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APPLICATION OF LANGMUIR PROBE DIAGNOSTIC IN CASCADED ARC PLASMA ENHANCED DEPOSITION

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ABSTRACT

In expanding beam deposition method, an argon cascaded arc is used as a plasma source; the deposition is realized by injecting reaction gas (silane or hydrocarbons) together with hydrogen or oxygen into the expanding plasma. In this work, the question has been addressed to how the injected gases alter charged particle density and temperature. A quantitative study by Langmuir probe diagnostics shows that the injection of the reaction gases causes significant variations of the charged particles density and temperature.

INTRODUCTION

The cascaded arc plasma has been developed as a plasma source for plasma enhanced thin film deposition technique since the late 80's. This technique presents a very attractive future for its application in both electronic and mechanical industry. Using a cascaded arc as a plasma source in plasma deposition, very fast deposition of α–C:H film (> 100 nm/s), and α–Si:H film (> 10 nm/s) are available /1/. Besides the amorphous carbon and silicon, diamond and graphite thin films have also been produced with good quality by using this method /2/.

One of the distinguishing features of the cascaded arc plasma enhanced deposition is the use of an argon cascaded arc as a basic source of plasma. The deposition is realized by injecting the reaction gases (SiH_4, or CH_4 and C_2H_2) at the nozzle into the expansion part of this plasma source. Additionally, hydrogen is used during the deposition, since in both amorphous silicon and carbon deposition hydrogen is very effective for passivation of the dangling bonds. Oxygen is used as an etching reagent especially in diamond deposition /2/. In this paper, we present the results of how the charged particle density and temperature in the expanding beam are influenced by injecting hydrogen, oxygen or silane gases. The electron and ion density and electron temperature are determined by Langmuir probe measurements.

EXPERIMENTAL

The cascaded arc plasma source is an example of a wall stabilized thermal plasma /3/, widely used as a plasma source or a light source. A cascaded arc consists of a cathode (or more cathodes), an anode plate with nozzle and several cascaded plates which are electrically isolated from each other. A cascaded arc can be operated in broad pressure, arc current and electron density ranges. Comparing this source with, for example, a hollow cathode arc, not only the operational condition ranges are widely expanded, but also the lifetime of the arc itself is significantly extended.

In the experiment, two parallel tungsten wires both with lengths of 7 mm and diameters of 0.4 mm are used as a Langmuir double probe. A floating signal generator with triangle waveform is used as the probe source. The probe signals are collected by an A/D converter and then stored in a personal computer. The basic assumptions of the Langmuir probe theory are satisfied in the experiment. The random measuring error due to the experimental settings was about 10%.

RESULTS AND DISCUSSION

1.Argon plasma source

Figures 1 and 2 show the charged particles density and electron temperature in the expanding argon plasma. The measurements were taken at an axial position of 250 mm from the nozzle at the axis of the plasma beam. Both electron density and temperature rise with increasing argon flow or arc current.

A full explanation of the variations of the charged particle density and temperature with change of argon flow rate and arc current requires a full modellization, because at the same time the other plasma characteristics (diameter of the plasma beam, distribution of electromagnetic forces, etc.) could change as well /4/. Here, we will qualitatively discuss the correlation between the variation of charged particles density in the expansion with the variation of the pressure in the cascaded arc.

In /5/ for the same cascaded arc as in this work, the results of direct measurements of the pressure in the arc as function of argon flow rate and arc current, have been presented. In particular, it has been found, that with increasing arc current from 15 A to 75 A, the gas pressure near the exit of the arc increases approximately 3 times (for example at $Q = 3.5$ slm, from 50 mbar to 150 mbar). Variation of argon flow rate from 1 slm to 9 slm, results in an increase of the gas pressure in the arc of almost 14 times (for example at $I = 45$ A, from 20 mbar to 280 mbar).

From Figures 1 and 2 it is easy to find, that with the same variation of: a) arc current, and b) argon flow rate, charged particles density changes a) from $5 \cdot 10^{18}$ m^{-3} to $3 \cdot 10^{19}$ m^{-3}, and b) from 10^{18} m^{-3} to $5 \cdot 10^{19}$ m^{-3}, respectively. Thus, the variation of charged particles density correlates qualitatively with the variation of the pressure in the cascaded arc. As the plasma in the arc is in partial LTE and not too far from equilibrium it is to be expected that the electron density rises with downstream pressure. This has also been found by Beulens et. al. /6/, from a two–dimensional non–equilibrium model. It is clear, that the higher source current strength will also lead to a higher electron density in the expansion. For a fully understanding of the electron density increase, a further experimental investigation of argon plasma properties in the expansion is required.

Without additional heating and/or cooling by energy transfer to the heavy particles the electrons will expand adiabatically, and $n_e \simeq T_e^{1.5}$. In addition to this simple adiabatic expansion picture there may be additional heating and cooling effects. These heating mechanisms have been mentioned in /4/. The first is Joule heating by convective current, arising because of finite ∇p_e. These convective currents are expected to increase with arc current and flow, simply because of the increase in n_e. The other two heating mechanisms are electron heat conduction and energy gain by three body recombination. Finally the energy coupling between electrons and heavy particles may play a role. The energy coupling time $\tau_{ei}^{\epsilon} = (M_i/2m_e) \cdot \tau_{ai}$ will not change much as the n_e variation compensates for the T_e variation. The flow velocity may increase with flow giving less time for energy equilibration between electrons and ions. Again to obtain a full understanding more measurements are required.

2. H_2/Ar plasma mixture

We observe a dramatic decrease of n_e by injecting hydrogen into the argon plasma. This decrease indicates a strong recombination mechanism. In pure argon the density decreases with distance from nozzle, but in that case it is mainly due to the radial expansion; i.e. the total ion fluence remains approximately constant /4/. When hydrogen is seeded in the argon arc, the density decreases the factor of 10^3 compared to the pure argon case and here another recombination mechanism must be responsible.

In atomic plasmas the only mechanism is that of the three body recombination of atomic ions (like in argon):

$$Ar^+ + e + e \longrightarrow Ar^* + e, \tag{1}$$

$$H^+ + e + e \longrightarrow H^* + e. \tag{2}$$

another and much more efficient recombination route:

$$H^+ + H_2^{v,j} \longrightarrow H_2^+ + H, \tag{3}$$

$$H_2^+ + H_2 \longrightarrow H_3^+ + H, \tag{4}$$

$$H_2^+ + e \longrightarrow H + H, \tag{5}$$

$$\left\{\begin{array}{l} H_3^+ + e \longrightarrow H_2 + H, \\ H_3^+ + e \longrightarrow H + H + H. \end{array}\right. \qquad \begin{array}{r}(6)\\(7)\end{array}$$

The molecular reactions (3) – (7) are expected to be much faster than the atomic reactions (1) and (2) /7/, because reactions (1) – (2) are determined by the slow three–body recombination. On the other hand it is well known, that dissociative recombination of molecular positive ions with electrons (5) – (7) occurs very fast /8/. That fact present the principal possibility to explain experimental results.

In a plasma mixture, the component with the lowest ionization potential, in the present case is hydrogen, will be preferentially ionized. Thus, in the conditions of experiment in the H_2/Ar mixture with more than 5–8% of hydrogen in the total flow rate, practically all of positive ions in the beginning of the expansion must be the protons. Further one must suppose the presence of fast charge transfer reaction (3), with following reactions of dissociative recombination (5) – (7). Those reactions cause a cooling of the plasma and a dramatic drop of the charged particles density.

The obtain decrease of T_e might be connected with several reasons: 1) with the higher hydrogen concentrations the electron–ion energy transfer to the dominant H^+ ion becomes faster since lighter ions decelerate electrons more effectively; 2) for higher hydrogen concentrations the heavy particles temperature may become lower because of the enhanced heat conductivity; then the electrons are cooled too by energy transfer; 3) with hydrogen admixture the acoustic properties can change in particular for the ions. This may lead to a deeper expansion cooling and thus again to a lower T_0 and therewith T_e; 4)vibrational excitation of hydrogen molecules, and dissociative recombination of molecular ions also might be important reasons for "cooling" of electrons, as in both cases electron energy is converted to vibrational and translational energy of the neutral atoms and molecules.

3. O_2/Ar plasma mixture

To avoid the oxidation and erosion of the copper cascaded plates, oxygen has been injected beyond the arc source into the expansion plasma at the nozzle position. The Langmuir double probe measurements were performed at an axial position of 120 mm away from the nozzle. The results show that the charged particles density drops slightly when rising the oxygen flow component (Figure 4). One of the possible explanation is the radial expansion of the plasma, which decrease local particles density. Another possibility it is a consecutive reactions of charge transfer of argon ions with oxygen molecules (exothermic in that case), and dissociative recombination of oxygen molecular positive ions, could be responsible for the decrease of n_e:

$$Ar^+ + O_2 \longrightarrow Ar + O_2^+, \tag{8}$$

$$O_2^+ + e \longrightarrow O + O, \tag{9}$$

or/and:

$$Ar^+ + O_2 \longrightarrow ArO^+ + O, \tag{10}$$

$$ArO^+ + O_2 \longrightarrow O_3^+ + Ar, \tag{11}$$

$$O_3^+ + e \longrightarrow O + O + O. \tag{12}$$

Limiting point for those reactions is non–resonant charge exchange (8), (10) and example, the rate constant for the reaction (9): $k_{rec} = 1.95 \cdot 10^{-13} (300/T_e)^{0.7}$ $m^3 \cdot s^{-1}$ [16]. It is important to note, that "slow" electrons recombine faster.

The electron temperature in the plasma rises a little when oxygen appears in the plasma. The reasons might be the same as in case of pure argon plasmas: convective current circulating in the vessel, which heats the electrons, three–body recombination, electron heat conductivity and/or a change of the frequency of electron–ion interactions, which cool the electron gas.

4. $SiH_4/H_2/Ar$ plasma mixture

One of the main experimental difficulties of using a Langmuir probe to determine the charged particles density and electron temperature in a $SiH_4/H_2/Ar$ plasma mixture is the fast deposition of amorphous silicon on the probe surface. This may introduce an additional error to the experimental data. In those circumstances it is important to keep the probe clean. The probe is cleaned during each measurement by bombarding of pure argon plasma at large negative bias to the probe. Besides, by choosing a short measuring time one can keep the probes clean enough for the probe measurements.

It might be expected that a $SiH_4/H_2/Ar$ plasma mixture may be somewhat similar as a H_2/Ar plasma mixture, since silane molecules will be dissociated into hydrogen and Si_xH_y radicals in the plasma. From the result of Figure 5 one can see that the charged particles density drops further at the small silane flow range and after the point of ≃ 3–4% of silane in the flow, density decreasing very slow at increasing silane flow rate. Such a behavior of the charged particles density can be connected with additional appearance of dissociative recombination channels of the SiH_n^+ radicals /9/:

$$SiH_n^+ + e \longrightarrow SiH_{n-1} + H, \qquad (13)$$

or/and with appearance of new hydrogen molecular ions H_2^+ and H_3^+ at dissociation of Si_xH_y, with the following reactions of dissociative recombination (5)–(7).

At the same time, the electron temperature goes to the inverse direction as that in the case of H_2/Ar plasma mixture. The reason of the temperature rising when silane appears in the plasma might be the same as in case of pure argon, and oxygen/argon mixtures.

Some uncertainties at interpretation of experimental data might be connected with the deposition of amorphous silicon on the probe surface. Since the deposition rate is so fast (few nanometers per second under our experimental conditions), this influence is almost impossible to avoid completely. The upper limit of the error in the charged particle density value can be estimated to be 30% if one assumes that the increase of the temperature is only due to the amorphous silicon deposition on the probe surface.

CONCLUSION

Langmuir probe diagnostic is used for the quantitative study of the variations of the electron temperature and density if hydrogen, oxygen and silane gases are ejected into an argon expanding plasma which can be used for thin film deposition.

In the pure argon case, the charged particles density (at an axial position of 250 mm away from the nozzle, flow rate of 1 slm to 10 slm, arc current of 15 A to 75 A arc current and 0.5 mbar background pressure) varies around 10^{19} m^{-3}. The density rises with increasing argon flow or arc current. Injection of hydrogen, oxygen or hydrogen/silane gas mixture into the argon arc, leads in all cases to a decrease of the charged particle density in the plasma. This decrease may amount to orders of magnitude, three in the case of hydrogen injection.

The electron temperature of the pure argon plasma (at an axial position of 250 mm away from the nozzle, flow rate of 1 slm to 10 slm, arc current of 15 A to 75 A arc current and 0.5 mbar background pressure) varies between 2000 K and 4000 K and it increases with both flow rate and arc current. T_e also increases in the cases of small oxygen or silane gas mixture injection. But in hydrogen injection case, T_e decreases. The main drop of T_e occurs at small hydrogen concentration range. After 5–8% hydrogen in total flow rate, T_e changes very slightly.

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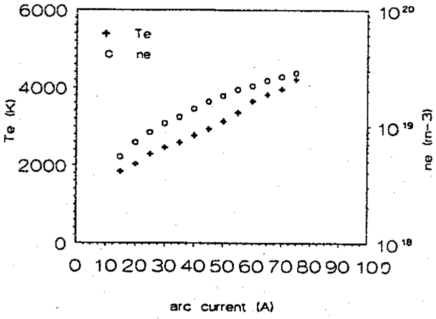

Fig.1 Arc current influence on T_e and n_e

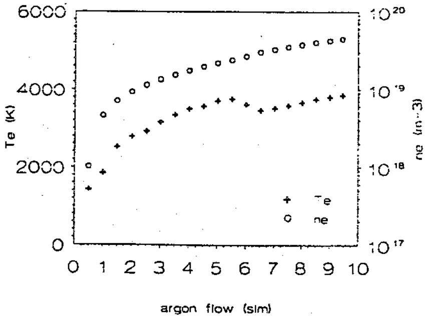

Fig.2 Argon flow influence on T_e and n_e

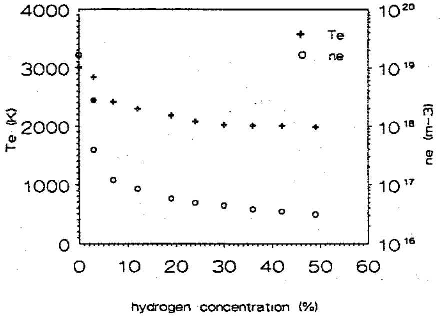

Fig.3 T_e and n_e of a H_2/Ar mixture

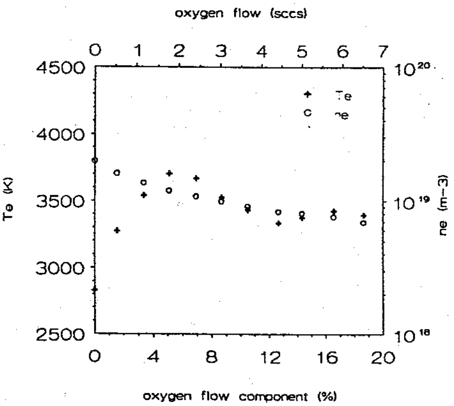

Fig.4 T_e and n_e of an O_2/Ar mixture

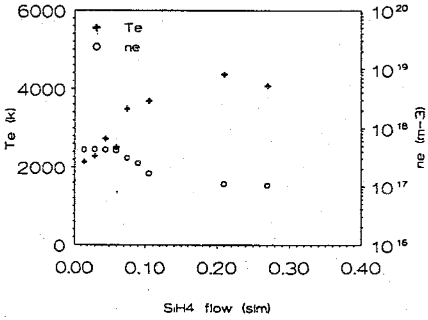

Fig.5 T_e and n_e of a $SiH_4/H_2/Ar$ mixture