas phase to the growing film. Figure 3 indicates that by varying the percentage of helium in the mixture from 17% to 83%, the conversion efficiency increases from 0.45 to 1.5; this can be attributed to the helium capability to increase the activation of methane by a dissociation process in the plasma. Argon also can improve the activation of methane by effective collisions of Ar with CH_4 in the plasma.[15] So the conversion efficiency increases with

adding Ar up to 67%. However, the etching capability of argon with large mass causes the conversion efficiency to decrease at very high Ar concentration.

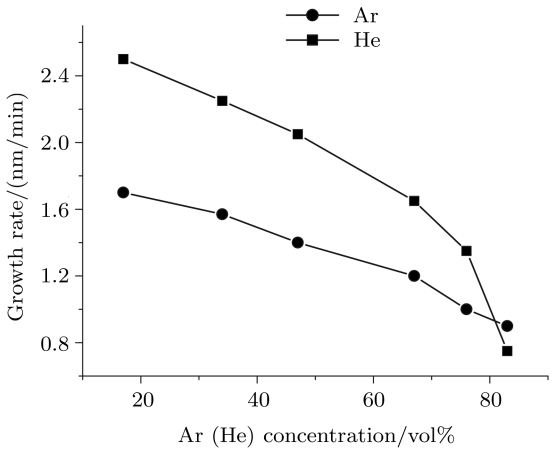


Fig.2. Growth rate as a function of Ar or He concentration for DLC films deposited in $CH_4 + Ar$ or $CH_4 + He$ DBD plasmas. Discharge conditions: total gas pressure = 100 Pa, discharge gap = 10 mm, power supply, 28 kV and 1.1 kHz.

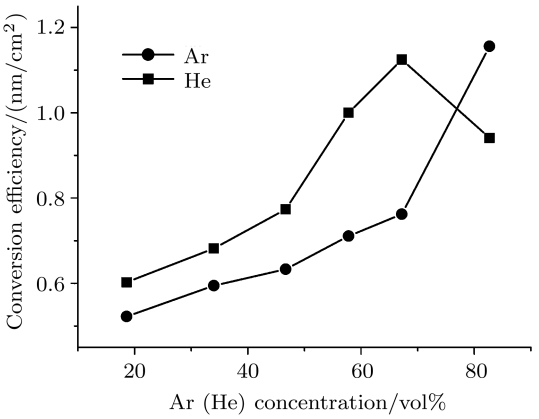


Fig.3. Conversion efficiency as a function of Ar or He concentration for DLC films deposited in $CH_4 + Ar$ or $CH_4 + He$ DBD plasmas. Discharge conditions: total gas pressure = 100 Pa, discharge gap = 10 mm, power supply, 28 kV and 1.1 kHz.

Figure 4 shows breakdown voltage of $CH_4 + Ar$ (He) versus Ar (He) concentration. With increasing volume concentration of Ar (He) from 17% to 83%, the breakdown voltage of $CH_4 + Ar$ decreases from 490 to 370 V, while that of $CH_4 + He$ increases from 500 to 570 V. The different trends can be attributed to the different ionization energy between Ar (15.759 eV) and He (24.586 eV).

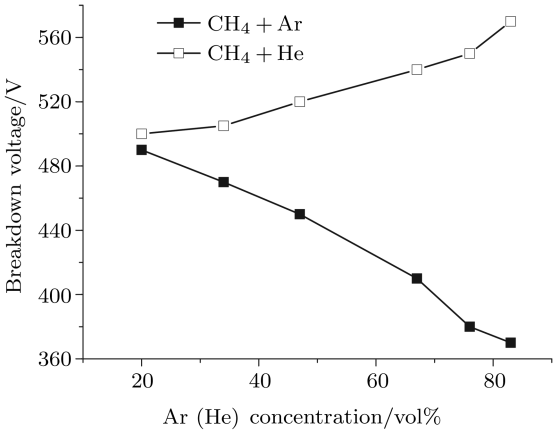


Fig.4. Breakdown voltage of $CH_4 + Ar$ (He) as a function of Ar or He concentration under the conditions of total gas pressure = 100 Pa, discharge gap = 10 mm, power supply, 28 kV and 1.1 kHz.

4. Theoretical model

The discharge processes of DBD plasmas have been discussed widely.[1,5,6] Applying a rising voltage to the gas gap, the discharge is ignited once the local electric field reaches the breakdown voltage of gas, and then the gas voltage remains approximately constant, i.e., gas breakdown voltage V_{BD}, so the electrical field strength in the gas gap is

$$E = \frac{V_{BD}}{d}, \tag{1}$$

where d is the gas gap, V_{BD} is the gas breakdown voltage.

Gas molecule density at several hundreds of Pa is around $10^{18}\,cm^{-3}$, average free path of ion is about 10^{-3} cm, which is much less than the gas gap (0.1–1 cm). So ions will undergo a large number of collisions during their passing through the gas gap, and the ion velocity can be expressed as

$$v_D = \mu E, \tag{2}$$

where μ is the mobility. At a lower electric field strength, μ can be expressed as follows:

$$\mu = \frac{e}{2m_i\gamma_m}, \tag{3}$$

where e is the elementary charge, m_i is the ion mass, and γ_m is average collide frequency and expressed as

$$\gamma_m = \frac{\bar{v}}{\bar{\lambda}}. \tag{4}$$

Here $\bar{v} = \sqrt{\dfrac{8kT}{\pi m_i}}$ is the thermal velocity, k is Boltzmann's constant, T is gas temperature. The mean free

path and gas density may be expressed as $\bar{\lambda} = 1/N\sigma$ and $n = p/kT$, where σ is the collision cross-section, p is gas pressure.

Combining Eqs.(3) and (4), one may obtain

$$\mu = 0.31\frac{e}{n}\left(\frac{1}{m_i k_{\rm B} T}\right)^{1/2}\frac{1}{\sigma}. \tag{5}$$

When reduced field E/n is not vanishingly small, the velocity distribution function of the ions is much different from that of neutral gas particles. By two-temperature treatment of the Boltzmann equation, the gas distribution is modelled as a Maxwellian but the ions are treated as at ion temperature $T_{\rm eff}$, which is much higher than the neutral gas temperature.[16] In this treatment of the Boltzmann equation, μ can be expressed as

$$\mu = 0.375\frac{e}{n}\left(\frac{\pi}{m_i k_{\rm B} T_{\rm eff}}\right)^{1/2}\frac{1+\alpha}{\sigma}, \tag{6}$$

$$\frac{3}{2}k_{\rm B}T_{\rm eff} = \frac{3}{2}k_{\rm B}T + \frac{1}{2}m_i v_{\rm D}^2(1+\beta). \tag{7}$$

Here α, β are adjustment factors, $v_{\rm D}$ is the ion drift velocity defined as Eq.(2).

According to strict gas dynamics, Langevin deduced the ion mobility at low E/n when ions move in other gas,

$$\mu = 0.47\frac{e}{n}\left(\frac{1}{m_i k_{\rm B} T}\right)^{1/2}\left(\frac{m_i + m_\alpha}{m_i}\right)^{1/2}\frac{1}{\sigma}, \tag{8}$$

where m_α and m_i are neutral molecule mass and ion mass, respectively. This is the Langevin equation.

Similar to Eqs.(6) and (7), at a relatively high E/n, the ion mobility for ions in other gas can be expressed as

$$\mu = 0.47\frac{e}{n}\left(\frac{1}{m_i k_{\rm B} T_{\rm eff}}\right)^{1/2}\left(\frac{m_i + m_\alpha}{m_i}\right)^{1/2}\frac{1+\alpha}{\sigma}. \tag{9}$$

Additionally, for ions in a mixed gas, their mobility can be expressed as follows by using Blanc's law:[17]

$$\frac{1}{\mu_i} = \sum_{j=1}^{n}\frac{f_j}{\mu_{ij}}, \tag{10}$$

where μ is the mobility of the ith ion in the pure jth (j is Ar or CH_4) gas at a given partial pressure.

The ion energy, W, can be obtained by

$$W = \frac{1}{2}m_i(\mu E)^2. \tag{11}$$

5. The ion energy calculation and discussions

The gas voltage is fixed approximately at the gas breakdown voltage when a discharge is ignited. We have measured the breakdown voltage of CH_4 diluted with Ar (He), as shown in Fig.4, with total gas pressure of $CH_4 + Ar$ (He) being 100 Pa, the gas gap fixed at 10mm, and the Ar (He) volume concentration changed from 17% to 83%. These discharge conditions are also used when carrying out theoretical analysis of ion energy and the deposition of DLC films.

In CH_4 plasmas used for the deposition of a-C:H films, the CH_3^+ and CH_4^+ are the predominant hydrocarbon ions, which often show similar behaviours because their ionization cross-sections by electron impact on CH_4 are very similar and much larger than those of other hydrocarbon ions.[18] In this discussion, only CH_4^+ and Ar^+ (He^+) kinetic energies are theoretically calculated as a function of Ar (He) concentration, as shown in Fig.5. With increasing Ar (He) concentration from 17% to 83%, the kinetic energy of CH_4^+ increases from 69.6 to 92.1 eV (in $CH_4 + Ar$) or from 43.9 to 128.5 eV (in $CH_4 + He$), while the kinetic energy of inert ions decreases from 97 to 78.8 eV (Ar^+) or from 145.2 to 75.5 eV (He^+). It is just the increase of CH_4^+ kinetic energy that leads to the increase of hardness of DLC films, as shown in Fig.1. However,

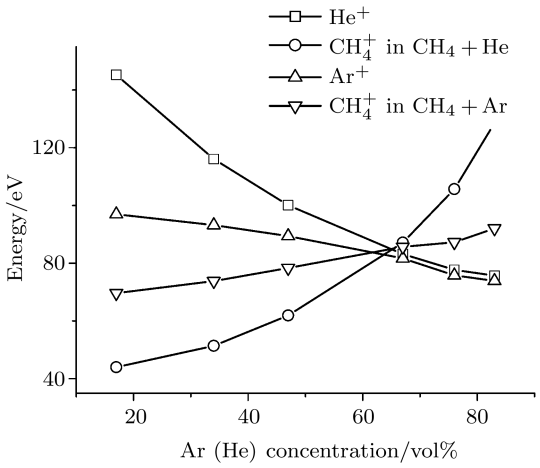


Fig.5. CH_4^+ and Ar^+ (He^+) kinetic energies in $CH_4 + Ar$ (He) DBD plasmas as a function of Ar (He) concentration under the conditions of total gas pressure = 100 Pa, discharge gap = 10 mm.

Fig.1 also shows that the hardness of DLC films falls down at the concentration of Ar ($> 67\%$) or He ($> 76\%$); this can be attributed to the structural

change from a diamond-like to a polymer-like film due to the thermal effect related to the impinging of high-density Ar^+ or He^+. The strong etching capability of Ar^+ ions with a heavy mass will lead to the decrease of the conversion efficiency at high concentration Ar ($> 67\%$), as shown in Fig.3. In contrast, the conversion efficiency at high concentration of He ($> 76\%$) will increase.

The calculated results of ion kinetic energy cannot make clear the different actions between He and Ar. Figure 6 shows the dependence of ion mobility on the Ar (or He) concentration.

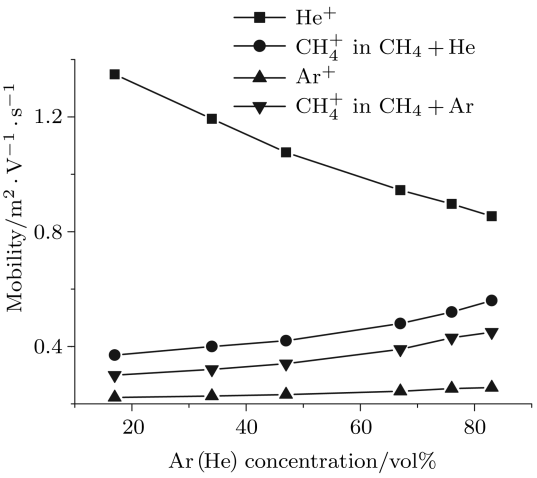


Fig.6. CH_4^+ and Ar^+ (He^+) ion mobility in $CH_4 + Ar$(He) DBD plasmas as a function of Ar (or He) concentration under the conditions of total gas pressure = 100 Pa, discharge gap = 10 mm.

Increasing the concentration of Ar or He from 17% to 83% leads to the increase of CH_4^+ mobility from 0.30 to 0.45 $m^2 \cdot V^{-1} \cdot s^{-1}$ (in $Ar + CH_4$), or from 0.37 to 0.56 $m^2 \cdot V^{-1} \cdot s^{-1}$ (in $He + CH_4$), while Ar^+ mobility increases slightly from 0.22 to 0.25 $m^2 \cdot V^{-1} \cdot s^{-1}$, and He^+ mobility reduces obviously from 1.34 to 0.85 $m^2 \cdot V^{-1} \cdot s^{-1}$. These results show the distinction between the behaviours of Ar and He. According to Eqs.(1) through (10), we can conclude that the difference in mass and in ionization energy between Ar and He may affect their ion mobilities. However, this problem needs to be studied further.

6. Conclusions

Ion energy analysis based on the binary-body collisions and DLC film deposition has been carried out in both CH_4/Ar and CH_4/He DBD plasmas. The calculated results of ion kinetic energy show that, for the discharge condition of fixed gas pressure of 100Pa and increasing Ar (or He) concentration from 17%–83%, the CH_4^+ kinetic energy is increased from 69.6 to 92.1 eV (in $CH_4 + Ar$) or from 43.9 to 128.5 eV (in $CH_4 + He$), correspondingly, the hardness of DLC films deposited increases and reaches a maximum at Ar (He) concentration of 67% (76%), then decreases due to the impinging of high-density Ar^+(He^+). Adding Ar or He into CH_4 causes different effects on the ion mobility due to the difference between their masses and ionized energies.

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