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J. W. Coburn^a; Eric Kay^a

^a IBM Research Laboratory, San Jose, California

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Tetrafluoromethane Injected into a dc Argon Glow Discharge

J. W. COBURN and ERIC KAY

IBM Research Laboratory
San Jose, California 95193

ABSTRACT

Low partial pressures (10^{-5} to 10^{-3} Torr) of tetrafluoromethane have been injected into a dc argon glow discharge (85×10^{-3} Torr, 1000 V) and the discharge-induced removal rate of the CF_4 molecules from the vapor phase has been studied with a mass spectrometer as a function of the discharge current and the CF_4 concentration. The ultimate disposition of the CF_4 is believed to be in the form of polymeric deposit on the walls of the discharge vessel. The removal rate of CF_4 is proportional to the discharge current and also proportional to the concentration of CF_4 in the low concentration regime. At higher partial pressures of CF_4 ($\sim 1 \times 10^{-3}$ Torr) the removal rate tends to saturate, becoming independent of the CF_4 concentration.

INTRODUCTION

As part of a study of the ionic and radical species created in glow discharges involving molecular gases, measurements have been made of the extent to which a dc argon glow discharge affects the concentration of small quantities of tetrafluoromethane (CF_4) injected into the discharge. Information of this type will assist

in the interpretation of results of studies in which ionic species are extracted directly from the discharge and may be of interest in the area of plasma polymerization in that the ultimate disposition of the CF_4 removed from the gas phase is expected to be in the form of a condensed deposit, presumably as polymeric material.

EXPERIMENTAL

The experimental apparatus has been described previously [1] and consists of a planar diode glow discharge system in which species from the discharge can be extracted through a sampling orifice into a differentially pumped low-pressure region containing an electrostatic energy analyzer and a quadrupole mass filter. Both ionic and neutral species can be extracted from the discharge, but in this study only neutral species are considered. The discharge is established by applying a dc voltage (500 to 3000 V) to a water-cooled Fe target electrode, 20 cm^2 in area with about 85×10^{-3} Torr of Ar in the discharge chamber. The interelectrode spacing is about 3 cm and consequently the volume of the glow discharge itself (~ 0.1 liter) is very much less than the total volume of the discharge chamber (92 liters). However, the concentration of neutral CF_4 , which is injected into the large discharge chamber at partial pressures in the range of 10^{-5} up to 10^{-3} Torr, is dramatically decreased by the initiation of a glow discharge. The extent to which this concentration reduction occurs is dependent upon the residence time of the species in the discharge chamber and in this apparatus, in which both the Ar and CF_4 are flowing through the system continuously, the residence time can be varied from about 29 sec to 40 min at Ar pressures in the range of 85×10^{-3} Torr. This corresponds to Ar flow rates of 0.27 and 3.26×10^{-3} Torr-liter/sec, respectively ($1 \text{ std cm}^3/\text{min} = 1.266 \times 10^{-2}$ Torr-liter/sec).

In this study the CF_4 neutral concentration is monitored by using the electron impact ionization chamber associated with the quadrupole mass filter to ionize a representative fraction of the neutral CF_4 molecules extracted from the discharge volume through the sampling orifice. The CF_3^+ fragment created by the electron impact ionization of CF_4 is used to monitor the CF_4 concentration. It is assumed that CF_3 neutral radicals created in the discharge do not contribute to the observed CF_3^+ signal primarily because the ionization chamber is not on a line-of-sight with the discharge.

RESULTS AND DISCUSSION

An example of a typical measurement is shown in Fig. 1 in which the CF_4 concentration (denoted by P) is plotted as a function of time

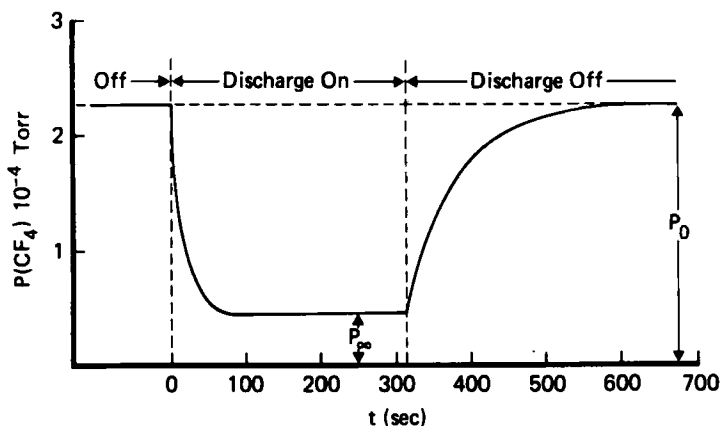


FIG. 1. Transient response of the CF_4 concentration to initiation and termination of a dc argon glow discharge: argon pressure = 87 mTorr; discharge voltage = 1700 V; discharge current = 7.2 mA; $\tau = V/S = 70$ sec (pumping time constant with discharge off).

as the glow discharge is initiated at $t = 0$ and terminated at $t = 310$ sec. The object of this study is to investigate the extent to which relatively straightforward vacuum physics concepts can be used to characterize the behavior of P , the CF_4 concentration. The transient behavior of P will be represented by a modified version of the pumping equation:

$$V \frac{dP}{dt} = Q - SP - \eta(P, I) \quad (1)$$

where

- V = volume of discharge chamber (liters)
- P = CF_4 partial pressure (Torr)
- Q = CF_4 injection rate (Torr-liters/sec)
- S = pumping speed of auxiliary pumping system and sampling orifice for the removal of CF_4 from the discharge chamber (liters/sec)
- I = total externally measured discharge current (mA)
- $\eta(P, I)$ = removal rate of CF_4 caused by the glow discharge (Torr-liters/sec) ($1 \text{ Torr-liter/sec} = 3.54 \times 10^{19}$ molecules/sec)

The analytical form of $P(t)$ following initiation of the discharge ($0 < t < 100$ sec in Fig. 1) is not known in general whereas the form of $P(t)$ following termination of the discharge is the simple exponential solution of Eq. (1) where $\eta(P, I) = 0$. However, there are several ways in which one can evaluate $\eta(P, I)$. A consideration of the steady-state solutions to Eq. (1) indicate that:

$$\eta(P_{\infty}, I) = V \frac{dP}{dt} \Big|_{P=P_{\infty}} \quad (2)$$

$$\eta(P_0, I) = -V \frac{dP}{dt} \Big|_{P=P_0} \quad (3)$$

$$\eta(P_{\infty}, I) = S(P_0 - P_{\infty}) \quad (4)$$

Each of the quantities on the right-hand side of these equations can be measured and therefore each of these three equations represents a way of determining $\eta(P, I)$ experimentally.

It was experimentally most convenient to use the method indicated by Eq. (2) to determine the P dependence (CF_4 concentration) of $\eta(P, I)$, and the results are shown in Fig. 2. These data were determined by measuring the initial slope of the $P(t)$ curve as the discharge was turned off for a range of CF_4 partial pressures. The units of $\eta(P, I)$ in Fig. 2 are molecules of CF_4 removed from the gas phase per electron flowing in the external target electrode circuit. This current represents the sum of the positive ion current incident on

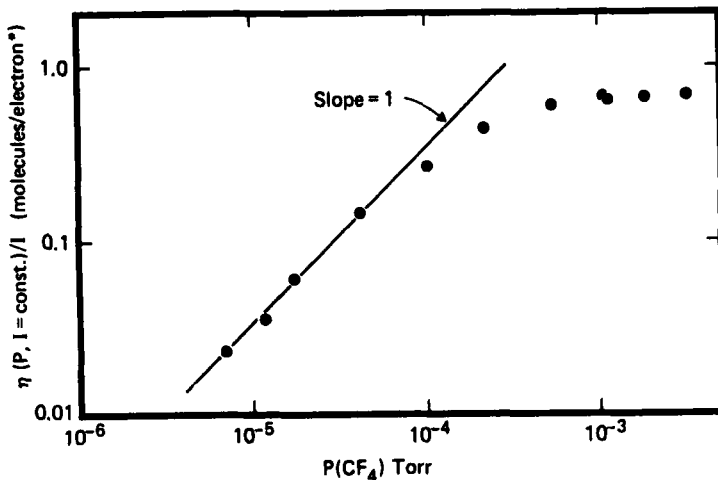


FIG. 2. Dependence of η on the CF_4 concentration: argon pressure = 86 mTorr; discharge voltage ~ 1400 V; discharge current ~ 72 mA; $\gamma = V/S = 42$ sec. *The units for η/I are CF_4 molecules removed per electron measured in the external target electrode circuit. See text for further discussion.

the target electrode plus the secondary electron current leaving the target electrode, and since secondary electron emission coefficients are usually 0.1 or less [2] for incident ion energies involved [3] in this work, it is necessary to multiply $\eta(P, I)$ by about a factor of 10 in Fig. 2 in order to relate approximately the CF_4 removal rate to the current of high-energy electrons (i.e., those formed on the target electrode by Ar^+ ion impact and accelerated into the discharge by the electric field in the cathode dark space) passing through the discharge volume. The shape of the pressure dependence of η shown in Fig. 2 is indicative of the transition region from the low-pressure case ($\eta \propto P$) where the removal rate of CF_4 presumably due to polymerization is limited by the concentration of CF_4 , to the high-pressure case ($\eta \sim \text{const}$) where saturation of the process responsible for the removal of CF_4 from the discharge volume has occurred. One cannot infer from this saturation observation that the addition of higher concentrations of CF_4 will not increase the removal rate or polymerization rate of CF_4 in the discharge because at higher CF_4 concentrations the entire nature of the glow discharge will be influenced by the CF_4 , and gas-phase collisions between CF_4 and dissociation products of CF_4 will probably play an important role in the discharge chemistry.

The experimental problems associated with maintaining a constant value of P for varying discharge currents complicated the determination of the dependence of η on I , the discharge current. Consequently, it was necessary to use the method indicated by Eq. (4) with a constant flow of CF_4 into the system (i.e., $P_0 = \text{const}$). P_∞ was measured as a function of I , and a value of η was determined in each case. However, in this approach both I and P_∞ are varying and it was necessary to use the data of Fig. 2 to remove the dependence of η on P_∞ . The resulting determination of $\eta(P_\infty = \text{const}, I)$ is shown in Fig. 3.

As might be anticipated from the complexity of the glow discharge environment, little can be deduced from this data alone concerning the reaction mechanisms responsible for the removal of CF_4 from the gas phase. The general process almost certainly involves the dissociation of CF_4 and eventual reaction and condensation of the radical fragments at the walls of the vacuum system. Reactions between the radicals themselves in the gas phase or between the radicals and neutral CF_4 molecules are not expected to be important because of the relatively low partial pressures of CF_4 which are used, and in fact no neutral high molecular weight species are observed mass spectrometrically. The approximate linear dependence of η on I (Fig. 3) does not imply that the dissociation of CF_4 is primarily caused by electron impact. In fact, preliminary numerical estimates indicate that the CF_4 removal rate is too large to be accounted for by electron-impact-induced dissociation of the CF_4 by the secondary electrons from the target electrode. Dissociative charge transfer

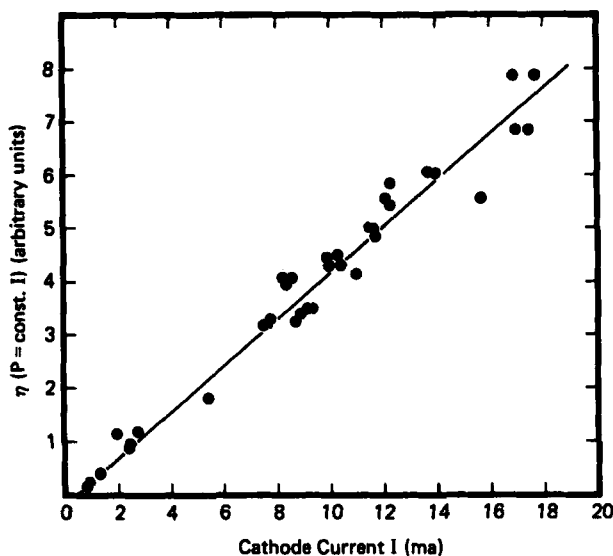


FIG. 3. Dependence of η on the discharge current: argon pressure = 85 mTorr; $\tau = V/S = 42$ sec.

with Ar^+ ions is a possibility as is a resonant collision between a CF_4 molecule and a metastable Ar atom. (The concentration of Ar^+ ions and metastable Ar atoms is comparable to the electron concentration.) If CF_4 chemisorbs on the electrode surfaces, dissociation of such chemisorbed molecules can occur either by Ar^+ ion bombardment of the cathode or electron bombardment of the grounded anode. The vacuum pumping characteristics of CF_4 in the vacuum system suggests that chemisorption is not important but the observation is not conclusive.

A check on the applicability of these concepts which have been used to characterize the behavior of CF_4 in an Ar discharge can be obtained from using the pressure dependence of η as shown in Fig. 2 in Eq. (1) and comparing the result with the observed transient response of P (e.g., Fig. 1, $t < 100$ sec). Reasonable agreement is obtained for low initial concentration of CF_4 (i.e., $P_0 < 10^{-4}$ Torr). When higher values of P_0 are used, the initial region of the transient decay is in reasonable agreement with the expected curve, but after P has decreased about a factor of 10 or so, the agreement becomes very poor in that $\left| \frac{dP}{dt} \right|$ observed experimentally is much less than the $\left| \frac{dP}{dt} \right|$ expected from combining

Eq. (1) and Fig. 2. The reason for this disagreement is not known at the present time. It is hoped that additional measurements combined with studies of the ionic species extracted from the discharge volume will provide further insight as to the dominant processes influencing the removal of CF_4 from the glow discharge volume.

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