Dependence of plasma parameters in low-pressure RF discharges on total mass flow rate and composition of sputtering gas

W. Lu and K. Komvopoulos
Department of Mechanical Engineering, University of California, Berkeley, CA 94720

Abstract

The effects of the total mass flow rate and composition of sputtering gas on the plasma parameters in low-pressure radio-frequency (RF) discharges were studied experimentally using Ar and N_2 gas mixtures with N_2 contents in the range of 0–50 vol%. Based on a theoretical analysis and some approximations for the low-pressure RF discharges produced in the sputtering system of this study, the effective ionization rate in the plasma discharges is related to the measured absorbed RF power, working pressure and bias voltages on the target and substrate surfaces. This relationship provides insight into the effect of the total mass flow rate on the plasma parameters affecting RF sputtering deposition of thin films. The effective rate of plasma ionization decreases with increasing the total mass flow rate of sputtering gas. This effect becomes more significant when a reactive gas (such as nitrogen) is incorporated in the sputtering gas. Conversely to reactive sputtering gas, the effective rate of plasma ionization in pure Ar discharges changes only slightly with increasing the total mass flow rate in the range of 5–50 sccm. The effect of the total mass flow rate on the self-biased target voltage, effective ionization rate and ion-current density is secondary compared to that of the composition of the sputtering gas. The obtained results suggest that the effect of the total mass flow rate on the growth, microstructure and nanohardness of reactively RF sputtered thin films of nitrogenated amorphous carbon (reported in a previous publication) is associated with changes in the ion-current density or power density on the growing film surface.

Submitted to *Applied Physics Letters* on January 5, 1999.

INTRODUCTION

Reactive plasma discharges offer a wide spectrum of possible surface modifications for engineering materials. In the context of supply-rate-limited and pumping-rate-limited competing factors in chemical vapor deposition and plasma etching, the total mass flow rate of the reactive gas is considered to be an important parameter affecting the process kinetics.[1] Despite this realization, the effect of the total mass flow rate (and composition) of sputtering gas on the plasma parameters of radio-frequency (RF) discharges has not been studied systematically. At a fixed working pressure, the total mass flow rate of the sputtering gas may affect the growth rate, microstructure and mechanical properties of the deposited films. Indeed, recent studies[2] on reactive RF sputtering of nitrogenated amorphous carbon films have shown that although the total mass flow rate of the Ar/N_2 sputtering gas mixture does not affect the chemical composition of the deposited films, it exhibits a noticeable effect on the growth rate, microstructure and nanohardness of the films. These trends have been attributed to changes in the plasma parameters of the film growth environment caused by variations in the total mass flow rate. Therefore, for ultra-thin film deposition by RF sputtering, the effect of total mass flow rate of sputtering gas (noble or reactive) on the plasma parameters is of particular interest. Based on considerations for the plasma discharges occurring in the capacitive RF sputtering system used in this study (Perkin-Elmer Randex-2400), the characteristics of the low-pressure RF discharges were analyzed in light of experimental results demonstrating the effects of the total mass flow rate and composition of sputtering gas on plasma parameters.

EXPERIMENTAL

The RF sputtering experiments were conducted using Ar and N_2 gas mixtures with N_2 contents in the range of 0–50 vol% and total mass flow rates varying from ~6 to 50 sccm. The experiments were performed at a constant forward RF power of 750 W, self-biased substrate voltage of –200 V (applied by the substrate tuning technique[3]), and working pressure of ~3 mTorr. The self-biased target voltage, reflected RF power and chamber pressures before plasma ignition and during steady-state sputtering were measured and correlated to the total mass flow rate.

THEORETICAL

For ultra-thin film deposition by RF sputtering, low working pressures (typically 3-10 mTorr) of sputtering gas yield low deposition rates and increased energetic ion bombardment. The latter is critical to film densification and the re-sputtering of weak atomic bonds. The most important plasma parameters in glow discharges for thin-film deposition are the electron and ion temperatures T_e and T_i, respectively, plasma density n_0, and kinetic energy E_i and current density J_i of the ions bombarding the target or substrate surfaces. The product of the latter two parameters E_iJ_i determines the power density on the target or substrate surfaces during film deposition. In traditional RF sputtering deposition, the plasma generated by low-pressure discharges is not in thermal equilibrium and the electric power is coupled most efficiently to plasma electrons. In low-pressure plasma discharges, the electron temperature T_e greatly exceeds the ion and neutral temperatures in the bulk plasma T_i and T, respectively. Typically, T_e is in the range of 2–5 eV (plasma temperatures are usually given in equivalent electron-volt units, 1 eV = 11605 K), whereas T_i and T are a few times the room temperature (i.e. ~0.026 eV). [4,5]

The low-pressure discharges in this study are weakly ionized discharges. For example, for Ar plasma at working pressure of 3 mTorr and absorbed RF power in the range of 100–1000 W, the plasma density is $n_0 \approx 2–8 \times 10^{10}$ cm^{-3} with neutral gas density $n_g \approx 10^{14}$ cm^{-3}.[6] Sputtering film depositions were performed in a 70-cm-diameter and 30-cm-height vacuum chamber using a ~20-cm-diameter target fixed at a distance of ~7 cm above a substrate holder of surface area equal to that of the target (i.e. $A_S = A_T$). For a working pressure of 3 mTorr and low-energy ions ($T_i \approx 0.05$ eV), the ion-neutral mean free path l_i is ~1 cm, the electron-neutral mean free path is ~4 cm, and the sheath mean thickness produced in these capacitive discharges is ~1 cm.[4] At a pressure of 3 mTorr, the neutral-neutral mean free path l for argon and nitrogen is about 1.4 and 1.2 cm, respectively.[7] Hence, the Knudsen number Kn, defined as $Kn = D/\lambda$, where D is a characteristic dimension of the vacuum chamber (i.e. chamber diameter), is in the range $1 < Kn < 100$. This implies that the gas flow in the present system is in the intermediate flow regime,[8] in which plasma transport is predominantly diffusive and the sheathes generated by the low-pressure discharges can be approximated as collisionless sheathes.

For weakly ionized discharges, the electron energy approximately follows a Maxwellian distribution at the electron temperature T_e. Based on particle balance considerations for a steady-state discharge of pure Ar plasma and the method and data given in Ref. 4, the electron temperature T_e in the low-pressure discharges in the sputtering system of this study is estimated to be 3.5, 2.9 and 2.6 eV for 3, 6 and 10 mTorr, respectively. Since T_e is determined by particle conservation alone, it is independent of the plasma density and, hence, the input RF power.[5] The kinetic energy of bombarding ions E_i is the sum of the energy gained by ions accelerating through the sheath electric field and the ion kinetic energy introduced into the sheath. The mean velocity of ions entering the sheath is equal to the ion sound velocity u_B (or Bohm velocity) corresponding to a directed energy of $T_e/2$, $u_B = (T_e/M_i)^{1/2}$, where M_i is the ion mass. (For $T_e \approx 3.5$ eV and Ar plasma, $u_B \approx 2.9 \text{ x } 10^3$ m/s.). In the discharges of RF sputtering film deposition, both sheath voltages on the target and the substrate are significantly greater than $T_e/2$, especially in the presence of a substrate bias voltage. Hence, the plasma discharge in the sputtering system can be approximated as a uniform cylindrical plasma of radius r and length l oscillating at a frequency of 13.56 MHz between the target and substrate surfaces, assuming that radial losses can be neglected as relatively small, for simplicity.

For 3-mTorr RF discharges, the electron Debye length l_{De}, defined as the scaling distance over which significant charge densities can spontaneously exist, $l_{De} \approx 743(T_e/n_e)^{1/2}$, where T_e is given in eV and the electron density n_e is given in cm^{-3}, is much smaller than l_i ($l_{De} << l_i$). For example, for T_e = 3.5 eV and $n_e = 10^{10}$ cm^{-3}, $l_{De} \approx 0.014$ cm $\approx l_i/71$. In this situation, the ion velocity at the plasma-sheath edge u_s is equal to u_B.[4] Thus, for collisionless sheathes, it can be assumed that the rate of ion loss to the target and substrate surfaces per unit area is $n_s u_B$, where n_s is the ion density at the plasma-sheath edges in the low-pressure discharges, related to the bulk plasma density n_0 by[5]

$$n_s \approx 0.86 n_0 (3 + \frac{l}{2 l_i})^{-1/2}$$

(1)

Consequently, the overall discharge power balance for the approximately cylindrical plasma yields, $P_{abs} = n_s u_B A E_T$, where P_{abs} is the power absorbed by the plasma, A is the total surface area for particle loss comprising the target and substrate surface areas, and E_T is the total energy lost per ion lost from the plasma system given by $E_T = E_c + E_e + E_i$, where E_c is the collisional energy lost per electron-ion pair created and depends only on T_e for a given discharge gas (for T_e = 3.5 eV, it can be found that $E_c \approx 40$ eV),[4] E_e is the mean kinetic energy lost per electron lost ($E_e = 2T_e$ for Maxwellian electrons), and E_i is the mean kinetic energy lost per ion lost to the substrate or target surfaces (i.e. the kinetic energy of bombarding ions). As discussed earlier, the kinetic energy of bombarding ions is approximately equal to the dc potential of the sheath, i.e. $E_i = e(V_0 - V)$, where V_0 is the bulk plasma potential (typically ~10 V) and V is the target or substrate bias voltage that can be measured directly. Hence, based on the above considerations, the power balance equation can be written as

$$P_{abs} = n_s u_B A_T (2E_c + 4T_e + 20 - eV_T - eV_S) = n_s u_B A_T (E' - eV_T - eV_S) \qquad (2)$$

where E¢ ($E' = 2E_c + 4T_e + 20$) is equal to ~114 eV for 3-mTorr Ar discharges, and V_T and V_S are the target and substrate bias voltages, respectively. Substituting Eq. (1) into Eq. (2), the absorbed power can be expressed in terms of the plasma density,

$$P_{abs} = 0.86 n_0 u_B A_T (E' - eV_T - eV_s)(3 + \frac{l}{2 l_i})^{-1/2} \qquad (3)$$

The above power-balance equation indicates that for a discharge at fixed working pressure, target-substrate geometry, absorbed RF power and substrate bias, decreasing the plasma density in the discharge increases the magnitude of the target bias voltage. This provides an explanation for the changes in the target bias voltage caused by variations in the composition of the sputtering gas mixture observed during RF sputtering deposition of nitrogenated amorphous carbon films.[2]

In view of the particle balance in the steady-state RF discharges described previously, the number of ions lost to both target and substrate surfaces is equal to the number of ions generated in the bulk plasma at a given effective ionization rate. This consideration leads to the following relationship,

$$n_s u_B \cdot 2pr^2 = K'_{iz} n_g pr^2 l \qquad (4)$$

where K'_{iz} is the effective ionization rate expressed in s^{-1} and n_g is the neutral gas density given by $n_g = pN_A / RT$, where p is the working pressure, N_A the Avogadro number, and R is the gas constant. As can be deduced from Eqs. (1) and (4), the effective ionization rate K'_{iz} depends on the plasma density n_0, that is affected by the total mass flow rate. For diffusive discharges examined in this study, a faster gas flow may cause more charged particles to be lost to the vast chamber space and walls. Nevertheless, considering the high bias voltages on the target and substrate surfaces, this kind of energy loss can be neglected as very small. However, the effective ionization rate at a given pressure may differ from the real ionization rate in the bulk plasma due to the loss of some charged particles to the chamber space and walls.

Using Eqs. (2) and (4), the effective ionization rate is expressed in terms of the absorbed RF power, working pressure and bias voltages on the target and substrate surfaces,

$$K_{iz}{}' = \left[\frac{2RT}{elA_T N_A}\right] \cdot \frac{P_{abs}}{(\frac{E'}{e} - V_T - V_S)\cdot p} = C \cdot \frac{P_{abs}}{(\frac{E'}{e} - V_T - V_S)\cdot p}$$

(5)

where $C = 2RT / elA_T N_A$ is constant in this study. Thus, the effective ionization rate can be used to examine the effect of the total mass flow rate on the plasma parameters by substituting in Eq. (5) the values of the different parameters measured during sputtering at different total mass flow rates.

RESULTS

In the experiments described above, the reflected RF power P_R, target bias voltage V_T, and working pressure p_2 were measured after the RF plasma reached a steady state. Table I shows typical experimental data for an Ar/N_2 sputtering gas mixture with 50 vol% N_2. While the chamber pressure p_2 remained almost constant after the ignition of pure Ar plasma (i.e. $p_1 = p_2$, where p_1 is the chamber pressure before the plasma ignition), a comparison of the pressure values given in Table I shows that the chamber pressure changed appreciably in the case of the Ar/N_2 plasma, especially at relatively low mass flow rates. Figure 1 shows that a similar behavior occurred at significantly different N_2 contents. Since reactive N atoms can be chemically or physically adsorbed on fresh surfaces, these surfaces can be regarded as adsorption sites. Thus, the chamber pressure p_2 decreased after the ignition of the Ar/N_2 plasma, even though the total mass flow rate and the pumping speed of the vacuum system were kept constant. As evidenced from Table I and Fig. 1, less variation of the chamber pressure after the ignition of the Ar/N_2 plasma is encountered with increasing the total mass flow rate of the gas mixture Q_m. This is because the introduction of N_2 gas at higher flow rates reduces the relative amount of consumed N_2 and, thus, the effect of N adsorption sites becomes secondary.

Figure 2 and Table I show the dependence of the self-biased target voltage V_T on the total mass flow rate Q_m for different sputtering gas compositions. The trend for the magnitude of the target voltage to increase with the N_2 content and total mass flow rate is in good agreement with the observations of a previous study.[2] In view of Eq. (3) and the trends shown in Table I and Fig. 2, it may be argued that increasing the N_2 content and total mass flow rate of the Ar/N_2 sputtering gas decreases the plasma density in the discharges. It should be pointed out that the Ar/N_2 discharges are much more complex than pure Ar discharges because for molecular gases the collisional energy loss E_c can be 2–10 times higher than that for a noble gas at the same electron temperature.[9] The approximation of the Ar/N_2 plasma by pure Ar plasma, however, does not change the trends observed in the present experiments.

Figure 3 shows the effective ionization rate $K_{iz}^{'}$ as a function of the total mass flow rate Q_m for different sputtering gas mixtures. For all gas compositions, the effective ionization rate decreases with increasing the total mass flow rate, especially at higher N_2 contents. In view of the trends shown in Fig. 3, it may be interpreted that for a pure Ar plasma the effect of the total mass flow rate is marginal and becomes significant by increasing the N_2 content in the sputtering gas mixture. This result indicates that if the chamber pressure is maintained constant (i.e. ~3 mTorr in this study), increasing the total mass flow rate of the sputtering gas results in more ion or electron losses in the diffusive discharges due to the associated higher pumping speeds. Consequently, for a given sputtering gas composition, higher total mass flow rates yield lower plasma densities in the discharges, even though the density change, reflected by the change of the ion-current density J_i ($J_i = en_s u_B$), is not very profound, as evidenced from Fig. 4. The ion-current density decreases primarily with increasing the N_2 content in the gas mixture and secondarily with increasing the total mass flow rate. Since the substrate bias was fixed at –200 V during sputtering, the power density on the substrate surface (= $E_i J_i$) exhibits the same trends as the ion-current density. For a kinetic energy of bombarding ions of ~200 eV, the ion-current density plays an important role in the film growth process, affecting the microstructure and mechanical properties of the deposited films.[10] These trends of the ion-current density and power density on the substrate surface are in good agreement with those reported previously for the growth and nanomechanical properties of amorphous carbon films deposited under similar conditions.[2]

COMCLUSIONS

In conclusion, the composition of the sputtering gas mixture exhibits a significant effect on the effective rate of plasma ionization and 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 film properties is less significant compared to that of the sputtering gas composition. The results of this investigation illustrate the significance of the total mass flow rate and composition of sputtering gas on the plasma parameters in low-pressure RF discharges and provide some new insight into the reasons for the changes in the growth and nanomechanical properties of RF sputtered carbon films observed in earlier studies.

ACKNOWLEDGEMENTS

The authors are grateful to Mr. Dujiang Wan for experimental assistance. This work was partially supported by the Surface Engineering and Tribology Program of the National Science Foundation under Grant No. CMS-9734907, and the Computer Mechanics Laboratory at the University of California at Berkeley.

REFERENCES

[1] B. Chapman, *Glow Discharge Processes*, John Wiley, New York (1980).

[2] W. Lu and K. Komvopoulos, J. Appl. Phys. **85,** (1999) in press.

[3] J.S. Logan, IBM J. Res. Develop. **14**, 172 (1970).

[4] M. A. Lieberman and A. J. Lichtenberg, *Principles of Plasma Discharges and Materials Processing*, John Wiley, New York (1994).

[5] M. A. Lieberman, G.S. Selwyn, and M. Tuszewski, MRS Bull. **21**(8), 32 (1996).

[6] W. Lu and K. Komvopoulos, unpublished work.

[7] M. Konuma, *Film Deposition by Plasma Techniques*, Springer-Verlag, Berlin, Germany (1992).

[8] M. Ohring, *The Material Science of Thin Films*, Academic Press, Boston (1992).

[9] C. Lee and M. A. Lieberman, J. Vac. Sci. Technol. **A13**, 368 (1995).

[10] K. S. Fancey, C. A. Porter, and A. Matthews, J. Vac. Sci. Technol. **A13**, 428 (1995).

Table I. Experimental parameters of the low-pressure RF discharges of an Ar/N_2 gas mixture with 50 vol% N_2 under different total mass flow rates.

Total mass flow rate Q_m (sccm)	Reflected RF power P_R (W)	Absorbed RF power P_{abs} (W)	Working pressure[1] p_1 (mTorr)	Working pressure[1] p_2 (mTorr)	Target bias voltage V_T (V)
6	13	737	3.02	2.59	-1730
8	12	738	3.02	2.70	-1740
10	8	742	3.13	2.85	-1750
16	7	743	3.19	3.06	-1750
20	13	737	3.03	2.91	-1750
26	7	743	3.15	3.06	-1760
30	12	738	3.13	3.04	-1770
36	7	743	3.14	3.08	-1780
40	12	738	3.18	3.12	-1780

[1] p_1, working pressure before plasma ignition; p_2, working pressure at steady-state plasma conditions.

List of Figures

FIG. 1 Effect of the total mass flow rate (Q_m) on the ratio of the chamber pressure at steady-state plasma conditions (p_2) to the chamber pressure before plasma ignition (p_1) for different N_2 contents in the Ar/N_2 sputtering gas.

FIG. 2 Self-biased target voltage (V_T) versus total mass flow rate (Q_m) for different N_2 contents in the Ar/N_2 sputtering gas.

FIG. 3 Effective ionization rate ($K_{iz}^{'}$) in low-pressure RF discharges versus total mass flow rate (Q_m) for different N_2 contents in the Ar/N_2 sputtering gas.

FIG. 4 Ion current density (J_i) versus total mass flow rate (Q_m) for different N_2 contents in the Ar/N_2 sputtering gas.

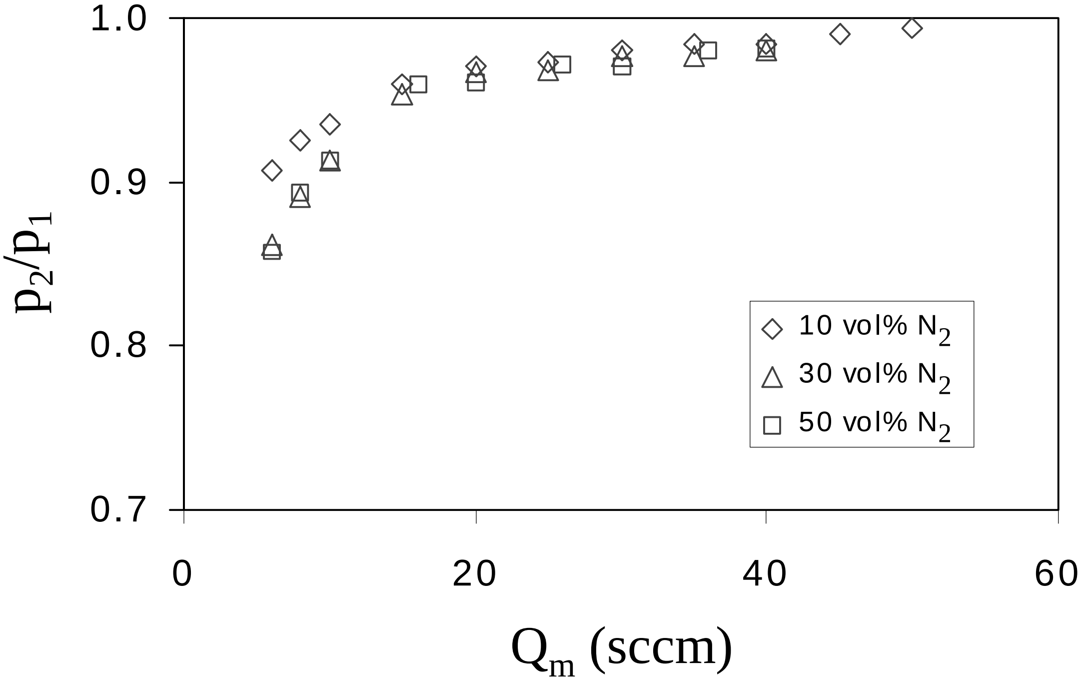


Figure 1

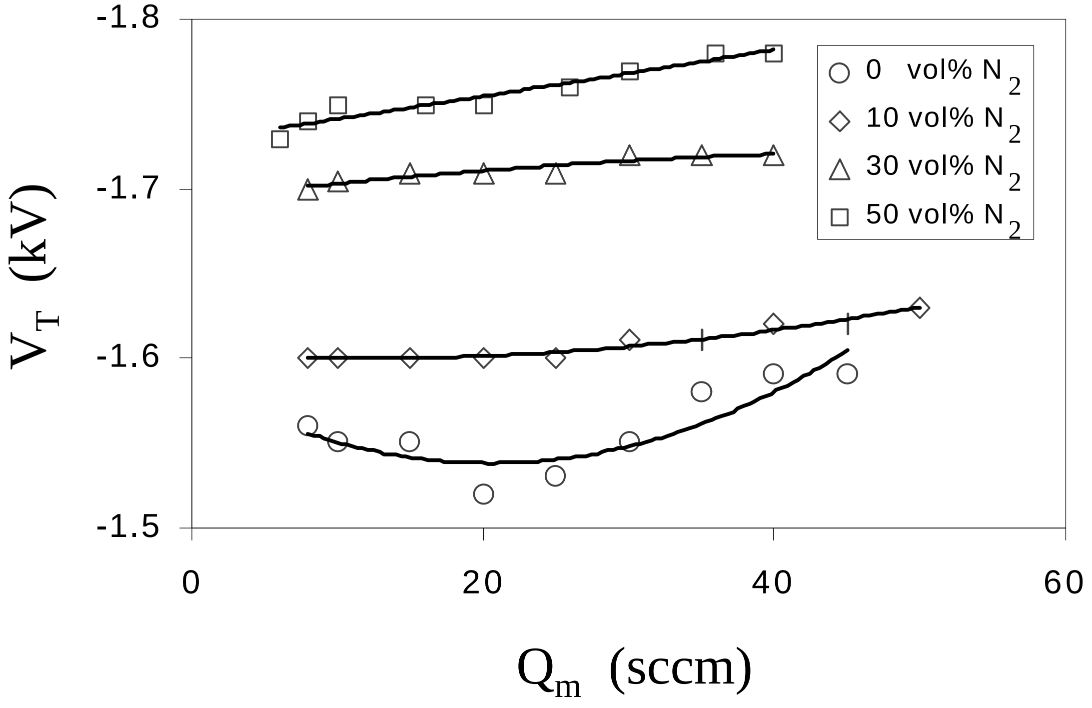
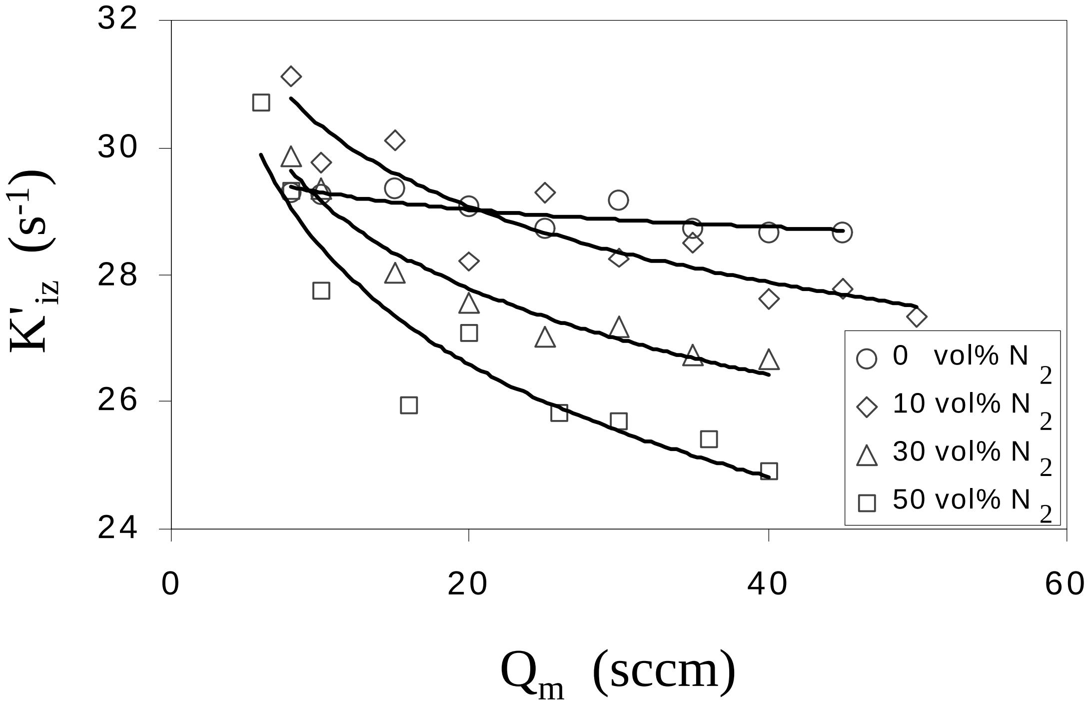

-1.8
-1.7
-1.6
-1.5
0
20
40
60
V_T (kV)
Q_m (sccm)
○ 0 vol% N_2
◇ 10 vol% N_2
△ 30 vol% N_2
□ 50 vol% N_2

Figure 2



32
30
28
26
24
0
20
40
60
K'iz (s-1)
Qm (sccm)
○ 0 vol% N2
◇ 10 vol% N2
△ 30 vol% N2
□ 50 vol% N2

Figure 3

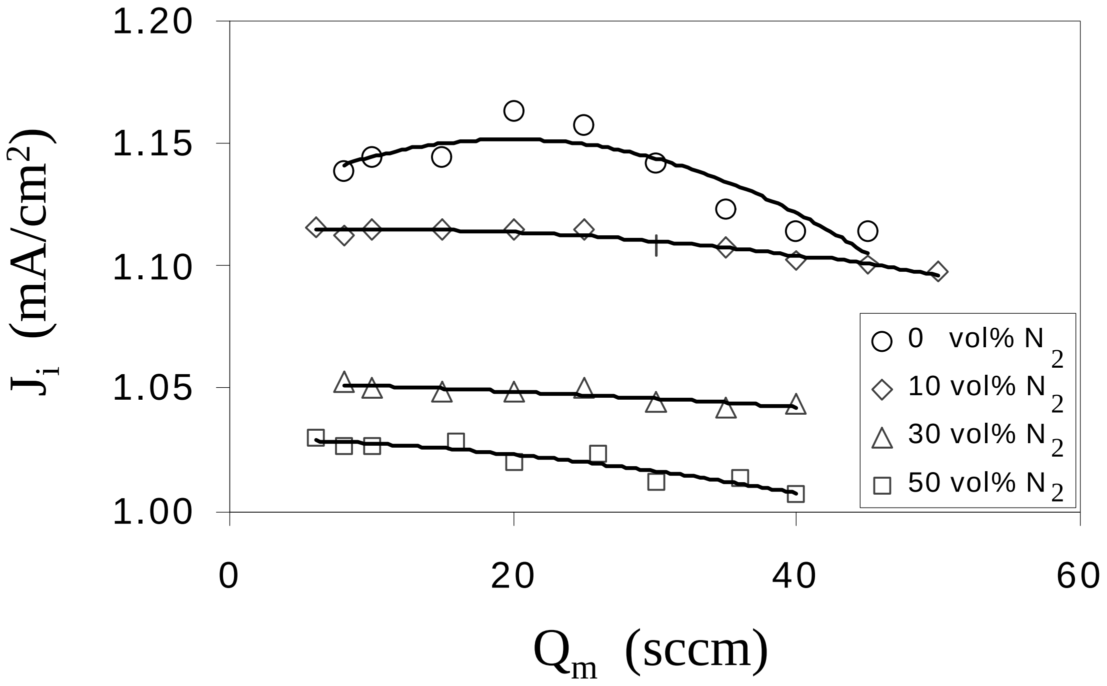

1.20
1.15
1.10
1.05
1.00
J_i (mA/cm^2)
0
20
40
60
Q_m (sccm)
○ 0 vol% N_2
◇ 10 vol% N_2
△ 30 vol% N_2
□ 50 vol% N_2

Figure 4