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Influence of ion species ratio on grid-enhanced plasma source ion implantation*

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Grid-enhanced plasma source ion implantation (GEPSII) is a newly proposed technique to modify the inner-surface properties of a cylindrical bore. In this paper, a two-ion fluid model describing nitrogen molecular ions N_2^+ and atomic ions N^+ is used to investigate the ion sheath dynamics between the grid electrode and the inner surface of a cylindrical bore during the GEPSII process, which is an extension of our previous calculations in which only N_2^+ was considered. Calculations are concentrated on the results of ion dose and impact energy on the target for different ion species ratios in the core plasma. The calculated results show that more atomic ions N^+ in the core plasma can raise the ion impact energy and reduce the ion dose on the target.

Keywords: plasma simulation, plasma sheath, two-ion fluid model, grid-enhanced plasma source ion implantation

PACC: 5240K, 5265

1. Introduction

Plasma source ion implantation (PSII) is a well-known technique to modify surface properties of materials such as metals, polymers, ceramics and semiconductors.[1,2] One of the promising features of this technique is that it can implant targets that are not line-of-sight accessible. Because many industrial components such as dies, pipes and bushings require inner surface modification, PSII for inner surface modification has attracted considerable interest of physicists and material scientists.[3−6]

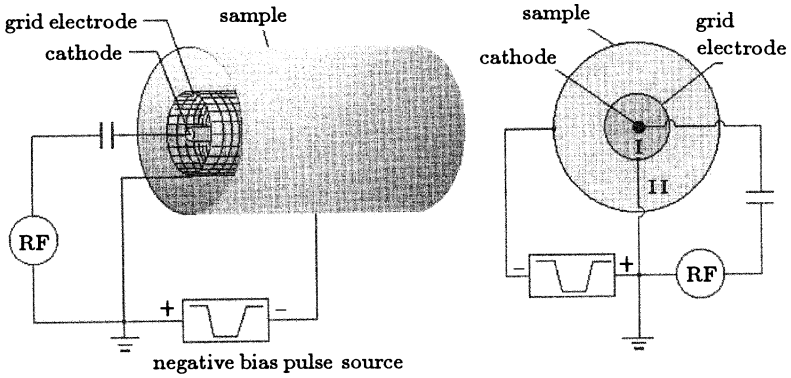


Fig.1. Schematic diagrams of the GEPSII experiment considered. The right one is the cross-sectional diagram, in which region I is the core plasma region, region II is the diffusion plasma region. Note that the applied pulse shapes are trapezoidal.

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Grid-enhanced PSII (GEPSII) is a newly developed method in our laboratory for inner surface modification of a cylindrical bore,[6−8] which is modified from the previous experiment [4,9] with a central grounded electrode inside the bore along its radial direction. In this new method, three coaxial electrodes (a central cathode, a coaxial cylindrical grid electrode and the inner surface of a tubular target) divide the cylindrical bore into two regions: the core plasma region and the diffusion plasma region (see Fig.1). Plasma is produced by RF discharge established in the core plasma region between the central cathode and the grounded grid electrode. The plasma can diffuse through the grid electrode to the target. When a negative voltage pulse is applied to the target, positive ions in the diffusion plasma region can be accelerated into the target. Experimental studies have shown some advantages of this new technique over the previous one. First of all, plasma is generated inside the bore, so the plasma density is relatively high and uniform along the axis of the bore, which ensures ion dose uniformity on the target along the axial direction. In addition, metallic atoms can be produced by RF sputtering of the cathode, which makes it possible to realize metallic implantation and deposition on the inner surface.

The feasibility and superiority of the GEPSII technique has been further verified by our calculation of ion sheath dynamics using the collisionless fluid model.[10] Later, for the purpose of giving some guidance to optimize the GEPSII experiment, we investigated the effects of grid and target radius and ion-neutral collisions on the GEPSII process utilizing the collisional fluid model.[11] However, our previous calculations only simulate nitrogen molecular ions N_2^+ without considering the fact that there is a mixture of ion species (N^+ and N_2^+) present in the GEPSII experiment using nitrogen plasma.[12]

Although carrying the same charge, N^+ and N_2^+ have different mass and collision cross-section, and accordingly they will have different velocities when travelling through the sheath. Hence, it is necessary to simulate them separately. In addition, it has been pointed out by Tang *et al*[13] that the ion species ratio in the plasma is critical in predicting both the dose and energy of the implanted ions. For example, if there are 25% N^+ and 75% N_2^+ in a nitrogen plasma, the average number of atoms produced per ion equals 1.75 ($0.25 \times 1 + 0.75 \times 2 = 1.75$). When the target is biased at 50kV, after implantation, each implanted N^+ is converted into one nitrogen atom with 50keV energy, and each implanted N_2^+ is converted into two nitrogen atoms with 25keV energy. Since nitrogen plasma is used in the GEPSII experiment, both the two ions (N^+ and N_2^+) should be considered in calculations.

In this paper, a two-ion fluid model is used to simulate the GEPSII process, which, in its physical content, is identical to that we used before, but is modified by taking into consideration the two ion species. Our goal is to investigate the effect of ion species ratio on the dose and energy of the implanted ions in GEPSII.

2. Model description

In the GEPSII process, at time t=0, a high negative voltage pulse ϕ is applied to the inner surface of a cylindrical bore, then the sheath expands inward until the sheath edge reaches the grounded grid electrode. When the sheath stops expanding, the ions (N^+ and N_2^+) will be extracted from the core plasma through the grid and accelerated into the target wall. The two-ion fluid model simulating the ion sheath dynamics between the grid electrode r_a and the target r_b is similar to our previous collisional fluid model,[11] except that two ion species (N^+ and N_2^+) are considered now.

In this model, Poisson's equation is modified to explicitly consider the contribution of n_{i1} and n_{i2}, the densities of N^+ and N_2^+, respectively,

$$\frac{1}{r}\frac{\partial}{\partial r}r\frac{\partial \phi}{\partial r} = -\frac{e}{\varepsilon_0}(n_{i1} + n_{i2} - n_e). \tag{1}$$

Then, $n_0 = n_{i1}|_{r_a} + n_{i2}|_{r_a}$ is the plasma density at the grid electrode. The electrons are assumed to be in thermal equilibrium and obey the Boltzmann's relation

$$n_e = n_0 \exp(e\phi/kT_e). \tag{2}$$

The two ion species are assumed source free and cold, their densities and velocities are determined by their equations of continuity and motion

$$\frac{\partial n_{i1}}{\partial t} + \frac{1}{r}\frac{\partial}{\partial r}(r n_{i1} v_{i1}) = 0, \tag{3}$$

$$\frac{\partial n_{i2}}{\partial t} + \frac{1}{r}\frac{\partial}{\partial r}(r n_{i2} v_{i2}) = 0, \tag{4}$$

$$\frac{\partial v_{i1}}{\partial t} + v_{i1}\frac{\partial v_{i1}}{\partial r} = -\frac{e}{M_1}\frac{\partial \phi}{\partial r} - \frac{F_{c1}}{M_1}, \tag{5}$$

$$\frac{\partial v_{i2}}{\partial t} + v_{i2}\frac{\partial v_{i2}}{\partial r} = -\frac{e}{M_2}\frac{\partial \phi}{\partial r} - \frac{F_{c2}}{M_2}. \tag{6}$$

Here F_{c1}/M_1 and F_{c2}/M_2 in Eqs.(5) and (6) are the collision drag force terms for N^+ and N_2^+, respectively. Under low-pressure PSII conditions, F_c can be written as [14,15]

$$F_c = \frac{\pi}{2} n_n \sigma_i v_i |v_i| M = \frac{\pi}{2} \frac{|v_i| v_i}{\lambda_i} M,$$

where n_n is the neutral background gas density, σ_i is the ion collision cross-section and λ_i is the ion mean free path. For N^+, σ_{i1} can be assumed to be 10^{-15}cm^2 and for N_2^+, σ_{i2} to be 10^{-14}cm^2.[16]

Equations (1)–(6) can be normalized using the following variables:

$$\rho = r/D, \quad \psi = \phi/\phi_p,$$

$$N_i = n_i/n_0, \quad V_i = v_i/v_{max},$$

$$T = t\omega_{pi}, \quad \alpha_i = \frac{\pi}{2}\frac{D}{\lambda_i} = \frac{\pi}{2} D n_n \sigma_i,$$

where $v_{max} = \sqrt{\dfrac{-2e\phi_p}{M_1}}$ is the velocity a collisionless atomic ion N^+ would gain in falling through the full potential drop ϕ_p; $\omega_{pi} = \sqrt{\dfrac{n_0 e^2}{\varepsilon_0 M_1}}$ is the ion plasma frequency, and $D = \sqrt{\dfrac{-4\varepsilon_0\phi_p}{e n_0}}$ is the ion-matrix overlap length.[3]

Substituting Eq.(2) into Eq.(1), and using the dimensionless variables, we obtain

$$\frac{1}{\rho}\frac{\partial}{\partial\rho}\rho\frac{\partial\psi}{\partial\rho} = 4(N_{i1} + N_{i2} - \exp(e\phi_p\psi/kT_e)), \quad (7)$$

$$\frac{\partial N_{i1}}{\partial T} + \frac{1}{\sqrt{2}}\frac{1}{\rho}\frac{\partial}{\partial\rho}(\rho N_{i1} V_{i1}) = 0, \quad (8)$$

$$\frac{\partial N_{i2}}{\partial T} + \frac{1}{\sqrt{2}}\frac{1}{\rho}\frac{\partial}{\partial\rho}(\rho N_{i2} V_{i2}) = 0, \quad (9)$$

$$\frac{\partial V_{i1}}{\partial T} + \frac{1}{\sqrt{2}} V_{i1}\frac{\partial V_{i1}}{\partial\rho} = \frac{1}{2\sqrt{2}}\frac{\partial\psi}{\partial\rho} - \frac{\alpha_{i1}}{\sqrt{2}} |V_{i1}| V_{i1}, \quad (10)$$

$$\frac{\partial V_{i2}}{\partial T} + \frac{1}{\sqrt{2}} V_{i2}\frac{\partial V_{i2}}{\partial\rho} = \frac{1}{2\sqrt{2}}\frac{M_1}{M_2}\frac{\partial\psi}{\partial\rho} - \frac{\alpha_{i2}}{\sqrt{2}} |V_{i2}| V_{i2}. \quad (11)$$

The above equations can be used to describe the ion sheath dynamics of PSII with the plasma consisting of two ion species, and also can be extended to multi-ion species plasma. However, it should be pointed out that the physical mechanism of the GEPSII process determines its special initial and boundary conditions.

As to the initial conditions for Eqs.(7)–(11), the variable mobility model [17] we used previously is also modified to consider the two ion species N^+ and N_2^+. Hence, the equations included in the model are the source free steady-state continuity equations and equations of drift for the two ion species, and Boltzmann's relation for electrons:

$$\frac{1}{r}\frac{\partial}{\partial r}(r n_{i1} v_{i1}) = 0, \quad (12)$$

$$\frac{1}{r}\frac{\partial}{\partial r}(r n_{i2} v_{i2}) = 0, \quad (13)$$

$$v_{i1} = \mu_{i1} E, \quad (14)$$

$$v_{i2} = \mu_{i2} E, \quad (15)$$

$$n_e = n_0 \exp(e\phi/kT_e), \quad (16)$$

where $\mu_i = \dfrac{2e\lambda_i}{\pi M |v_i|}$ is the ion mobility coefficient in low-pressure cases.[18] The above equations are solved by the finite difference method using the boundary conditions of $n_i = n_{i1} + n_{i2} = n_e = n_0$ at $r = r_a$ and $v_i = v_B$ at $r = r_b$. Here, n_0 is the plasma density at the grid and v_B is the Bohm velocity. The exact values of n_{i1} and n_{i2} are determined by the ion species ratio in the core plasma. The calculated initial ion velocity is small compared with that when the voltage pulse is applied, so we assume that the ions are initially motionless.

The normalized boundary conditions for the two-ion fluid model are ψ=0 and $N_i = N_{i1} + N_{i2} = 1$ at the grid electrode ρ_a ($\rho_a = r_a/D = 1.0$), and $\psi = \psi_t$ at the target ρ_b ($\rho_b = r_b/D = 2.0$). As we used before, the applied voltage pulse at the target ψ_t is assumed to be trapezoidal with its normalized rise time T_r=17, plateau time T_p=66 and fall time T_f=17, which approximately corresponds to a rise and fall time of $\approx 1\mu$s for a plasma density of $n_0 = 5\times10^9\text{cm}^{-3}$.

Using the above initial and boundary conditions, Eqs.(7)–(11) in the normalized two-ion fluid model are solved with a finite difference method just as we used before.[10,11] A normalized grid spacing Δr=0.005 and a time step ΔT=0.001 are used in our simulation.

3. Results and discussions

The parameters used in the calculations include: electron temperature T_e=1eV, source plasma density $n_0 = 5\times10^9\text{cm}^{-3}$, full target potential ϕ_p=–10kV and its rise and fall times $t_r = t_f \approx 1\mu$s. For the neutral background gas pressure of 1.33×10^{-1}Pa, α_{i1} is about 0.1 and α_{i2} about 1.0.

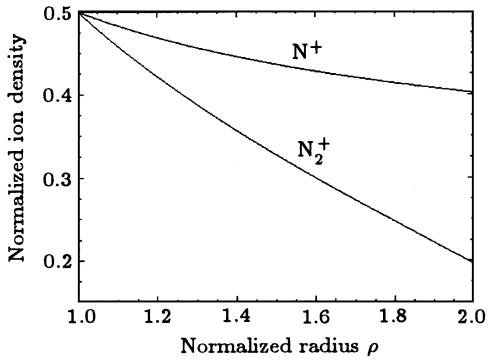


Fig.2. Normalized initial ion density in the diffusion plasma region between the grid electrode and the target for ion species ratio of N^+=50% and N_2^+=50% in the core plasma.

The initial ion densities within the diffusion plasma region calculated by the variable mobility model are presented in Fig.2. Determined by the plasma diffusion mechanism, the initial steady-state densities of both N^+ and N_2^+ decrease along the radial direction from the grid electrode to the target. For the ion species ratio of N^+=50% and N_2^+=50% in the core plasma, the normalized ion densities of the two species at the grid are equal ($N_{i1}|_{\rho_a} = N_{i2}|_{\rho_a} = 0.5$), but at the target, N_{i2} is much lower than N_{i1}. Such a difference can be explained by their different mobility coefficients. With longer mean free path and smaller mass, the atomic ion mobility coefficient μ_{i1} is larger than the molecular ion mobility coefficient μ_{i2}, which means that there will be more N^+ than N_2^+ diffused to the target under the same conditions. Therefore, the initial steady-state densities of N^+ and N_2^+ within the diffusion plasma region cannot be equal to each other even if they are equal in the core plasma.

Figure 3(a) shows the normalized velocity of N^+ and N_2^+ at the target during the pulse. The increase and decrease of the ion velocities at the two ends of the pulse are mainly caused by the voltage pulse rising and falling. The impact velocity of N^+ rises faster and its maximum value is higher, which can be explained as follows. First, the ion impact energy at the target is the result of electric field acceleration and collision deceleration from a given position to the target. N^+ and N_2^+ can obtain the same electric field acceleration as both of them carry one positive charge. However, since the collision cross-section of N_2^+ is higher than that of N^+, N_2^+ will lose more energy by collisions before impacting the target, so the impact energy of N_2^+ is lower. In addition, the mass of molecular ions M_2 is the double of M_1, and so the impact velocity of N^+ will be higher than N_2^+ even when their impact energies are equal, which can further explain the higher velocities of N^+ at the target. It should be pointed out that the ion impact velocities cannot be affected by their ratios in the core plasma.

Figure 3(b) gives the normalized ion densities at the target for the ion species ratio of N^+=50% and N_2^+=50% in the core plasma. For N^+ or N_2^+, the ion density decreases rapidly in the initial period, and the rate of decrease gradually slows down as the sheath expands to the grid electrode. After the sheath edge reaches the grid electrode, the ion density drops sharply to its stable value. The density of N^+ is higher than that of N_2^+ in the initial period, which can be attributed to its initial higher density as seen in Fig.2. The density of N^+ reaches its relatively lower stable value earlier due to the higher velocity of N^+.

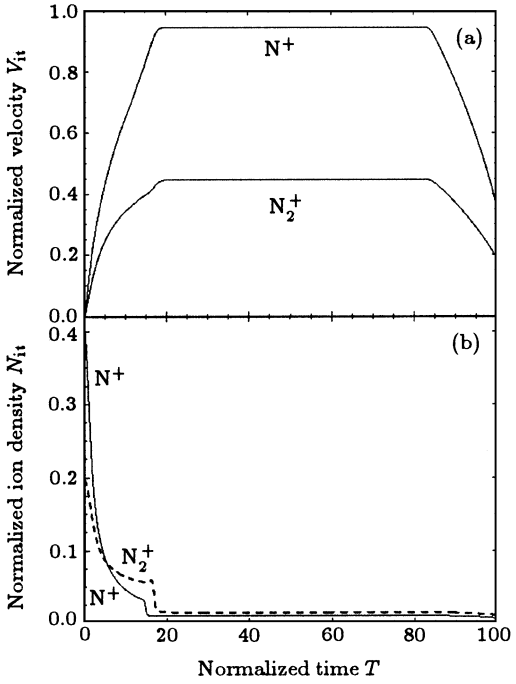


Fig.3. Normalized ion velocity (a) and ion density (b) at the target for the ion species ratio of N^+=50%, N_2^+=50% during the pulse.

The normalized ion dose at the target vs time for different nitrogen species ratios is presented in Fig.4. The normalized ion dose N_d is the time integral of the normalized ion flux $N_{it}V_{it}$ and is given by

$$N_d = \int_0^T N_{it}V_{it}\,dT. \qquad (17)$$

Therefore, N_d is determined by the time-dependent ion density N_{it} and impact velocity V_{it} at the target,

as shown in Fig.3. Figures 4(a) and 4(c) can be easily explained by the fact that higher ratio of one ion species in the core plasma will certainly result in its higher dose. However, when their ratios are equal (see Fig.4(b)), the dose of N^+ is higher than N_2^+, implying that there are more ions of N^+ than of N_2^+ reaching the target at one time due to its higher impact velocity.

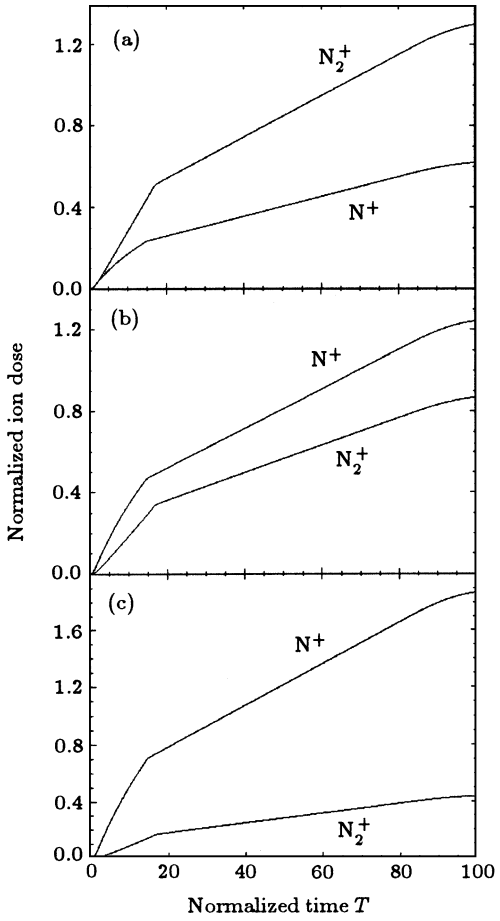


Fig.4. Normalized ion (N^+ and N_2^+) dose at the target vs time for different nitrogen species ratios of (a) N^+=25%, N_2^+=75%, (b) N^+=50%, N_2^+=50% and (c) N^+=75%, N_2^+=25%.

As Tang *et al*[13] has mentioned, one nitrogen molecular ion N_2^+ impacted the target will be eventually converted into two nitrogen atoms implanted into the target. In view of such an idea, we give the normalized nitrogen atom dose of N^+ and N_2^+ at the target vs time for different nitrogen species ratios in Fig.5, from which we can see that except when the N^+ ratio is very high in the core plasma, the nitrogen atom dose mainly comes from N_2^+ implantation.

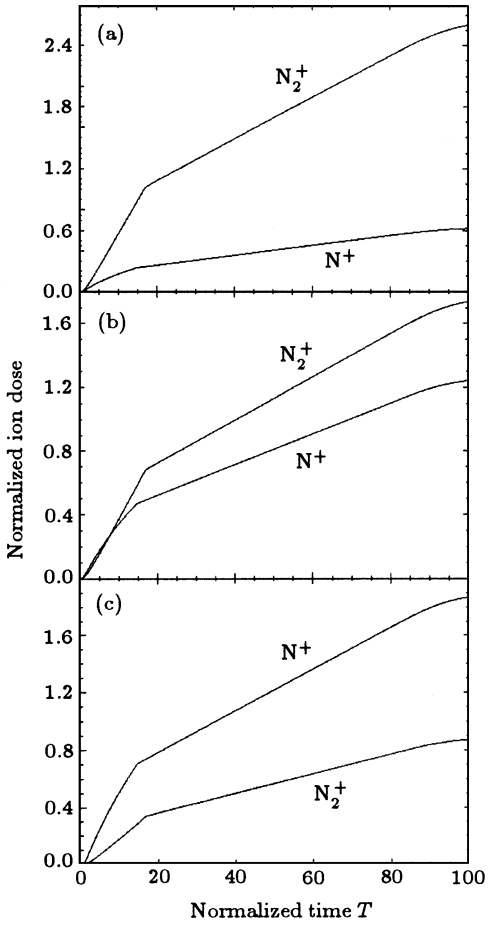


Fig.5. Normalized nitrogen atom dose of N^+ and N_2^+ at the target vs time for three different nitrogen species ratios as in Fig.4.

The time-averaged ion energy distribution at the target during a pulse for different nitrogen species ratios is given in Fig.6. In all the three given cases, besides a few ions visible at the lower energy end, most ions are concentrated on the two energy peaks positioned at about E_{it}=0.38 and E_{it}=0.88, which correspond to the maximum impact energies of N_2^+ and N^+, respectively. The population of ions in the higher energy peak of E_{it}=0.88 increases with increasing ratio of N^+ in the core plasma, which verifies that more N^+ in the plasma is favourable to increase the ion impact energy at the target. Interestingly, the near mono-energy implantation of N^+ or N_2^+ can be explained

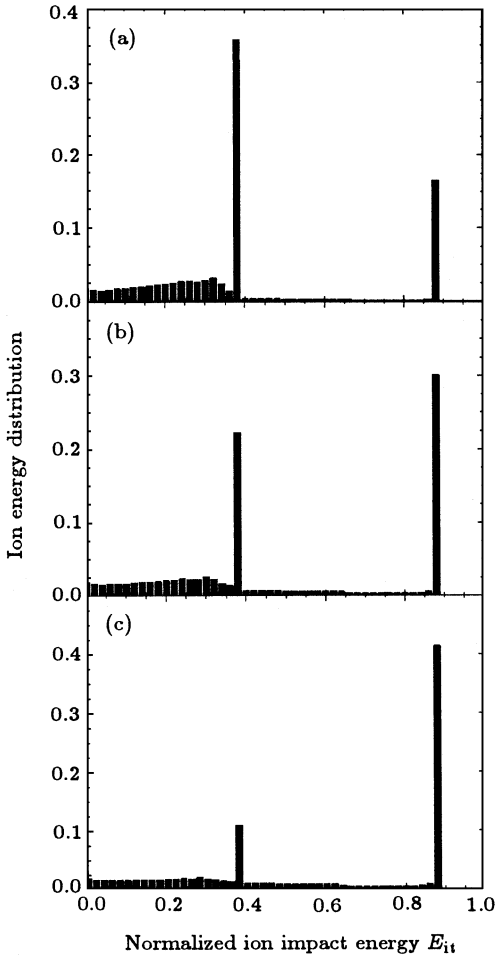


Fig.6. Time-averaged ion energy distribution at the target for three different nitrogen species ratios as in Fig.4.

by the sheath evolution process in GEPSII: In GEPSII, the ion sheath will stop expanding when the sheath edge reaches the grid electrode, and then all the ions extracted from the core plasma region through the grid will experience the full target potential fall, and finally reach the target with their maximum impact energy. Therefore, a fixed ion sheath width of GEPSII ensures the near mono-energy ion implantation as long as the pulse duration is long enough.

4. Conclusions

In conclusion, we have investigated the effect of nitrogen ion species ratio on the GEPSII using a two-ion fluid model. The calculated results have demonstrated that higher ratios of N_2^+ in the core plasma can result in higher nitrogen atom dose on the target. However, more N_2^+ in the plasma can lower the ion impact energy. Under our present GEPSII conditions, the ion species ratio in the core plasma is about N^+=25%, N_2^+=75%. Hence, based on the above calculation, we think we should change the RF discharge conditions (gas pressure, RF power and driving voltage) in real experiments to raise the N^+ ratio in the core plasma, which can increase the ion impact energy on the target, and the induced lower ion dose can be compensated by prolonging the processing time.

References

[1] Conrad J R, Radtke J L, Dodd R A, Worzala F J and Tran N C 1987 *J. Appl. Phys.* **62** 4591

[2] Chu P K and Chan C 2001 *Surf. Coat. Technol.* **136** 151

[3] Sheridan T E 1993 *J. Appl. Phys.* **74** 4903

[4] Sun M, Yang S Z and Li B 1996 *J. Vac. Sci. Technol.* A **14** 367

[5] Zeng X C, Liu A G, Kwok T K, Chu P K and Tang B Y 1997 *Phys. Plasmas* **4** 4431

[6] Liu B, Zhang G L, Cheng D J, Liu C Z, He R and Yang S Z 2001 *J. Vac. Sci. Technol.* A **19** 2958

[7] Liu B, Liu C Z, Cheng D J, Zhang G L, He R and Yang S Z 2001 *Nucl. Instrum. Meth. Phys. Res.* B **184** 644

[8] Zhang G L, Wang J L, Liu C Z, Yang W B, Fan S H and Yang S Z 2003 *Acta Phys. Sin.* **52** 2213 (in Chinese)

[9] Sun M, Yang S Z and Yao W Q 1998 *J. Vac. Sci. Technol.* A **16** 2718

[10] Wang J L, Zhang G L, Fan S H, Yang W B and Yang S Z 2002 *Chin. Phys. Lett.* **19** 1473

[11] Wang J L, Zhang G L, Fan S H, Yang W B and Yang S Z 2003 *J. Phys. D: Appl. Phys.* **36** 1192

[12] Yu W, Zhang L Z, Li X W, Han L, Chen Y M and Fu G S 1999 *Acta Phys. Sin.* **48** 1701 (in Chinese)

[13] Tang B Y, Fetherston R P, Shamim M, Breum R A, Chen A and Conrad J R 1993 *J. Appl. Phys.* **73** 4176

[14] Sheridan T E and Goeckner M J 1995 *J. Appl. Phys.* **77** 4967

[15] Qiu H T, Wang Y N and Ma T C 2002 *Acta Phys. Sin.* **51** 1332 (in Chinese)

[16] Phelps A V 1991 *J. Phys. Chem. Ref. Data* **20** 557

[17] Lieberman M A and Lichtenberg A J 1994 *Principles of Plasma Discharges and Materials Processing* (New York: Wiley) p137–138

[18] Smirnov B M 1981 *Physics of Weakly Ionized Gases* (Moscow: Mir) p217