Optical Emission Spectroscopy Diagnostics of HMDSO/O_2 Magnetized Plasma

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Abstract Based on general plasma enhanced chemical vapor deposition (PECVD), a novel plasma set-up equipped with horizontal electronic field and perpendicular magnetic field is built in this study for a purpose of obtaining a high density plasma source. In order to characterize plasma parameters, optical emission spectroscopy (OES) was used to diagnose the electron temperature and electron density in plasma. The electron temperature calculated through Stark broadening function is in the range of 1.0–5.0 eV while the electron density is in the range of 5.0–10.0 $\times$ 10^{15} cm^{-3}. The electron density is three orders of magnitude higher than that in normal plasma. OES results also indicate that oxygen concentration pays an essential role both on the dissociation of Hexamethyldisiloxane (HMDSO) molecule for Si precursor and on oxidation reactions of fragments, which supplies the theoretical research of plasma chemical reaction mechanism.

Keywords OES · Plasma parameters · Magnetically enhanced plasma source

1 Introduction

Due to excellent performances, such as chemical stability, excellent barrier diffusion against water vapor or gases, and good transparent, silicon oxide coating attracts a great interest in organic electronics and food packaging surfaces [1–3].

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P. Zhao et al. (eds.), *Advanced Graphic Communications and Media Technologies*, Lecture Notes in Electrical Engineering 417,
DOI 10.1007/978-981-10-3530-2_137

Comparing to many manufacturing methods of silicon oxide (SiO_x) coating, PECVD exhibiting lots of advantages such as good adhesion, homogenous, pin hole free and convenience to mediate structural component [2, 4] becomes much popular method. However, the deposition rate for this technology is so low (less than 30 nm/min in practical [5]) that the application of silicon oxide products in industrial scale is seriously hampered.

Recently, the addition of magnetron field to the plasma discharge area was developed to increase ionized species density and thus to enhance the deposition rate [6]. In our previous study [7], the magnetic field confined plasma source was built where the magnetic field in electrode configuration generated the electron Hall current in an endless loop and thus decreases the diffusion rate of ions, electron, and charged species. Similarly, Rank et al. [6] has observed that addition of a magnetic field could not only enhance the properties of capacitive coupling RF discharge sources but also improve the pretreatment speed rate of plastic webs. So, it can be deduced that the power efficiency could be highly improved by magnetized plasma. Essentially, the existence of magnetic field in the plasma could effectively constraint the electron mobile path in the discharge area, resulting in speeding up the ion collision rate and thus enhancing ionization degree [8].

As for silicon dioxide film deposited by PECVD, discharge and deposition principles for normal plasma source were systematically investigated and various diagnosis technologies were developed [9], but the plasma parameters and reaction mechanisms of plasma sources coupled with magnetron field is seldom studied. This is because the confined electron mobility after the magnetron affiliation will have a significant influence on the trajectory of charged particles, which makes feedback current and voltage inaccurate. Although some diagnostics methods become invalid to effectively investigate plasma parameters, especially for Langmuir probe (LP) and mass spectroscopy (MS), OES could compensate above shortcomings and is verified to be an effectively way to perform diagnostic function of magnetron enhanced plasma [10]. Therefore, magnetron enhanced plasma parameters are investigated by OES to disclose the chemical reaction principle in this study.

2 Brief Theories for Stark Broadening Function

According to Gig-Card theory [6, 9], electron density can be generally calculated by Stark broaden function through the full width at half maximum (FWHM) that a globally neutral, homogeneous and isotropic system exists in thermal equilibrium. Herein, FWHM is determined by width of special line at a center of decisive wave number, which consists of all kinds of widths such as natural (or instrumental), Doppler, Zeeman, Stark, Lorenz, as consist into $\Delta\lambda_0$ in the formula $\lambda = \lambda_0 \pm \Delta\lambda_0$. Stark broadening can be available through subtracting the factual spectral FWHM $\Delta\lambda_{1/2}$ by all kinds of other broadening widths for the purpose of electron density N_e.

Consuming the existence of local heat dynamic equilibrium the optical relativity strength I_{nm} can be formulated as follows:

$$I_{nm} = \frac{1}{4\pi} h\gamma_{nm} N_n A_{nm} D \tag{1}$$

where *n, m* correspond to up/down principal quantum number respectively; γ_{nm}, A_{nm} are optical frequency and self-transition rate, respectively; D is the plasma depth at the observing direction, N_n is upper energy level of distribution density, and h is Planck constant. Given the same ionization species of different levels obeys to Boltzmann distribution, we get

$$\frac{N_n}{N_1} = \frac{g_n}{g_1} \exp\left(-\frac{x_{1n}}{KT_e}\right) \tag{2}$$

where N_1 are the basic energy level of distribution density, g_1, g_2 are the basic or excited ionized statistics averaged equally, respectively; x_{1n} is excited potentials of n level (eV), KT_e is electron temperature (eV).

The similar other optical relative strength can also be written as:

$$I_{pq} = \frac{1}{4\pi} \frac{g_p}{g_1} h\gamma_{pq} A_{pq} D N_1 \exp\left(-\frac{x_{1p}}{KT_e}\right) \tag{3}$$

Comparing Formula (2) with Formula (3) we get the Formula (4) for electron temperature:

$$\frac{I_{nm}}{I_{pq}} = \frac{g_n \gamma_{nm} A_{nm}}{g_p \gamma_{pq} A_{pq}} \exp\left(\frac{x_{1p} - x_{1n}}{KT_e}\right) \tag{4}$$

In this Formula, parameters, except I_{nm} and I_{pq} through optical emission spectroscopy, can be obtained in Ref. [11], and then KT_e can be calculated.

3 Experimental

The experiment equipment used here can be traced back to our previous study [6]. The roll-to-roll electrodes are connected to 40 kHz pulsed discharge source (duty ratio is set at 50%). hexamethyldisiloxane (Arish, USA. 98+ %) is used as precursor of Si and oxygen gas of 99.9% purity is used as the dilution gas. The flow ratio of HMSDO and oxygen is set at 2:1, and the working pressure is kept constant at 1.5 Pa with the basic pressure of 10^{-3} Pa. The optical emission spectroscopy (AvaSpec-ULS2048-8, AVANTES B.V., Netherlands) has a grating logarithm of 300 lines/mm and slim depth of 10 μm to provide the resolution of 0.8 nm in the wavelength range of 300–900 nm.

4 Results and Discussion

Figure 1 depicts OES results of plasma when the applied power, pressure and precursor and oxygen ratio were set at 300 W, 1.2 Pa and 2:1, respectively. One can see that when discharge was performed in pure oxygen, only several peaks for molecule CO in 525.31, 558.42, 597.18, 615.63 and 635.75 nm were detected in the range of 520–635 nm, although the strong oxygen signal appear at 777.44 and 844.75 nm. CO species could be traced to oxygen plasma etching effect of flexible substrate of polyethylene terephthalate (PET).

Once the precursor HMDSO was inputted, the strong lines appeared at 391.02, 427.57, 486.22 and 656.40 nm, which contribute to CH, SiO, H_α and H_β species, respectively, as shown in Table 1. The dissociated fragmentations of HMDSO lead to generation of complex mixture of active species, such as SiC and CH_x, leading to organic component deposited in polymeric film. It is consistent with our previous results [7] that the stoichiometric value of silicon oxide was $SiO_{1.32}$, and carbon content was ca. 23.5% in complex mixture. Choudhury et al. [12] also observed the existence of CH, SiO, H and O radicals in HMDSO/O_2 plasma, and found that the peak intensity of CH, SiO, H and O were almost equal, resulting in an organic character in the film structures. Saloum et al. [13] has studied the correlation between the plasma parameters and coating structures in remote RF hollow cathode technology and found the similar species.

However, the absence of SiH species at 414.7 nm in our data inferred the strong oxidization reaction in our plasma source, which was favorable to the subsequent formation of SiO and H_2 since SiH radical was always an essential transition state during the dissociation process of HMDSO [14]. It is notice that the intensities of H_α and H_β were much higher than others like SiO and CH species, which confirm the strong ionization of CH_x in this plasmas source. The highest intensity of CO species further verifies the oxidization from CH and H fragments to avoid the formation of SiH through combination of Si and H radicals.

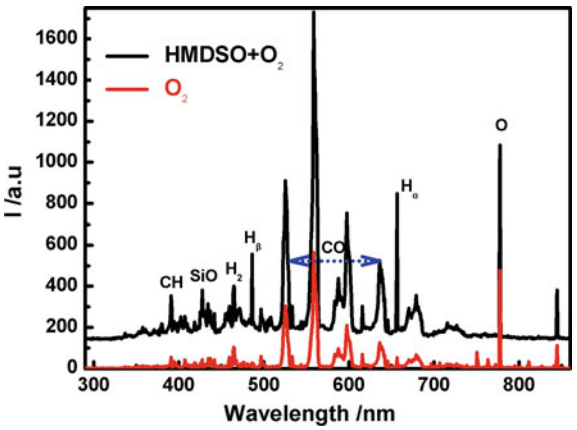

Fig. 1 OES of discharge plasma with O_2 and HMDSO + O_2 mixtures

Table 1 Species detected by OES in HMDSO/O_2 plasma [16]

Species	Transition	Wavelength (nm)
CH	$X^2\prod - B^2\sum -$	391
SiH		414.7
SiO		427.57
CO	$B^1\sum - A^1\prod(v, v')$ (0, 0)	451.1
	-id-(0, 1)	483.5
	-id-(0, 2)	519.8
	-id-(0, 3)	561.0
	-id-(0, 4)	608.0
	-id-(0, 5)	662.0
H	H_β: H(n = 4) → H(n = 2)	486.22
	H_α: H(n = 3) → H(n = 2)	656.4
H_2	Fulcher α : $d^3\prod_u - a^3\sum_g^+$	453–464, 570–650
	$^5P - {}^5S_0$	777.44
O	$^3P - {}^3S_0$	844.75

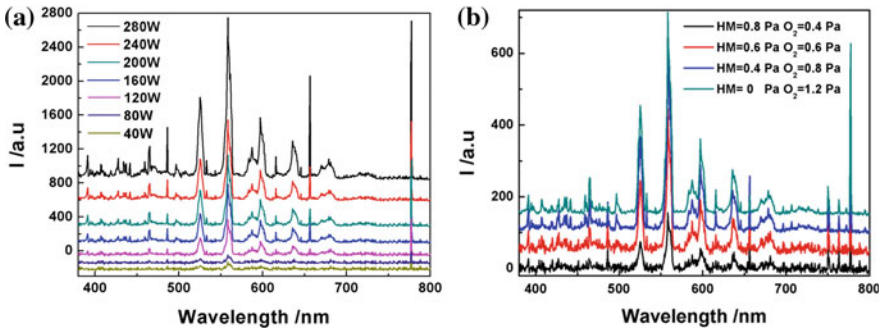

Fig. 2 OES of discharge plasma with HMDSO/O_2 mixtures as a function of discharge power (**a**) and HMDSO/O_2 ratios (**b**)

Regarding the oxidation rate and deposition rate related to the chemical reaction and subsequent coating structure, there are two factors needed to be further studied: applied power and HMDSO/O_2 ratio. Figure 2a shows the OES of HMDSO/O_2 plasma as function of applied power. One can see that the peak locations keep constant while their intensities are increased along with discharge power. Considering four typical species, O in 777.44 nm, H in 486.22 nm, CO in 451.1 nm and CH in 391.02 nm, one can find that although O in 777 nm increases much fast with discharge power, the relativity of O/H, CO and CH keep constant. On the contrary, the oxidation degree of HMDSO strongly depends on the O_2 concentration as shown in Fig. 2b, since O intensity decreased and H_β intensity increased with the inputted HMDSO. Thus, it can concluded that the high intensity

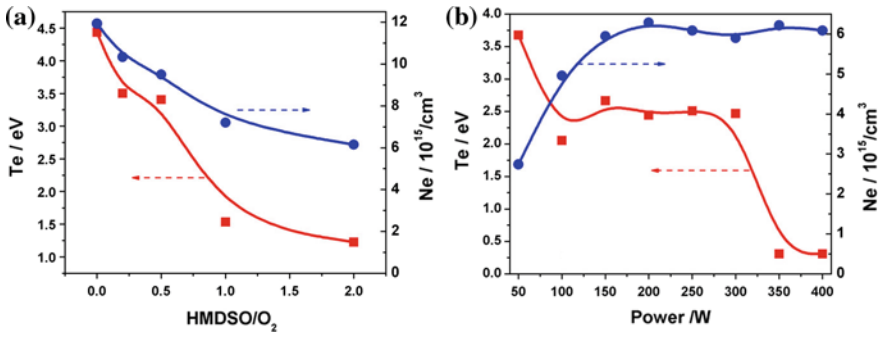

Fig. 3 Electron temperature and intensity of mixture plasma with different $HMDSO/O_2$ ratios (**a**) and discharge power (**b**)

of O plays a positive contribution to the species oxidization, such as CH or H into CO or H_2O, respectively while the decrease of CO intensity indicate further ionization of CH_x fragment.

In comparison with the densities of species in their fundamental state, the emission intensity by the activated species is a function of the excited states. OES can be utilized to measure relative concentrations based on the actinometrical method [15]. Lasorsa et al. [16] has found that the competition between Si–O at the substrate and Si–C species in the plasma phase is sensitive to variations of electron temperature in PECVD. So, in our study, all intensities were calibrated by O in 777.42 nm in order to analyze the reaction principles. The lines of H_β 486.2 nm, C=O 451.1 nm, C–H 391.02 nm were utilized to calculate the electron temperature and ionized density according to the Formula (4).

Figure 3a shows that both electron temperature and density were decreased from 4.5 to 1.2 eV and 12 to 6.0×10^{15} cm^{-3} respectively, with the precursor concentration. With the increase of precursor, the atomic oxygen species, which etches the polymeric surface under high initial density, was consumed by breaking CH or Si–C bonds to form H_2O and CO, leaving Si–O species in deposition process, since electrons impact cause an increase of more than two or three orders than that in normal plasma phase. Compared with Fig. 2b, when the ratio varied from zero to 2, the high fragmented degree of precursor and relatively low oxidation counterpart of fragments will lead to more organic formation in finally deposited layer.

On the other hand, at the constant working pressure, the electron temperature decreases from 3.7 to 2.5 eV with increment of discharge power from 40 to 100 W, and keep a constant value until 300 W, finally dropped to a low level of 0.5 eV, as shown in Fig. 3b. At the same time, the electron density increases from 1.7 to 6.0×10^{15} cm^{-3} and then keep constant regardless of discharge power. Therefore, it can be concluded that discharge power has a positive effect on the decrement of electron temperature, and lead to electron impact and speeding up the chemical reaction rate for precursor/oxygen phase process to obtain a high stoichiometric ratio of SiO_x as verified by species composition in plasma phase shown in Fig. 2a.

Furthermore, the relationship of composition structure of deposited film with plasma phase should be built, as will be investigated in the next process.

5 Conclusions

In this paper, OES was adapts to explore the principle mechanism of polymerization reaction in the magnetized plasma for purpose of explaining the essence of the magnetized plasma. OES results indicated that the species in plasma phase depended on the oxygen concentration. When the precursor was inputted, the electron temperature and density calculated through Stark broaden function, decreased from 5.0 to 1.0 eV and 10.0–5.0 $\times$ 10^{15} cm^{-3}, respectively, indicating the O etching effect. On the other hand, the discharge power had a positive effect on the decrements of both electron temperature and acceleration of the chemical reaction for precursor/oxygen plasma phase.

Acknowledgements This article was financially supported by Key Construction Discipline Program of Beijing Municipal Commission of Education (PXM2014-014207-0000029), Youth Science Fund Project of Beijing University of Agriculture and Youth Teacher Foundation of Da Bei Nong Group of Beijing University of Agriculture (14ZK006).

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