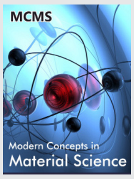
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Research article

The Effects of Total Mass Flow Rate and Gas Composition in Reactive Radio-Frequency Sputtering of Ultrathin Films

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Abstract

The effects of total mass flow rate and gas composition in low-pressure plasma discharges, typical of radio-frequency (rf) sputtering, were investigated in the context of deposition experiments with nitrogen-containing amorphous carbon ultrathin films. An analysis of low-pressure rf discharges is presented to illuminate the dependence of effective ionization rate on the absorbed power, target and substrate bias voltages, and working pressure and provide insight into the effects of total mass flow rate and gas composition on key plasma parameters. The effect of the gas composition on the ion-current density of bombarding plasma ions is shown to be more significant than that of the total mass flow rate. The correlation of the effective ionization rate, ion-current density, and total mass flow rate established by the experiments and analysis of this study explains the variations in growth rate and microstructure of thin and ultrathin films deposited by low-pressure rf discharges.

Keywords: Deposition parameters; Low-pressure plasma discharges; Radio-frequency sputtering; Thin and ultrathin films

Highlights

- Effects of total mass flow rate and gas composition on key plasma parameters
- Effective ionization rate versus ion-current density and total mass flow rate
- Effective ionization rate versus absorbed power, bias voltage, and working pressure
- Stronger effect of gas composition on ion-current density than total mass flow rate
- Insight into growth rate and microstructure variations of radio-frequency sputtered carbon thin and ultrathin films

Introduction

Radio-frequency (rf) sputtering is one of the most widely used thin-film deposition methods. This method uses low-energy neutral atoms or clusters of atoms as film-forming precursors, and its low input energy, process temperature, and working pressure make it an efficient method for depositing thin films. Characteristically, Ar^+ ion bombardment during film growth tailors the film microstructure and properties without altering its chemical environment. The film composition can also be modified by a reactive plasma, such as nitrogen plasma. Thus, the film microstructure, composition, and properties can be tweaked by accordingly adjusting the deposition parameters controlling the low-pressure plasma discharges in rf sputtering, such as forward rf power, ion current density, target voltage, working pressure, plasma ion density, and substrate bias voltage [1-5]. Particularly, the effect of substrate biasing on the microstructure and mechanical properties of sputtered films has been extensively studied because it directly influences the ion bombardment energy, which, in turn, affects the intensity of collision cascades between the impinging Ar^+ ions of the plasma and the atoms at the growing film surface. The resulting atomic interactions at the film surface promote film densification, intermixing of the film atoms with the surface atoms of the substrate [6], growth of diamond nanocrystallites [7], and formation of a layered film structure [8]. The bias voltage for maximum sp^3 hybridization in rf sputtered amorphous carbon (a-C) films has been reported to be in the range of –100 to –200 V [9]. Higher voltages intensify the ion bombardment, subsequently instigating film damage, thermal spikes that may induce transformation from sp^3 to sp^2 carbon atom hybridization, and film resputtering.

The foregoing studies and several others indicate that reactive plasma discharges offer a wide spectrum of possible surface modifications. In the context of supply-rate/pumping-rate-limited competing factors in chemical vapor deposition and plasma etching processes, the total mass flow rate and reactive gas composition are important process parameters [10]. However, the effects of the former parameters on the low-pressure plasma discharges encountered during rf sputtering has not been thoroughly studied. For a fixed working pressure, the total mass flow rate of the sputtering gas may affect the growth rate, microstructure, and properties of the deposited film. Indeed, it has been shown that the total mass flow rate of Ar/N_2 sputtering gas affects the growth rate, microstructure, and nanomechanical properties of nitrogen-containing amorphous carbon (a-CN_x) films deposited by reactive rf sputtering, but not the chemical composition, although the effect is secondary compared to that of the gas composition [11]. These trends can be attributed to changes in plasma parameters influencing the mechanical and chemical environment of the deposited film. Therefore, knowledge of the effect of the total mass flow rate of sputtering gas (either noble or reactive) on key plasma discharge parameters of rf sputtering is of profound importance in deposition of thin films with desirable properties.

In consideration of the plasma discharges encountered under capacitive rf sputtering conditions, the characteristics of low-pressure rf discharges were examined in this study in the context of analytical and experimental results demonstrating the effects of total mass flow rate and sputtering gas composition on important plasma parameters (i.e., effective ionization rate and ion-current density) affecting the growth rate and mechanical properties of a-CN_x films. The results presented below provide explanation for the differences in growth rate, microstructure, and properties of thin and ultrathin films deposited by reactive rf sputtering.

Experimental Method

Deposition of a-CN_x thin films was accomplished with a capacitive rf sputtering system (Perkin-Elmer Randex-2400) in the presence of Ar/N_2 gas (0–50 vol% N_2) under working conditions of total mass flow rate $f \approx 6$–50 sccm, forward rf power $P_f = 750$ W, self-biased substrate voltage $V_S = -200$ V (applied by a substrate tuning technique [12]), and working pressure $p \approx 3$ mTorr. The self-biased target voltage V_T, reflected rf power, and chamber pressure measured before plasma ignition p_1 and under steady-state sputtering conditions p_2 were correlated to the total mass flow rate and composition of the Ar/N_2 gas mixture.

Analysis

A low working pressure (e.g., $p = 3$–10 mTorr) in rf sputtering yields low deposition rates and enhances energetic ion bombardment, which is conducive to film densification and resputtering of weakly bonded atoms. Important plasma parameters are the electron and ion temperature T_e and T_i, respectively, plasma density n_0, ion kinetic energy E_i, and ion-current density J_i [3,13,14]. The product $E_i J_i$ determines the power density on both the target and substrate surfaces during film deposition. Low-pressure discharges are weakly ionized, e.g., for a pure Ar plasma, $p = 3$ mTorr, and plasma-absorbed rf power $P_{ab} = 100$–1000 W, $n_0 \approx (2$–$8) \times 10^{10}$ cm^{-3} and neutral gas density $n_g \approx 10^{14}$ cm^{-3} [3]. For $p = 3$ mTorr, the neutral-neutral mean free path for Ar and N_2 is ~1.4 and ~1.2 cm, respectively [15]. For the intermediate gas flow range [3,16] examined in this study, plasma transport is predominantly diffusive and the generated low-pressure discharges yield an approximately uniform cylindrical plasma of radius r and length l, confined between collisionless electric sheathes and exhibiting negligible energy losses in the radial direction.

For low-pressure (e.g., 3 mTorr) rf discharges, the electron Debye length $\lambda_{De} \approx 743(T_e/n_e)^{1/2}$, where T_e is given in eV and the electron density n_e is given in cm^{-3}, is much smaller than the ion-neutral mean free path λ_i [3]. For example, for $T_e = 3.5$ eV and $n_e = 10^{10}$ cm^{-3}, $\lambda_{De} \approx 0.014$ cm $\approx \lambda_i/71$. Hence, the ion velocity at the plasma-sheath edge u_s is equal to the ion sound (Bohm) velocity $u_B = (T_e/M_i)^{1/2}$, where M_i is the ion mass [13]. Consequently, for collisionless sheathes, the ion-current density per unit area $n_s u_B$ on the target and substrate surfaces can be presumed to be equal, i.e., $J_i = e n_s u_B$, where n_s is the ion density at the plasma-sheath edges and is given by $n_s \approx 0.86 n_0 (3 + l/2\lambda_i)^{-1/2}$ [14]. Therefore, an overall discharge power balance for approximately cylindrical plasma gives [3]

$$P_{ab} = 0.86 n_0 u_B A_T (E' - eV_T - eV_S)\left[3 + \frac{l}{2\lambda_i}\right]^{-1/2} p \qquad (1)$$

where A_T is the target surface area and $E' \approx 114$ eV for 3 mTorr Ar discharges [3]. For a given p and fixed target-substrate geometry, P_{ab}, and V_S, Eq. (1) indicates that a lower n_0 intensifies V_T, which explains the changes in V_T due to gas composition variations in reactive rf sputtering of a-CN_x films [11].

The foregoing particle balance for steady-state rf plasma discharges yields that ion losses to the target and substrate surfaces are balanced by ions generated in the bulk of the plasma at an effective ionization rate. Thus,

$$2\pi r^2 n_s u_B = \pi r^2 l K_{iz}^{'} n_g \qquad (2)$$

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where $K_{iz}^{'}$ is the effective ionization rate (expressed in s^{-1}) and $n_g = PN_A/RT$, where N_A is the Avogadro number, R is the gas constant, and T is the neutral gas temperature, which is close to the ambient. Eq. (2) indicates that $K_{iz}^{'}$ indirectly depends on n_0, which might be a function of the total mass flow rate. For the diffusive discharges considered here, a higher gas flow rate may lead to more charged particle losses in the chamber space and walls. While the energy loss due to the foregoing particle losses can be neglected due to the high V_T and V_S, $K_{iz}^{'}$ may differ from the real ionization rate in the plasma bulk at a given pressure.

Using Eqs. (1) and (2), the effective ionization rate can be expressed as

$$K_{iz}{'} = C\frac{P_{ab}}{\left[\frac{E'}{e} - V_T - V_S\right]p} \qquad (3)$$

where $C = 2RT/elA_TN_A$ is a constant in this study. Thus, $K_{iz}^{'}$ can be used to indirectly interpret the effects of the total mass flow rate and sputtering gas composition on controlling plasma parameters by substituting in Eq. (3) the magnitudes of key process parameters measured under various sputtering conditions.

Results and Discussion

In the present experiments, p, P_f, and V_T were measured at steady-state plasma conditions. While the steady-state chamber pressure p_2 remained almost constant after the ignition of the pure Ar plasma (i.e., $p_1 \approx p_2$), Figure 1 shows an appreciable change in chamber pressure during the Ar/N_2 discharges, especially for a relatively low total mass flow rate Q_m. As adsorption of reactive nitrogen atoms occurred readily on the fresh surfaces of the chamber, p_2 decreased after plasma ignition, even though Q_m and the pumping speed were kept constant. Moreover, Figure 1 shows less change in chamber pressure due to plasma ignition with increasing Q_m. This is because the introduction of nitrogen gas at higher flow rates decreased the relative amount of consumed nitrogen, subsequently causing the effect of nitrogen-adsorbing sites to become secondary.

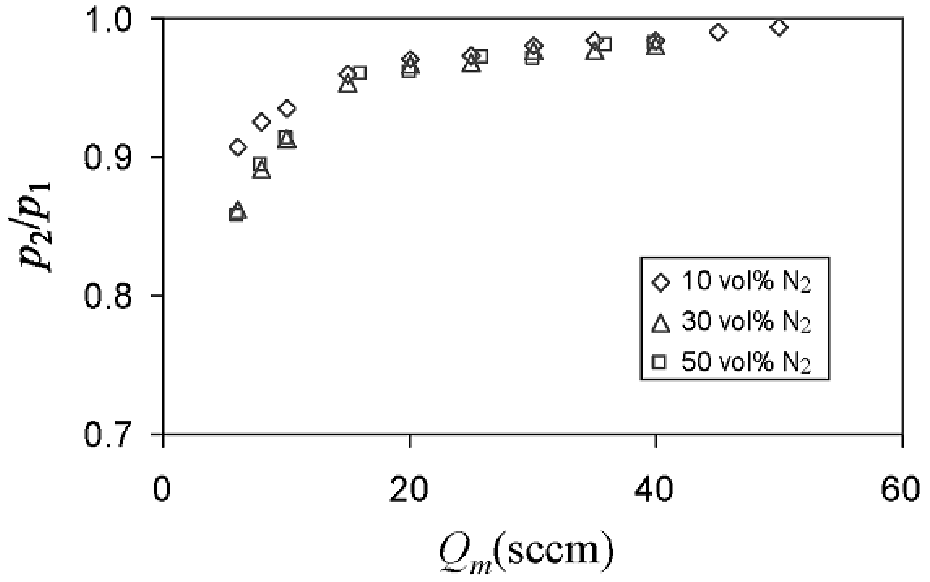

Figure 1: Effect of total mass flow rate Q_m on the ratio of the steady-state pressure p_2 to the pressure before plasma ignition p_1 for different N_2 contents of the Ar/N_2 sputtering gas.

Figure 2 shows the self-biased target voltage V_T versus total mass flow rate Q_m and gas composition. The trend for V_T to increase with the N_2 content and Q_m is in good agreement with previous findings [11]. In view of Eq. (1) and the tendencies shown in Figure 2, it can be inferred that the increase of the N_2 content and Q_m reduced the plasma density n_0. It is noted that Ar/N_2 discharges are considerably more complex than pure Ar discharges, and for molecular gases the collisional energy loss can be 2 to 10 times higher than that for a noble gas at a given electron temperature [17]. Nevertheless, the approximation of the Ar/N_2 plasma by a pure Ar plasma does not change the trends observed in the present experiments.

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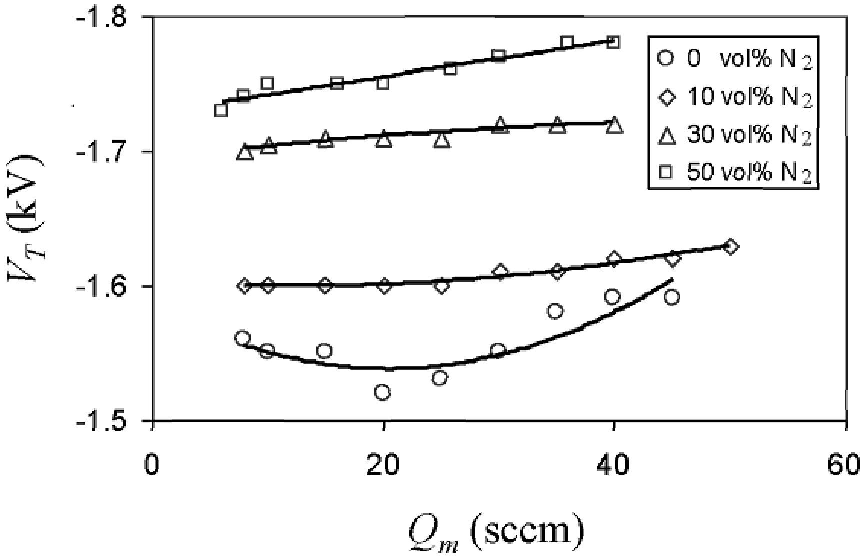

Figure 2: Self-biased target voltage V_T versus total mass flow rate Q_m and N_2 content of the Ar/N_2 sputtering gas.

Figure 3 shows the effective ionization rate $K_{iz}^{'}$ versus the total mass flow rate Q_m and gas composition. For all gas compositions, $K_{iz}^{'}$ decreased with the increase of Q_m, especially for higher N_2 contents. In view of the trends shown in Figure 3, it may be interpreted that although for pure Ar plasma the effect of the total mass flow rate was marginal, for an Ar/N_2 plasma with a relatively high nitrogen content the effect was significant. This indicates that, for a constant chamber pressure (i.e., ~3 mTorr), an increase in Q_m resulted in more ion or electron losses through diffusive discharges due to the corresponding higher pumping speed. Consequently, for a given sputtering gas composition, a higher total mass flow rate yielded a lower plasma density in the discharges, even though the density change (indicated by the change in ion-current density) was not very profound, as seen by the decrease of J_i primarily with increasing N_2 content and secondarily with increasing Q_m (Figure 4). Since V_T was fixed at –200 V during sputtering, the power density on the substrate surface exhibited the same trend as J_i. For $E_i \approx 200$ eV, J_i plays an important role in the film growth process, affecting the microstructure and nanomechanical properties of the deposited films [18].

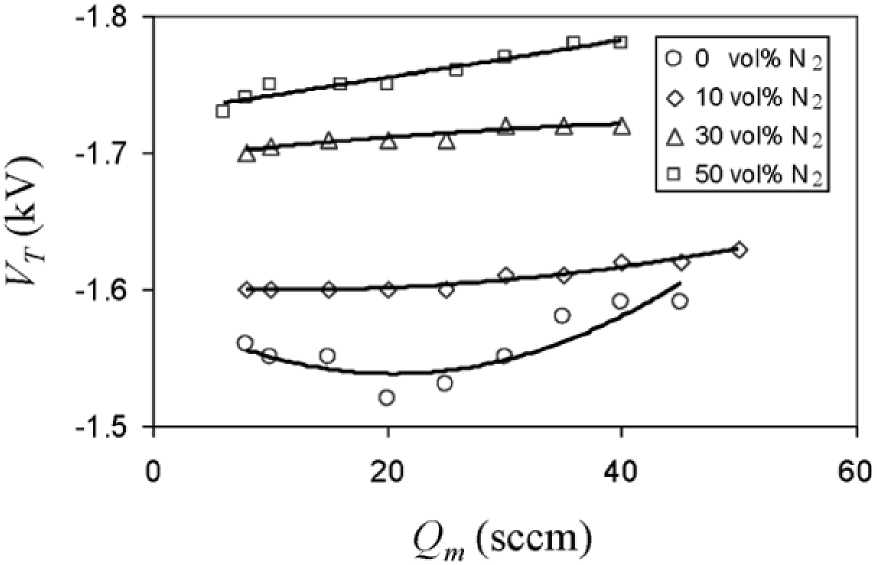

Figure 3: Effective ionization rate $K_{iz}^{'}$ in low-pressure rf discharges versus total mass flow rate Q_m and N_2 content of the Ar/N_2 sputtering gas.

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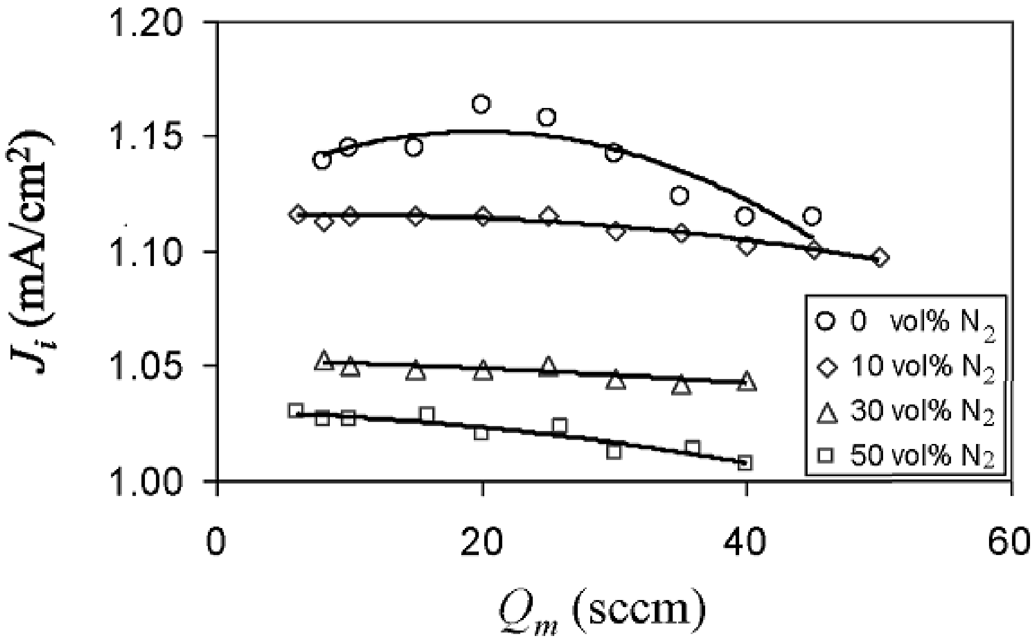

Figure 4: Ion-current density J_i versus total mass flow rate Q_m and N$_2$ content of the Ar/N$_2$ sputtering gas.

The foregoing trends of the ion-current density and power density on the substrate surface are in good agreement with those reported for the growth and nanomechanical properties of a-CN$_x$ films deposited under similar rf sputtering conditions [11]. Furthermore, the analytical and experimental results of this study reveal that a possible reason for the discrepancies in microstructure and properties of reactively rf sputtered thin and ultrathin films may be the effects of the total mass flow rate and sputtering gas composition on the effective ionization rate and ion-current density.

Conclusion

The composition of sputtering gas was shown to exhibit a significant effect on the ion-current density (or power density on the growing film surface) and, consequently, on the growth and properties of thin films deposited by reactive rf sputtering. However, the effect of the total mass flow rate on the plasma conditions and, in turn, the film characteristics was shown to be relatively less significant. The effective rate of plasma ionization decreased with the increase of the total mass flow rate, and this trend became more pronounced with the incorporation of a reactive gas (i.e., nitrogen) in the sputtering gas. The results of this study elucidate the effect of total mass flow rate and sputtering gas composition on important process parameters in low-pressure plasma discharges encountered during reactive rf sputtering and provide explanation for the variations in the growth rate and physical properties of reactively rf sputtered a-CN$_x$ films reported in the literature. Moreover, from a fundamental thin-film synthesis perspective, the present study sheds light into the interdependence of the effective ionization rate, ion-current density, and total mass flow rate, which is critical to understanding variations in the growth rate and structure characteristics of thin and ultrathin films deposited by low-pressure rf discharges.

Acknowledgment

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Conflict of Interest

None.

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