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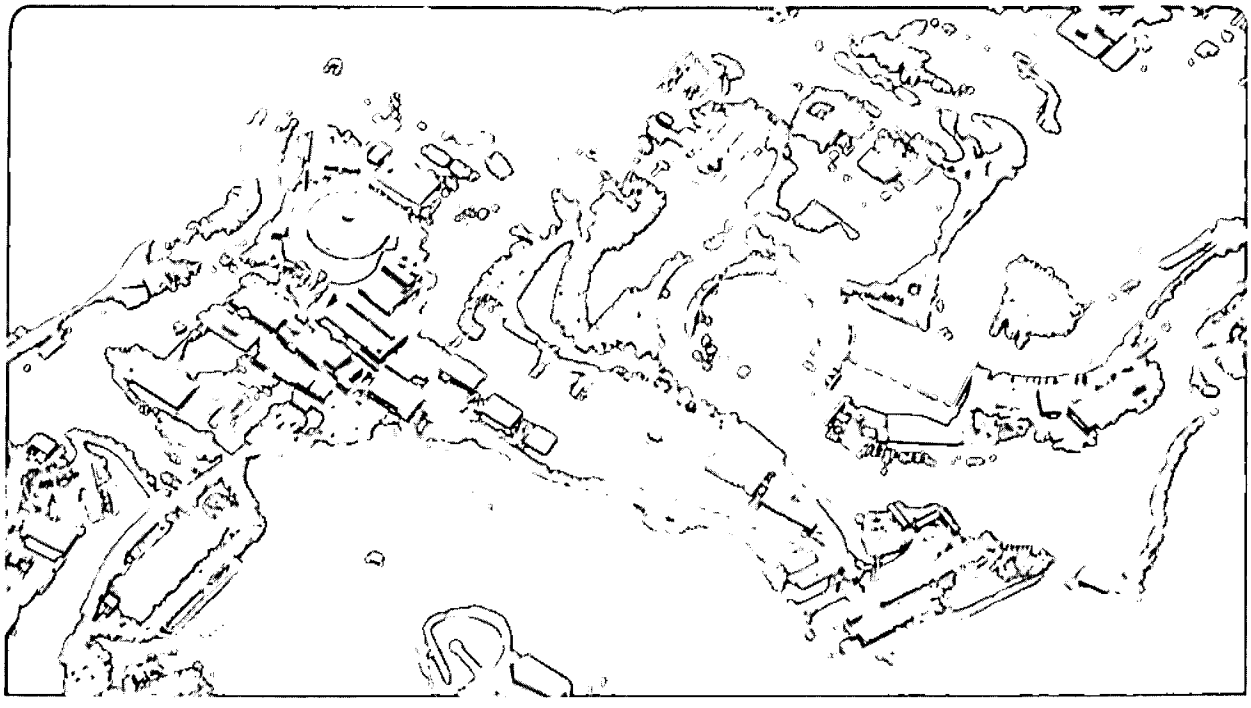

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Abstract

Aging of proportional counters in CF_4/iC_4H_{10} gases is studied as a function of gas composition. Wire deposits are analyzed by Auger electron spectroscopy. An apparent cathode aging process resulting in loss of gain rather than in a self-sustained current is observed in CF_4-rich gases. For tests with such gases, the current drawn is not a reliable measure of the extent of anode aging. Anode wire deposits are formed by the 95/5 and 90/10 mixtures of CF_4/iC_4H_{10}; etching of deposits is observed in the 50/50 and 80/20 mixtures and in pure CF_4. To understand anode aging in CF_4/iC_4H_{10} gases, we develop a four-part model considering: 1) plasma polymerization of the hydrocarbon, 2) etching of wire deposits by CF_4, 3) acceleration of deposition processes in strongly etching environments, and 4) reactivity of the wire surface. Gold-plated wires are resistant to aging resulting from chemical attack by CF_4; non-gold-plated wires are unacceptable for use in CF_4-containing gases. Application of the model to other fluorine-containing gases is discussed. Principles of low-pressure, rf plasma chemistry are used to predict the plasma chemistry in avalanches (≥ 1 atm, dc).

I. Introduction

Wire chambers are commonly used in high-energy physics experiments for particle detection and tracking. During the course of experiments using wire chambers, it is common to encounter problems that limit their useful lifetime. Although wire chambers represent a mature technology, wire aging studies have been largely empirical, and the causes of wire aging are still poorly understood. Wire aging studies have become more chemically oriented in recent years, however, and it has been suggested that plasma chemistry, in particular, may be a useful tool

for understanding the chemical reactions that lead to wire aging [1].

Plasma chemistry finds extensive application in microelectronics processing, which typically makes use of low-pressure (< 1 Torr), rf (13.6 MHz) plasmas. While the plasma characteristics of this regime are expected to differ from those of wire chambers (1 atm, dc), estimates of electron energies and E/p suggest that these parameters may be quite similar [2]. In previous work, we observed that the gaseous products formed in the avalanches in a proportional counter are, qualitatively, those expected if the chemical mechanisms in the avalanche are similar to the mechanisms in low-pressure discharges [3]. Moreover, other studies of atmospheric pressure plasmas have noted similarities to the low pressure regime and have generally concluded that reaction mechanisms in these two pressure regimes are similar [4,5,6]. For these reasons, we will draw on knowledge of the low-pressure, rf plasma regime to interpret results in wire chamber aging.

In plasma processing, CF_4-based gases are used for both etching and deposition processes, the distinction being made by the gas with which the CF_4 is mixed. In general, addition of oxygenated species shifts the chemistry of CF_4 plasmas towards etching while addition of hydrogenated species shifts the chemistry towards polymerization. Because a predominantly etching environment can be created from CF_4, it was reasonable to assume that this gas could be used to make a wire chamber gas more resistant to aging.

There is considerable interest in the use of CF_4-based gases for wire chamber applications in high-radiation environments such as at the SSC because these gases typically have high drift velocities [7,8,9], high primary ionization densities [7], and low electron diffusion [10]. One gas mixture of particular interest, CF_4/iC_4H_{10} (80/20), has been observed to have very good aging properties [11,12,13], and also to etch silicon-based deposits [14,15] and hydrocarbon deposits [15] from gold-plated wires. Although a complete understanding of the chemical mechanisms responsible for this etching is not necessary to use this gas mixture, some understanding is necessary to predict the aging properties of CF_4 with other than 20% iC_4H_{10} or in mixtures with other hydrocarbons. A mechanistic understanding is also necessary to predict the consequences of trace-level contaminants or intentional additives in the gas.

This work confirms the etching of anode deposits on gold-plated wires with CF_4/iC_4H_{10} (80/20) and shows that etching occurs over a range of CF_4/iC_4H_{10} mixtures. Deposition is shown to occur for some CF_4/iC_4H_{10} mixtures and for non-gold anode materials. A chemical model to explain the observed deposition or

etching in these gases is developed and practical guidelines suggested by the model are discussed.

We have previously reported that extensive and rapid anode aging occurs in CF_4 and that aging transients occur for CF_4/iC_4H_{10} mixtures [16,17]. As a consequence of further experimentation, we believe that that interpretation of results reflects an incomplete understanding of the chemical processes and aging mechanisms.

II. Experimental

The parameters varied in this work were primarily gas composition and wire material. Gases used were CF_4 and iC_4H_{10}, encompassing the full range of mixtures from pure CF_4 to pure iC_4H_{10}. Wire materials were most often Au (plated on W), Ni, and Cu. Stablohm (an alloy consisting of 75% Ni, 20% Cr, balance Al and Cu), Al, W, and C wires were used to a lesser extent.

All gases were purchased from Matheson Gas Products (Newark, CA). Unless otherwise noted, gas mixtures were premixed by Matheson and were used as received. Pure CF_4 (semiconductor grade, minimum purity 99.999%) was normally filtered with a model L-60 Nanochem filter (Semi-Gas Systems, San Jose, CA). Au/W wire was purchased from Luma Metall (Kalmar, Sweden). Stablohm, Al, Cu, and Ni wires were purchased from California Fine Wire (Grover City, CA). W wire was purchased from The Rembar Company (Dobbs Ferry, NY).

A. Accelerated Aging Tests

To age wires in a reasonable length of time (typically 1-10 days), accelerated aging tests were performed in which the current densities on the wires were two to three orders of magnitude higher than those encountered in actual wire chamber operation. The apparatus used to collect aging data has been described elsewhere [13,18]. Briefly, proportional counters (0.95 cm ID copper cathode, 50 μm dia anode wire, ~10 sccm gas flow rate) were irradiated with an ^{55}Fe point source (1 mCi, 3 mm dia). The irradiated length of wire was ~3.5 mm. Initial wire currents were typically 400 nA, corresponding to a current density of about 1.1 μA/cm. The current drawn by the wire was monitored by frequent sampling. Changes in the gain can be inferred from changes in the current because the two are linearly related. Barometric pressure and gas temperature were also monitored so that corrections for variations in the gain caused by changes in the gas density could be made. This correction was made according to the following formula:

$$I_n' = I_n/(c_n)^\alpha; \qquad c_n = (P_0T_n)/(P_nT_0), \tag{1}$$

where α is the empirically-determined density dependence of gas gain (typically, $4 < \alpha < 7$). The correction factor, c_n, is calculated assuming ideal gas behavior. For the analysis of each test, the gain (current) was plotted as a function of the total charge transfer, the assumption being that the extent of aging is closely correlated with the charge transferred. Aging rates are parameterized as the normalized rate of loss of gain, R:

$$R = -(1/G_0)(dG/dQ) = -(1/I_0)(dI/dQ), \tag{2}$$

where R has units of %/C/cm.

A fundamental assumption used to justify accelerated aging tests is that the aging rate is independent of the radiation dose rate. The validity of this assumption was not addressed in this work, but since the dose rates used in the accelerated tests are so much higher than those occurring in a wire chamber in normal operation, caution is warranted when attempting to draw parallels between the two operating regimes. In the case of CF_4/iC_4H_{10} (80/20), however, there is some evidence to suggest that aging properties are independent of dose rate [12].

B. Pulse Height

Aging was also characterized using the ^{55}Fe pulse height and energy resolution. Because the ^{55}Fe pulse height spectrum does not exhibit a narrow peak in CF_4/iC_4H_{10} gases [19], the counter gas was alternated between CF_4-based test gases, for the aging segments, and Ar/C_2H_6 (50/50), for the pulse height measurements. The ^{55}Fe spectrum in Ar/C_2H_6 has characteristic peaks that are useful for monitoring gain and gain uniformity and also a well-characterized degradation pattern resulting from aging [20].

To collect pulse height (PH) data, the counter gas was changed to Ar/C_2H_6 (50/50), the 1 mCi, 3-mm-dia ^{55}Fe point source used for aging was replaced with a 500 μCi ^{55}Fe line source (collimated width ~1 mm), and the anode potential was set to 2080 V. The collimated ^{55}Fe source was oriented perpendicularly to the wire axis so that pulse height spectra could be collected at distinct positions along the wire. The acquisition time for each spectrum was 5 min; the current during acquisition was usually ~0.35 nA.

C. Analysis of Deposits

Surface analysis of wires was performed with scanning electron microscopy (SEM) and Auger electron spectroscopy (AES). SEM photographs shown in this work were taken with a beam voltage of 10 kV and are at 1400x magnification. AES analysis provides definitive identification of elements on a surface to a depth of ~1 nm. AES was combined with argon ion beam sputtering of the surface to obtain a composition-depth profile [21]. It should be noted that no simple relationship between sputter time and depth exists due to the composition dependence of the sputtering rate. Because AES is insensitive to elements with $Z < 3$, it cannot be used to detect hydrogen. Therefore, hydrocarbons could not be distinguished from purely carbonaceous deposits by this technique.

III. Aging in CF_4

A simple model to explain the aging properties of CF_4/iC_4H_{10} (80/20) relates these properties to the presence of CF_4 in the gas. Because CF_4/iC_4H_{10} (80/20) did not age appreciably, we believed that a steady-state etching/deposition balance occurred, possibly resulting in a thin fluorohydrocarbon film on the wire surface. We further expected that because CF_4 is the parent for the reactive species responsible for the etching processes, the resistance to aging and the ability to etch anode deposits would correlate directly to the CF_4 content of the gas. It was therefore surprising to discover that pure CF_4 and CF_4-rich gases appeared to age rapidly.

Aging tests with CF_4 typically resemble the curves shown in Fig. 1, exhibiting a nonlinear transient behavior. To determine whether the transient was real or was an artifact, possibly related to the startup procedure of the aging tests, the transient was interrupted. If the transient was an artifact, it might occur again when the test was restarted. Aging tests were interrupted first by turning off the anode voltage and then by stopping the gas flow and opening the counter to air. In one test, the anode and cathode potentials were reversed to ensure complete dissipation of any accumulated charge. The ^{55}Fe source was not removed from the counter at any time during these interruptions. In all tests, the current returned to virtually the same value ($\pm 1\%$) that it had prior to the interruption, indicating that the decrease in current is real, the result of some aging process. These results are summarized in Table I.

To provide a meaningful basis for comparison of different aging curves, we use the functional form

$$I = A + B\exp(-Q^{1/2}/D) \quad (3)$$

to analyze the transients. The exponential dependence was chosen because it is the expected form for changes in gain [22]; the square-root within the exponential was chosen empirically, because of the good fits of the data to this functional dependence. We parameterize the aging transients with a gain change (I/I_0 = $I_{asymptote}/I_{initial}$ = $A/A+B$) and a decay constant, D. A chi-squared fit was performed over the interval 0-10 mC.

Fig. 2 shows decay constants and gain changes for several anode wire materials aged in CF_4. There is surprisingly little variation in these parameters considering the variety of different materials ($D = 1.27 \pm 0.45$ mC$^{1/2}$, $I/I_0 = 0.60 \pm 0.13$ for Au/W wires only; $D = 1.14 \pm 0.38$ mC$^{1/2}$, $I/I_0 = 0.57 \pm 0.16$ for all other wires). The approximate independence of the decay constant to anode material suggests that the initial aging in CF_4 may be due to a deposition on the wire rather than to a reaction with it. If so, fluorocarbon deposits would be expected on all wires but, as discussed in sections III.A and III.B, such deposits were not observed. Purifying the CF_4 had little effect on the transient for Au/W wires ($D = 1.22 \pm 0.46$ mC$^{1/2}$, $I/I_0 = 0.58 \pm 0.15$ without filter; $D = 1.31 \pm 0.47$ mC$^{1/2}$, $I/I_0 = 0.62 \pm 0.12$ with Nanochem filter), indicating that the CF_4, and not a trace component, is responsible for the aging. No clear dependence was observed for D or for I/I_0 with respect to gas flow rate over the range 1-15 sccm.

In an attempt to modify or eliminate the aging transient, anode wires were pretreated to create a film similar to that believed to form during aging. It was expected that by forming the film in advance, steady-state wire operation might be approached more quickly and the magnitude and possibly the duration of the transient reduced. Wires were pretreated in a barrel reactor [23] with a 13.56 MHz plasma of either 1) CHF_3 (200 W, 350 mTorr, exposure times of 30, 60, or 120 sec) to deposit a fluorocarbon film, or 2) SF_6/O_2 (96/4) (30 W, 200 mTorr, exposure times of 60 or 180 sec) to fluorinate the wire surface. Film thicknesses deposited by the CHF_3 plasma were measured by ellipsometry [24] (model L116A, Gaertner Scientific, Chicago, IL) on a silicon wafer used as a control, and were in the range 16-50 nm. AES revealed that the surface of Ni wires treated in the SF_6/O_2 plasma was fluorinated to a thickness comparable to that resulting from aging in CF_4 with total collected charge of 100 mC/cm but that the surface of Cu wires so treated was oxidized rather than fluorinated.

As shown in Fig. 2, neither pretreatment process resulted in a significant

change in the transient, although the decay constants for one set of wires treated in the CHF_3 plasma are marginally larger than those for untreated wires. The lack of effect resulting from pretreatment suggests that the rapid decrease in the current may not reflect anode aging.

A. Au/W Wires

Pulse height, energy resolution, and current for aging of an Au/W wire in CF_4 are shown in Fig. 3 (the procedures used to collect these data are described in section II.B). There is a slight increase in the pulse height with collected charge, while the energy resolution is essentially unchanged. This is surprising in view of the large decrease in current, which is essentially the pulse height integrated over the irradiated region of the wire. The lack of degradation of the pulse height suggests that very little degradation of the wire surface occurs or possibly that degradation of the wire surface occurs but disappears before the pulse height measurement is made. However, potential mechanisms for the disappearance of wire deposits, such as reaction with the ambient gas or evaporation, do not seem plausible for fluorocarbons. It is thus likely that no degradation of the wire surface occurred.

An unexpected occurrence in this measurement was that the post-interruption currents were typically 5-10% higher than their corresponding pre-interruption values (Fig. 3a). This behavior is very different than that observed when the aging tests were interrupted but pulse height measurements were not taken, in which case the pre- and post-interruption currents were virtually identical (Table I). This difference may be due to a modification of the anode surface resulting from exposure to the Ar/C_2H_6. The magnitude of the overshoot does not appear correlated to the amount of charge collected during this exposure, however: after 50 min at 400 nA in Ar/C_2H_6, the overshoot was still only about 10%. It is possible that the overshoot results from slight changes in the position of the ^{55}Fe source used to age the wire. That is, changes in the position of the source relative to the counter may increase the radiation flux to less-aged (higher-gain) areas while reducing the flux to more-aged (lower-gain) areas, so that the overall current on the wire increases.

A typical AES spectrum of an Au/W wire aged in CF_4 is shown in Fig. 4a. In addition to Au, only trace amounts of C and O are present. Such traces of C, and frequently O, are normally observed on surfaces exposed to air. Depth profiles (Fig. 4b) reveal no deposits in excess of the atmospheric carbon contamination. The appearance of these aged wires is indistinguishable from that of new wires (Fig. 5).

The lack of detectable deposits is consistent with the lack of degradation of pulse height or of energy resolution and with a previous study that had reported little aging in CF_4 [25].

Although suggested by the rapid decrease in the current, fluorocarbon deposition was not observed on wires aged by our standard procedure (i.e., with an irradiated region of ~3.5 mm). Fluorocarbon deposits were observed, however, on an Au/W wire aged in CF_4 that had been irradiated (using a 10 mCi, 6-cm ^{55}Fe line source) over a ~3 cm region with a current density of 0.36 μA/cm. No deposition was observed in a similar test in which the current density was reduced to 0.02 μA/cm. One possible explanation is that a combination of high current density and long residence time in the irradiated region may promote polymerization and adsorption of CF_x radicals.

B. Non-gold Wires

Pulse height, energy resolution, and current for aging of a Cu wire in CF_4 are shown in Fig. 6. Degradation is clearly evident for the Cu wire but, like the Au/W wire, there is still a discrepancy between the various measures of aging, with current dropping much faster than either pulse height or energy resolution. Because the energy resolution is a measure of the uniformity rather than the thickness of the deposits, its degradation pattern will not necessarily be correlated with those of the current or pulse height. The slightly more rapid degradation of both pulse height and energy resolution downstream relative to upstream of the center of irradiation suggests that convection of etching and/or polymerizing species is of some significance under the conditions used in these aging tests. Such convective effects are probably less important in real wire chambers where, unlike the aging tests, the plasma is neither spatially localized nor temporally continuous.

Non-gold wires that we have tested react to form a metal fluoride on the surface when aged in CF_4. Fig. 7a shows a typical AES depth profile of a Cu wire aged in CF_4. It is clear from the correlation between fluorine and the metal and the absence of carbon that a metal fluoride is present. Similar metal fluorides are observed on Al (Fig. 7b), Ni, and Stablohm wires. The morphology of the metal fluorides is smooth, resembling that of unused wires (Fig. 8). Growth of the copper fluoride is discussed further in section VI. The fluorination of non-gold wires by CF_4 provides an additional aging mechanism relative to gold wires, which may explain some of the variation observed in the aging transient for different wire materials (Fig. 2).

Small amounts of carbonaceous material were occasionally observed on top of the metal fluorides (e.g., Fig. 7a), although lack of carbon was more common (Fig. 7b). Bulk deposits clearly identifiable as fluorocarbons were observed only once on non-gold wires (Table II).

C. Cathode Effects

The lack of degradation of the pulse height spectra and the lack of deposits suggest that Au/W anode wires do not age in CF_4. If so, the observed decrease in anode current could not be due to anode aging and might therefore be due to cathode aging. Cathode aging would also explain the relative independence of the decay constant for CF_4 to anode material (Fig. 2) because copper cathodes were used for all of those tests. In addition, if the observed CF_4 aging is a cathode phenomenon, the beneficial effect of the iC_4H_{10} could be understood by its likely role of scavenging fluorine radicals or charge-exchanging with fluorocarbon ions *en route* to the cathode.

One means of investigating possible cathode aging was to separate anode and cathode effects by combining new and aged portions of counter tubes [26]. In the present case, cathode shells of counter tubes that had been aged in CF_4 were restrung with new anode wires. One such test resulted in a self-sustained breakdown, indicating the presence of cathode deposits. In a second test (Fig. 9), replacement of the anode wire did not restore the current to its initial value. The first aging segment shows the expected aging transient in CF_4. After an interval of 55 days the anode wire was replaced and the test was continued, with a recovery of the current from 43% to 70% of its initial value (point A). This recovery may be due to the length of time during which the tube was idle or to failure to replace the ^{55}Fe source in its original position. At the end of the second aging segment the anode wire was again replaced (point B). The time interval was reduced to 2.15 hr and great care was taken to ensure that the ^{55}Fe source was replaced in its previous position. The wire current was within ~5% of its previous value. This test was repeated in a different counter tube; the time interval for replacement of the anode wire was 1.3 hr, and the before and after values of the wire current agreed to within ~9%. These results indicate that some aging occurs, but not on the anode. Cathode aging is implied, but is not shown directly.

Possible effects of cathode material on aging in CF_4 were investigated using rectangular aluminum counter tubes with windows 1 cm dia. The design of these counters has been described previously [27]. Three cathode materials (Al, Au, and

Ni) were used; the latter two materials were plated onto the tube and the window foil. The aging transients were unchanged by using Au and Ni instead of Cu cathodes. In approximately half of the tests using Al cathodes, however, the magnitude of the transient was greatly reduced (Table III).

Trace amounts of fluorine, most probably in the form of a fluorocarbon, were observed on the cathode window foils from these tests. There was no indication of metal fluorides, nor was there any significant spatial variation in the composition of surface deposits. SEM imaging revealed no distinct deposits; from AES depth profiling the deposit thickness was estimated at ~10 nm.

A cathode aging phenomenon might be understood if charge accumulation on an insulating cathode layer accounts for the decrease in current observed in CF_4. The (insulating) native aluminum oxide may be of sufficient quality that a steady-state level of charge accumulation is achieved quickly, during startup of an aging test with the result that no transient is observed. For conducting cathode materials, charge accumulation cannot occur until a suitable (fluorocarbon) film is formed. Because formation of such a film results from reactions in the avalanche, film growth and the consequent charge accumulation are observable as a function of time after an aging test is started.

Deposition of a film on the cathode is not generally considered as a phenomenon that results in loss of gain. Rather, cathode films are expected to result in field emission and a self-sustained (Malter) breakdown [28]. However, if an insulating film on the cathode was sufficiently thick that the field emission threshold was not exceeded, the voltage drop at the cathode would reduce the effective anode potential and, hence, the gain. A voltage drop of about 100 V is needed to cause the ~50% reduction in gain typically observed for aging in CF_4. To remain below the threshold for field emission, measured to be $\sim 1.8 \times 10^5$ V/cm in the counters used for these tests, a cathode film therefore needs to be $\geq 5.6\,\mu$m thick. An upper limit on the mass of material available for reaction can be made by relating the energy dissipated by the avalanches in the time over which the rapid aging in CF_4 occurs and the dissociation energy of the C-F bond. This corresponds to about 7×10^{-4} g of material which, if evenly distributed on a cathode area of 1 cm^2, would form a layer about $7\,\mu$m thick. While this estimate suggests that cathode aging without self-sustained breakdowns may be a possibility, the cathode deposits observed were only ~10 nm, far thinner than that calculated to prevent field emission. We have been unable to explain the mechanism of cathode aging in CF_4.

D. Etching in CF_4

In view of the considerable evidence that Au/W anode wires do not age in CF_4, it was reasonable to ask whether CF_4 would etch deposits. Recovery in CF_4 was attempted with wires aged in CF_4/iC_4H_{10} (95/5) (see section IV), and was observed in the current, the pulse height, and the energy resolution. Recovery rates were rapid (typically >1000 %/C/cm), and full gain was restored after only 0.01 C/cm of charge. The extraordinary rapidity of this recovery is an indication of the efficacy of the etching reactions in CF_4.

Evidence of etching in CF_4 is also shown in Fig. 3 (a slight increase in the pulse height) and in the third segment of Fig. 9 (a slight increase in the current). These results may be due to removal of native contamination from the (new) wires used in these tests.

Deposits on Au/W wires that had been damaged by exposure to Ar/C_2H_6 (50/50) bubbled through silicone oil [13] were etched by CF_4/iC_4H_{10} (80/20) but not by dimethyl ether or by Ar/C_2H_6 (50/50), indicating that the recovery is due to a (chemical) etching process requiring fluorine and not to a (mechanical) ablation process. Due to the low energies of negative ions in an avalanche, ablation was not expected. Bubbling CF_4 through the silicone oil caused a change in the aging transient ($D \sim 6\ mC^{1/2}$; $I/I_0 \sim 0.85$) (compare to Fig. 2); AES revealed only atmospheric contamination on wires aged in this way.

IV. Deposition and Etching in CF_4/iC_4H_{10} Mixtures

As a means of understanding the chemistry that leads to etching in CF_4/iC_4H_{10} (80/20), it was useful to study the aging properties of a wide range of gas mixtures. This was also a useful step in the development of a general model for aging in CF_4/iC_4H_{10} gases.

CF_4/iC_4H_{10} (95/5): Heavy carbonaceous deposits are formed on Au/W wires aged in this gas mixture (Fig. 10a). Some variation in thickness with azimuthal position around the wire is evident. The AES spectrum is dominated by an intense C peak (Fig. 11); the thickness of the deposit masks the underlying metal. It is notable that the deposits are carbonaceous: the absence of fluorine indicates that they are formed primarily from the iC_4H_{10} and not from the CF_4. Depth profiling revealed a uniform composition throughout the deposit.

Heavy, rough deposits are also formed on non-gold wires aged in CF_4/iC_4H_{10} (95/5); these deposits typically have distinct morphology (Fig. 12a). Depth profiling revealed a stratified deposit structure, with a carbonaceous layer on

top and a metal fluoride underneath (Fig. 13). The carbonaceous layer shown in this figure (~1 min of sputter time) is considerably thicker than atmospheric contamination (typically 0.1 min of sputter time), but is much thinner than the visibly heavy deposits (e.g., Figs. 10a,b), which have thicknesses in excess of 10 min of sputter time.

CF_4/iC_4H_{10} (90/10): The deposits formed on Au/W wires by the 90/10 mixture are similar, both visually and chemically, to those formed by the 95/5 mixture, although they are not as thick or as extensive. There is also a sharper division in the azimuthal distribution of the deposits, with both coated and uncoated regions distinctly visible (Fig. 10b). Aging of non-gold wires was not investigated in this gas mixture.

CF_4/iC_4H_{10} (80/20): The appearance of Au/W wires tested in the 80/20 mixture (Fig. 10c) is indistinguishable from that of new wires (Fig. 5a). AES analysis revealed only trace deposits (atmospheric contamination) on these wires, consistent with a previous analysis of wires whose deposits were etched in this gas mixture [15] and with the lack of aging observed in our aging tests.

Non-gold wires aged in this gas mixture have heavy deposits (Fig. 12b). These deposits also have a layered structure with carbonaceous material on top of a metal fluoride. In one case, on an aluminum wire, the deposits were predominantly fluorocarbon.

CF_4/iC_4H_{10} (50/50): Au/W wires aged in this gas mixture have only trace carbonaceous deposits, similar to those observed on wires aged in the 80/20 mixture. The aging rate measured for Au/W wires in the 50/50 mixture was 0 ± 1 %/C/cm with total collected charge of 0.4 C/cm. The lack of apparent aging and of deposits suggested that this gas mixture might etch anode deposits. Indeed, recovery of a wire aged in CF_4/iC_4H_{10} (95/5) was at a rate of about 300 %/C/cm. Both current and pulse height recovered to within 4% of their initial values after 0.17 C/cm of collected charge. Only trace deposits were observed on a recovered wire.

Non-gold wires aged in the 50/50 mixture have heavy deposits that are similar both chemically and visually to those observed on non-gold wires aged in other CF_4/iC_4H_{10} mixtures.

CF_4/iC_4H_{10} (15/85) (mixed from two independently regulated flow streams): Recovery was attempted in this gas, but was largely unsuccessful. After an initial increase in the current of about 20%, the current began dropping at a rate approaching 2000 %/C/cm. This behavior is very different than that observed in the

recovery tests described above, in which the current increased and then remained constant. There was an increase of 10-15% in the pulse height, but the energy resolution was essentially unchanged from its severely degraded initial condition, suggesting that little or no recovery had occurred. The tendency of CF_4/iC_4H_{10} (15/85) to age is consistent with aging rates of 30-250 %/C/cm observed in CF_4/iC_4H_{10} (20/80).

iC_4H_{10}: We observed aging rates in this gas in the range 0-60 %/C/cm. Aging rates of about zero indicate that little deposition occurs on the anode, consistent with previous reports of aging in iC_4H_{10} [29]. A recovery attempt with iC_4H_{10} resulted in rapid aging observed in both current and pulse height. In this case it is possible that deposition was enhanced by the presence of deposits on the wire.

Aging and recovery rates for CF_4/iC_4H_{10} gas mixtures are shown in Fig. 14. Recovery results are listed in detail in Table IV. The data clearly show a region of aging between 0% and $\gtrsim$20% CF_4, a region of etching between $\lesssim$50% and $\gtrsim$80% CF_4, a region of aging between $\gtrsim$80% and $\lesssim$100% CF_4, and a small region of etching in the vicinity of 100% CF_4. Because aging transients similar to those shown in Fig. 1 occur in CF_4-rich gases, aging rates determined from the current in these gases were calculated for the asymptotic region of the curve. The signs and relative magnitudes of the aging rates are of more relevance than their absolute magnitudes. The magnitudes of recovery rates, in particular, should not be viewed as definitive because etching rates are expected to depend on the composition of the deposits being etched.

V. Chemistry of Wire Aging

The rf glow discharges (plasmas) used in plasma processing are partially ionized gases containing ions, electrons, and neutral species in both ground and excited states. The degree of ionization is small, typically about 10^{-5} of all species, but the degree of dissociation can be quite large, sometimes exceeding 10^{-1} of all species. Due to their higher concentration, the neutrals (radicals) are the primary chemical species responsible for deposition and etching processes.

Due to the difference in mobility between ions and electrons, all surfaces in contact with an rf plasma generally assume a negative potential with respect to the plasma. As a result, positive ions are accelerated into surfaces, and can have a synergistic effect on etching chemistries [30]. This process is distinctly different in an atmospheric-pressure wire chamber, where moderate energy electrons (5-10 eV)

and low energy negative ions (<1 eV) bombard the anode and near-thermal positive ions strike the cathode.

Energetic particles of a few eV can break chemical bonds in a surface, thereby creating adsorptive or reactive sites that may enhance reaction rates. Ions with energies $\gtrsim$30 eV may cause ablation (mechanical removal of material) as a result of momentum transfer. Energetic electrons are capable of breaking chemical bonds, but due to their low mass, electron bombardment does not lead to ablation.

The chemistry in a plasma is very complex, involving a large number of reactions between many types of species and occurring both in the gas phase and at the gas/surface interface. The chemistry is further complicated by the sometimes sensitive dependence of plasmas to such variables as pressure, electrode temperature, power density, gas flow rate, gas composition, including presence of ppm- or ppb-level impurities, and reactor geometry. It was beyond the scope of this work to investigate the effects of all of these parameters. For application to wire chambers, however, knowledge of the dependence on many of these parameters is not critical because most parameters are held constant in normal operation.

A. Chemical Model for Aging in CF_4/iC_4H_{10} Gases

One model for fluorine- and carbon-containing etch gases used in plasma processing is the F/C Ratio model [31]. Rather than attempting to describe in detail the chemistry of the discharge, this model views the plasma as a ratio of fluorine species to carbon species. That is, the F/C ratio is used as a qualitative parameter to account for the fact that etching and polymerization occur simultaneously in plasmas containing both fluorine and carbon. Anode aging in CF_4/hydrocarbon gases can be understood in terms of a four-part model based, in part, on the F/C ratio. Because of the difficulty in accurately modeling the multitude of chemical reactions in an avalanche, the advantage of using this sort of qualitative model is obvious.

1. Polymerization.

Plasma polymerization refers to the formation and deposition of polymeric material under the influence of a plasma. Plasma polymerization is believed to occur via a free-radical mechanism, which consists of three basic types of reactions: 1) Initiation, in which reactive species (radicals) are formed by dissociation, 2) Propagation, in which monomers are added to a growing polymer chain, and 3) Termination, in which two radicals combine, thereby destroying the reactivity of

both. Propagation reactions in plasma polymerization are believed to proceed primarily with unsaturated monomers, and there is a strong positive correlation between deposition rate and the degree of unsaturation of the monomer [32]. Deposition occurs when the polymer chain becomes sufficiently large to be involatile. There is an extensive literature on this subject [33], and plasma polymerization has been discussed as a model for wire aging processes [1,2,14].

With regard to small alkanes, one study of plasma polymerization has shown that polymerization rates are in the order $CH_4 > C_2H_6 > C_3H_8$ [32], from which it may reasonably be concluded that iC_4H_{10} polymerizes less-readily still.

2. Etching.

Etching refers to a chemical process in which gas-phase species react with a substrate to form volatile products. Etching chemistry is extremely complex. Qualitatively, CF_4 dissociates to form highly reactive F and CF_x radicals at the same time that electrons are released by the avalanche. These electrons have sufficient energy (5-10 eV) to break the chemical bonds (typically 4-5 eV) in a polymeric wire deposit. Upon recombination, some fluorine may be incorporated into the polymer matrix. Under repeated avalanches, the polymer can be reduced to stable, volatile products (e.g., CF_4, CHF_3, C_2F_6), which are removed from the wire.

Fluorocarbon deposition in CF_4 plasmas is also known [34,35] but, as discussed in sections III.A and III.B, such deposition was rarely observed in this work. The distinction as to whether etching or deposition will occur in CF_4 depends on the plasma characteristics. In wire chambers, it appears that etching is the favored process.

3. Scavenging-induced deposition.

Due to the large bond energy of HF (5.9 eV), fluorine radicals in a plasma react readily with hydrogen in a process known as radical scavenging. HF is a stable molecule and it does not contribute to etching. Thus, addition of hydrogen to a fluorine-containing plasma reduces the effective concentration of fluorine radicals available for etching.

Radical scavenging can also occur with the hydrogen in hydrocarbons. But in this case, production of HF is accompanied by production of carbon-enriched residues by reactions of the general form

$$m\,F + C_nH_{2n+2} \rightarrow m\,HF + C_nH_{2n+2-m}. \qquad (4)$$

Due to their high degree of unsaturation, the carbon-enriched residues will have a high tendency to polymerize and will be comparatively involatile. The greater the carbon-enrichment, the greater the likelihood that the residues will deposit onto a wire. The degree of carbon enrichment is related to the likelihood that hydrogen is scavenged (i.e., is related to the CF_4/hydrocarbon, or F/H, ratio). The combined effects of reduced etching (reduced fluorine radical concentration) and increased deposition may lead to serious aging in gases with a high CF_4/hydrocarbon ratio (i.e., in gases with low hydrocarbon content).

Note that scavenging-induced deposition (reactions of the form (4)) is expected to occur primarily *outside* of the avalanche volume (plasma), and is thus distinctly different than plasma polymerization. Although molecules in the avalanche volume are likely to undergo nearly complete fragmentation, the relatively long-lived fluorine radicals may migrate and react with unfragmented hydrocarbon molecules. Thus, the molecular size of a carbon-enriched residue may be correlated to the size of its parent hydrocarbon. It is therefore reasonable to expect that the likelihood that a residue will deposit onto a wire may be directly related to the size (molecular weight) of its parent. For example, a C_4 residue produced from isobutane may be less volatile and thus more likely to deposit onto a wire than a C_1 residue produced from methane. (In addition to being less volatile, larger alkanes are also more carbon-enriched than smaller alkanes.) Similarly, deposition may be influenced by the chemical nature of the hydrocarbon (e.g., unsaturation or the presence of heteroatoms).

4. Wire surface reactivity.

Many metals commonly used in wire-chamber wires react with fluorine-containing plasmas, some (Al, Cu, Ni) to form nonvolatile fluorides; others (Cr, W) to form volatile fluorides. Clear evidence of reaction of such wires with CF_4 avalanches was presented in section III.B of this work. No evidence of such reaction was observed for Au/W wires. For practical purposes, Au is considered inert to CF_4-based plasmas, although formation of a gold fluoride in such plasmas has been reported [36,37].

By combining the first three parts of this model, the qualitative dependence of aging on gas composition can be determined. The plasma polymerization rate of iC_4H_{10} is expected to increase with the iC_4H_{10} content of the gas, in the hypothetical case that the diluent gas, CF_4 in this case, is totally inert. Similarly, the

etching rate by CF_4 is expected to increase with the CF_4 content of the gas, again hypothesizing that the diluent gas, iC_4H_{10} in this case, is totally inert. Although these two dependences are probably nonlinear, their limiting behavior may be considered to be linear and they are shown as linear in Fig. 15. Scavenging-induced deposition is proportional to the CF_4/iC_4H_{10} ratio. Although this ratio becomes infinite as the iC_4H_{10} content approaches zero, it is clear that the hydrocarbon-related deposition must vanish in the limit of no hydrocarbon. Scavenging-induced deposition must therefore reach a maximum at some CF_4 concentration below 100%; it is shown in Fig. 15 as reaching a maximum at about 95% CF_4. The general trend of the data for aging behavior as a function of gas composition (Fig. 14) can be well explained by the sum of these three effects, shown in Fig. 15 as the dashed line. This model explains the divisions between deposition and etching regimes, and shows that a window in which etching will occur is expected for mid-range CF_4 concentrations.

Note that the relative magnitudes of the polymerization, etching, and scavenging-induced deposition effects shown in Fig. 15 are not intended to illustrate the chemistry of any particular CF_4/hydrocarbon mixture, but rather to provide a clear visual indication of the relation between the three effects. Note also that this model is only intended to explain why aging or recovery occurs in a particular gas mixture; it is not intended to predict magnitudes of aging or recovery rates. Finally, note that this model does not include all possible chemical effects and interactions. Not included, for example, is the catalysis of plasma polymerization by halogens [38]. This effect is expected to be small, however, since conventional plasma polymerization is only slightly accelerated by CF_4.

Extensive deposition was observed on non-gold wires aged in CF_4/iC_4H_{10} gas mixtures in cases when similar deposition was not observed on gold-plated wires. This difference indicates that the wire material influences the etching and deposition mechanisms. One possible means of interaction is a loading effect, resulting from the additional reaction pathway provided by fluorination of the wire material, which reduces the effective fluorine radical concentration for all CF_4/iC_4H_{10} mixtures. With the relative strength of etching reduced, there is a greater tendency to deposit at all CF_4 concentrations. It seems unlikely, however, that a significant fraction of the gas-phase fluorine radicals would be removed by reaction with the wire. Another possibility is that there is enhanced adhesion between gas-phase carbonaceous species and metal fluorides relative to gold.

B. Other CF_4-Based Gases

In analogy to CF_4/iC_4H_{10} (95/5), CF_4/C_2H_4 (95/5) (mixed from two independently regulated flow streams) was observed to form heavy carbonaceous anode deposits. Although C_2H_4 is a smaller molecule than iC_4H_{10}, it is more carbon-enriched and is unsaturated. In addition, the F/H ratio is larger in the CF_4/C_2H_4 mixture (19.6) than in the CF_4/iC_4H_{10} mixture (7.6), suggesting that more scavenging-induced deposition will occur in the former.

Previous results showing that CF_4/dimethyl ether (95/5) exhibits very little aging [39] indicate that the extent of scavenging-induced deposition is related to the chemical nature and possibly to the size of the hydrocarbon molecule. Dimethyl ether is expected to undergo relatively little scavenging-induced deposition because of its oxygen content: oxygen is expected to combine with carbon to form CO or CO_2, both of which are volatile.

We have previously reported that rapid aging (R~120,000 %/C/cm) occurs in $Ar/CF_4/O_2$ (50/40/10) [40]. This was an unexpected result because this gas mixture was expected to be strongly etching and therefore unlikely to cause deposition on anode wires. It is likely, however, that the rapid aging is only apparent, a result of the same phenomenon observed in pure CF_4. Indeed, the $Ar/CF_4/O_2$ was observed to etch anode deposits created by CF_4/iC_4H_{10} (95/5) (Table V). SEM analysis showed that an Au/W anode wire aged only in the $Ar/CF_4/O_2$ was visually clean, but AES revealed that C and O (probably atmospheric contamination) and F were present on the wire surface. It should be noted that gold fluorides can be formed in CF_4/O_2 plasmas [37], and that such fluorination, if it results from exposure to $Ar/CF_4/O_2$ avalanches, could cause some anode aging in addition to any possible cathode phenomena that may occur.

As a diagnostic probe of the etching chemistry, it was of interest to determine whether recovery of aged wires would occur in fluorine-containing gases other than CF_4. Two such gases tested were CHF_3 and CHF_3/CH_4 (82/18). These gases were chosen without regard to their potential utility in wire chambers. Recovery beginning with a rapid decrease in the current followed by an increase in the current was observed in both of these gases (Table V). The fact that etching was observed in these gases indicates that atomic composition rather than specific molecular configurations govern the chemistry. This is generally true for plasma etching and serves as the basis for the F/C Ratio model.

For the conditions used in the silicon etching studies of ref. [31], it was observed that etching generally occurs for F/C > 2. It is possible that similar

general guidelines may be established to predict the deposition or etching behavior of prospective wire chamber gas mixtures. Table VI lists several atomic ratios of gases investigated in this work that either deposit or etch. For these gases, scavenging-induced deposition dominates for F/H > 3 and no threshold for etching is observed in the range 0.8 < F/C < 4.0. Using F/C as an indication of etching and F/H as an indication of scavenging-induced deposition, C/H is an indication of the deposition/etching ratio. For the gases studied, deposition occurs for C/H > 1; etching for C/H < 1. Without more data for CF_4 in mixtures with hydrocarbons other than iC_4H_{10}, however, the general validity of these guidelines cannot be ascertained. In addition, the C/H ratio must be used cautiously because it does not explicitly account for fluorine.

C. Other Models for Aging in CF_4/iC_4H_{10}

It has been suggested that the relatively large dissociation energy of the C-F bond (5.2 eV) may make it less prone to dissociate in an avalanche. With less dissociation, fewer radicals would be produced, there would be less polymerization of the radicals, less deposition and, consequently, less aging [2].

It has also been suggested that the beneficial effect of iC_4H_{10} in CF_4/iC_4H_{10} gases is to reduce formation of fluorine radicals by cooling electrons in the avalanche to temperatures below that required for dissociative electron attachment to CF_4 [17]. (The peak for dissociative electron attachment to CF_4 occurs in the 7-8 eV range [41].) With less dissociative attachment, fewer fluorine radicals would be formed, and aging effects resulting from fluorine radicals would be reduced.

But prevention, or even reduction, of fluorine radical formation cannot be the dominant effect in CF_4/iC_4H_{10} gases. Although we have not directly observed fluorine radicals, there is ample evidence to suggest that they play a central role in determining the properties of these gas mixtures. In particular, the removal of anode deposits by some CF_4/iC_4H_{10} mixtures can be explained by an etching process requiring fluorine radicals. This is especially true for removal of silicon-based deposits, which may react with fluorine radicals to form volatile SiF_4. Finally, fluorine radicals are the primary reactive species in the model presented in this work.

D. Practical Guidelines

With a model for the observed aging, we are in a position to discuss some practical aspects of wire chamber operation with CF_4/iC_4H_{10} gases.

Because of possible cathode aging effects, use of pure CF_4 in a wire chamber may be detrimental. In addition, the deposition/etching balance in pure CF_4 is very sensitive to gas composition, with extensive deposition possibly resulting from trace hydrocarbon additives or contaminants. Accordingly, it is safer to operate at a gas composition within the etching window than with pure CF_4.

Non-gold wires react with fluorine radicals produced in an avalanche to form metal fluorides, which may promote further deposition. Such wires are therefore unacceptable for use in CF_4-based gases. Gold wires are essentially inert to fluorine-based plasmas, and can therefore have good aging properties in CF_4-based gases. Use of gold-plated wires does not necessarily ensure good aging properties in CF_4-based gases, however, since deposition may occur on wires of any material. It should be noted that gold can be etched in plasmas of $C_2Cl_2F_4$ [37] or $CClF_3$ [42]. Accordingly, these, and possibly other, chlorofluorocarbons should be avoided in wire chambers.

Two issues of relevance to the choice of wire chamber gases are flammability, for the obvious safety reasons, and minimized hydrogen content, to reduce the background noise from recoil protons in neutron radiation backgrounds. The range of the etching window places a lower limit on the hydrocarbon concentration. Applied to CF_4/iC_4H_{10}, the guidelines proposed in section V.B (that deposition occurs for $F/H > 3$ or for $C/H > 1$) require minimum iC_4H_{10} concentrations of 11.8% or 14.3%, respectively.

We have argued that the extent to which scavenging-induced deposition contributes to aging is directly related to the size of the hydrocarbon molecule. If so, the etching window may extend to lower hydrocarbon concentrations when CF_4 is mixed with hydrocarbons smaller than iC_4H_{10}. It may therefore be possible to make CF_4/CH_4 or CF_4/C_2H_6 mixtures that are nonflammable, have low hydrogen content, and also etch wire deposits.

VI. Metal Fluoride Film Growth on Cu Wires

Growth of metal fluorides on non-gold wires aged in CF_4 (section III.B) may be expected to be diffusion-limited. Indeed, diffusion-limited processes are well-known in plasma processing occurring, for example, in etching of Si in SF_6 plasmas [43] and in growth of SiO_2 on Si in O_2 plasmas [44]. If it is assumed that growth of the metal fluoride film is purely diffusion limited, the film growth rate can be expressed as

$$dz/dt = -D_i\ k_1\ dC_i/dz, \tag{5}$$

where D_i is the solid-state diffusivity of the fluorinating species, C_i is the near-surface gas-phase concentration of the fluorinating species, z is the thickness of the fluoride film, and k_1 is a constant that corrects for stoichiometry and fluoride density. It is permissible to use planar geometry because $z_{max} << r_{anode}$. Making the assumptions that the concentration gradient is linear and that C_i is linearly related to the current,

$$dz/dt = -D_i\ k_1\ C_i/z = -D_i\ k_1\ k_2\ I/z. \tag{6}$$

Using the relation $\int I dt = Q$, eqn. 6 becomes the classical parabolic rate equation with solution

$$z(t) = [k_3 Q + (z_0)^2]^{1/2}. \tag{7}$$

Fig. 16 shows the thickness of the copper fluoride layer (measured by the time required to sputter through it) as a function of the square root of the total charge collected during exposure to the CF_4 plasma. Two distinct regions are evident: a linear region of nonzero slope, indicating diffusion-limited growth, and a region of near-zero slope, in which essentially no further growth occurs. The maximum film thickness, determined directly by SEM observation of the cross section of a bisected wire, was 450±50 nm; for this film thickness, $k_3 = 1.3 \times 10^4$ nm^2/mC. Because the thickness measurements were destructive, each point shown in Fig. 16 was measured on a different wire. Errors associated with these measurements therefore include the variations in aging of the different wires as well as the uncertainty in the azimuthal location of the thickest part of the deposit. For these reasons, the error in the sputter-thickness measurements is estimated to be at least ± 15%.

The reason for the limiting film thickness is not understood at present. One possibility is that the primary diffusing species are ions and that diffusion is driven by an electric field. If there is a constant potential across the film, the field strength drops as the film grows so that at some film thickness, the field strength is sufficiently reduced that further diffusion is negligible. The limiting film thickness may explain why non-gold wires aged in CF_4 reach an asymptote and do not continue to age.

VII. Summary and Conclusions

There are three important results in this work. First, an apparent cathode aging that results in loss of gain and not in a self-sustained (Malter) breakdown occurs in CF_4. Second, a chemical model of aging in CF_4/hydrocarbon gases is developed and predictions of the model are used to suggest practical guidelines for use of CF_4-based gases. Third, principles of low-pressure, rf plasma chemistry are used to develop this model, and the correlations to observed phenomena are good.

A. Aging curves in CF_4 exhibit a nonlinear transient behavior in which the decrease in current is initially rapid, but then approaches a non-zero asymptote. This aging appears to occur on the cathode.

B. We use the functional form $I = A + B\exp(-Q^{1/2}/D)$ to describe the aging transient in CF_4. The parameterization of I is approximately independent of anode material ($D \sim 1.2$ mC$^{1/2}$; $I/I_0 \sim 0.6$).

C. Aging in CF_4/iC_4H_{10} gases is best characterized by pulse height measurements and by analysis of deposits on the wire. Because of apparent cathode effects, the current drawn in accelerated aging tests is not a reliable indicator of anode aging for CF_4-rich gases.

D. Gold-plated wires do not age in CF_4. Other metals (Al, Cu, Ni) react with fluorine radicals in the CF_4 discharge to form metal fluorides, which appear to grow by a diffusion-limited process. For Cu wires, the effective diffusion constant $k_3 \approx 1.3\text{x}10^4$ nm^2/mC, and the maximum fluoride film thickness is ~450 nm. Metal fluorides are observed at the interface between a carbonaceous deposit and the wire material of anodes aged in CF_4/iC_4H_{10} mixtures.

E. A four-part chemical model of the aging processes in CF_4/iC_4H_{10} is developed to explain why some CF_4/iC_4H_{10} mixtures form anode deposits and why others etch such deposits. The model considers 1) plasma polymerization of the hydrocarbon, 2) etching of wire deposits by CF_4, 3) acceleration of deposition processes in strongly etching environments, and 4) reactivity of the wire surface. This model may be generally applicable to CF_4/hydrocarbon gases.

F. Some practical implications of the model are 1) that mid-range concentrations of hydrocarbons in CF_4 are generally expected to etch wire deposits, while low hydrocarbon concentrations may result in considerable aging, and 2) that gold-plated wires are acceptable for use in CF_4-based gases while non-gold-plated wires are unacceptable.

G. Etching is observed over a wide range of CF_4/iC_4H_{10} mixtures and in

some CHF_3-based gases. The distinction as to whether or not etching occurs appears to be related to the atomic composition of the gas rather than to specific molecular configurations.

H. Principles of traditional plasma chemistry (low-pressure, rf) can be used with good results to predict the plasma chemistry in wire chambers (1 atm, dc). For CF_4-based gases, the chemical mechanisms occurring in the two plasma regimes are apparently similar.

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Table I

Summary of results for interruptions of aging tests with CF_4. Except where noted otherwise, CF_4 flow through the counter was maintained. The current after the interruption was corrected for gas density fluctuations (eqn. 1) with $\alpha = 6$.

Wire	Wire material	I before [nA]	I after [nA]	ΔI [%]	Δt [hr]	Comments
1	Au/W	286.4	285.9	−0.18	0.17	
1	Au/W	271.3	280.4	+3.35	0.53	open to air 0.28 hr
1	Au/W	192.7	195.3	+1.35	1.22	open to air 1.05 hr, forced convection
1	Au/W	193.9	195.3	+0.72	1.17	
2	Au/W	244.8	247.4	+1.06	18.02	
2	Au/W	231.6	232.4	+0.35	1.68	
2	Au/W	232.7	232.7	+0.00	3.47	
3	W	233.4	232.5	−0.39	0.20	
3	W	170.4	170.5	+0.06	0.28	apply +2080 V to shell, ground anode wire

Table II

Incidences of bulk fluorocarbon deposits on anode wires aged in CF_4.

Wire material	Number of wires analyzed	Number of wires with fluorocarbon deposits
Au/W	7	1[a)]
Al	2	0
Cu	10	0
Ni	3	0
Stablohm	1	0
W	2	1

[a)]Fluorocarbon deposits were observed only on the wire irradiated over a ~3 cm region with a current density of 0.36 μA/cm. See section III.A.

Table III
Summary of aging transients in CF_4 with Al cathodes. With Cu cathodes, average $R > \sim 3$ %/mC.

Wire material	Collected charge [mC]	I_{final}/I_{max}	Average R [%/mC]
Cu	9.56	0.987	0.14
Cu	7.67	0.979	0.27
Cu	25.9	0.970	0.12
Cu	5.62	0.939	1.09
Cu	3.05	0.926	2.43
Au/W	33.5	0.910	0.27
Stablohm	32.2	0.887	0.35
Cu	16.8	0.761	1.42
Cu	1.59	0.620	23.9
Cu	4.59	0.570	9.4
Cu	1.76	0.520	27.3

Table IV
Summary of recovery results for Au/W wires in CF_4/iC_4H_{10} gases. The wire recovered in the CF_4/iC_4H_{10} (80/20) was originally aged in Ar/C_2H_6 (50/50) bubbled through silicone oil; the other wires were originally aged in CF_4/iC_4H_{10} (95/5).

Recovery gas mixture CF_4/iC_4H_{10}	Aged PH [%]	Recovered PH [%]	Recovery rate, PH [%/C/cm]	Recovery rate, I [%/C/cm]	Total charge [C/cm]	Current density [μA/cm]
100/0	76	103	3700	3570	0.01	0.28
100/0	74	95	3100	2535	0.01	0.27
80/20	--	--	--	410	0.36	0.50
50/50	72	96	325	265	0.17	0.34

Table V

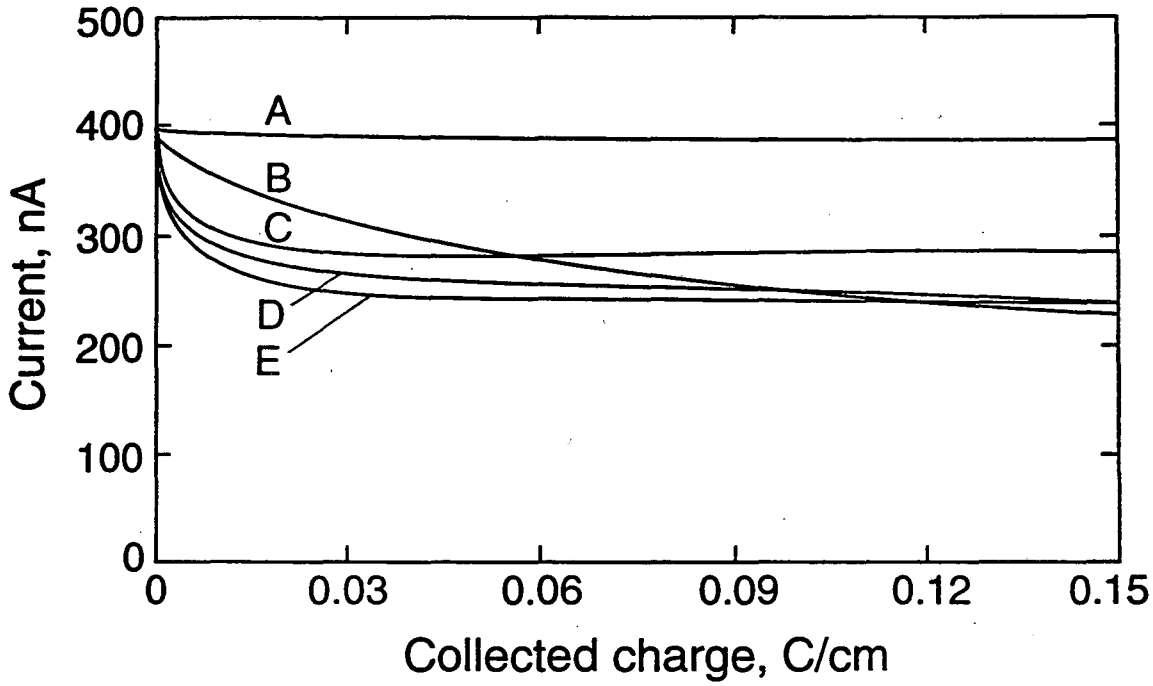
Summary of recovery results for Au/W wires in fluorine-containing gases. Deposits on these wires were formed by initial aging in CF_4/iC_4H_{10} (95/5).

Recovery gas mixture	Mixture ratio	Aged PH [%]	Recovered PH [%]	Recovery rate, PH [%/C/cm]	Recovery rate, I [%/C/cm]	Total charge [C/cm]	Current density [μA/cm]
$Ar/CF_4/O_2$	50/40/10	63	94	8400	16000	0.03	0.48
CHF_3	100	71	98	1000	990	0.09	0.43
CHF_3/CH_4	82/18	82	99	400	3830	0.05	0.43

Table VI

Atomic composition ratios and aging properties for selected gas mixtures.

Gas mixture	Composition	Aging behavior	F/C	(F-H)/C	F/H	C/H
CF_4	100	ETCH	4.00	4.00	--	--
$Ar/CF_4/O_2$	50/40/10	ETCH	4.00	4.00	--	--
CF_4/C_2H_4	95/5	DEPOSIT	3.62	3.43	19.00	5.24
CF_4/iC_4H_{10}	95/5	DEPOSIT	3.30	2.87	7.60	2.30
CF_4/iC_4H_{10}	90/10	DEPOSIT	2.77	2.00	3.60	1.30
CHF_3	100	ETCH	3.00	2.00	3.00	1.00
CHF_3/CH_4	82/18	ETCH	2.46	0.92	1.60	0.65
CF_4/iC_4H_{10}	80/20	ETCH	2.00	0.75	1.60	0.80
CF_4/iC_4H_{10}	50/50	ETCH	0.80	−1.20	0.40	0.50



XBL 927-5284

Fig. 1. Typical aging curves (current as a function of total collected charge) for CF_4 and CF_4/iC_4H_{10} gases. Curves shown are (gas,wire): A, CF_4/iC_4H_{10} (80/20), Au/W; B, CF_4/iC_4H_{10}, Stablohm; C, CF_4, Stablohm; D, CF_4, Cu; E, CF_4, Au/W.

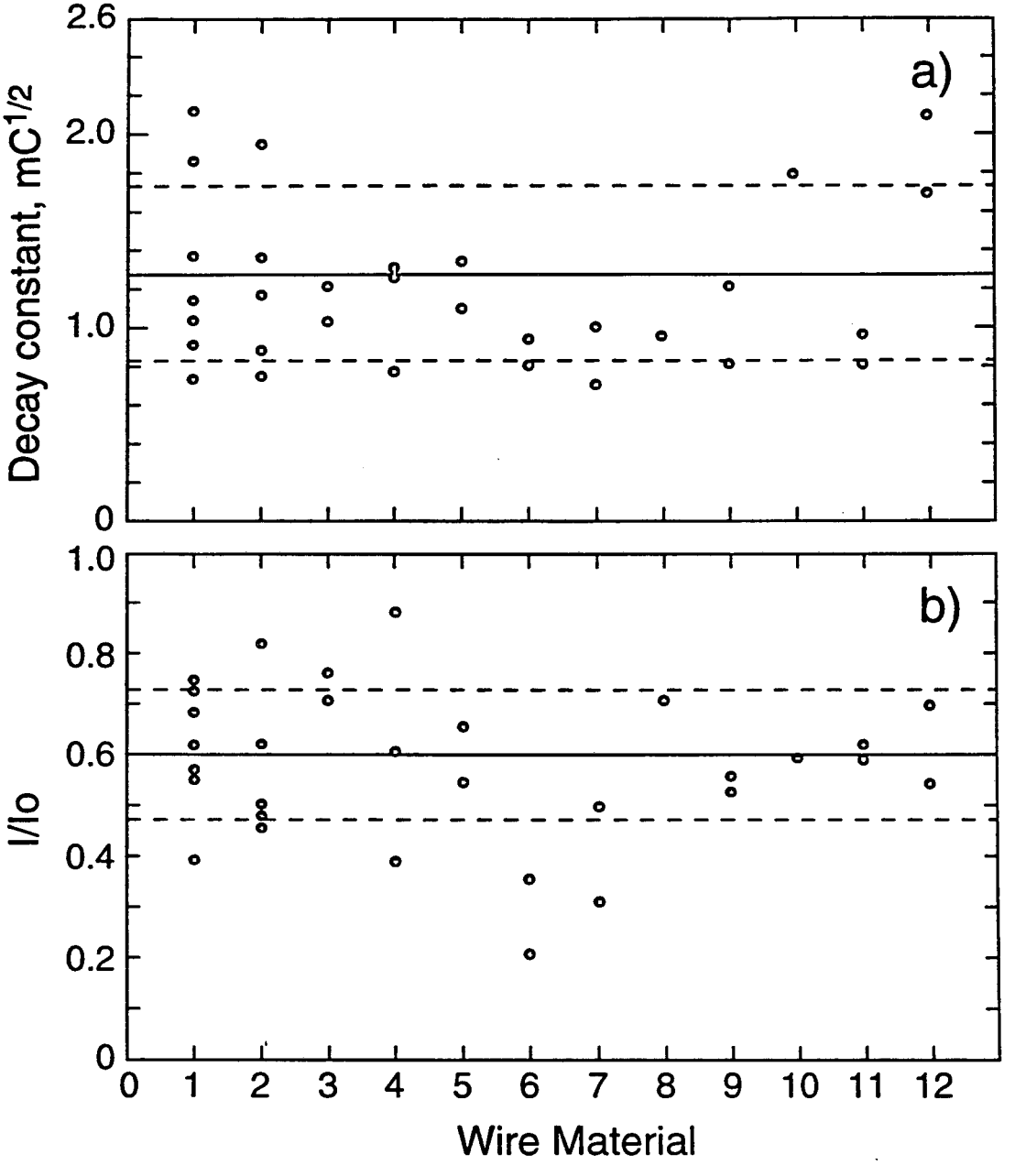


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Fig. 2. (a) Decay constants and (b) gain changes for various anode materials aged in CF_4. The solid line is the average for the Au/W wires; the dashed lines indicate the one-standard-deviation limits. Wire materials are: 1, Au/W; 2, Au/W, unfiltered CF_4; 3, Stablohm; 4, Ni; 5, Cu; 6, Al; 7, W; 8, C; 9, Ni pretreated in SF_6/O_2; 10, Cu pretreated in SF_6/O_2; 11, Au/W with nominal 50 nm CHF_3 film; 12, Au/W with nominal 37 nm CHF_3 film.

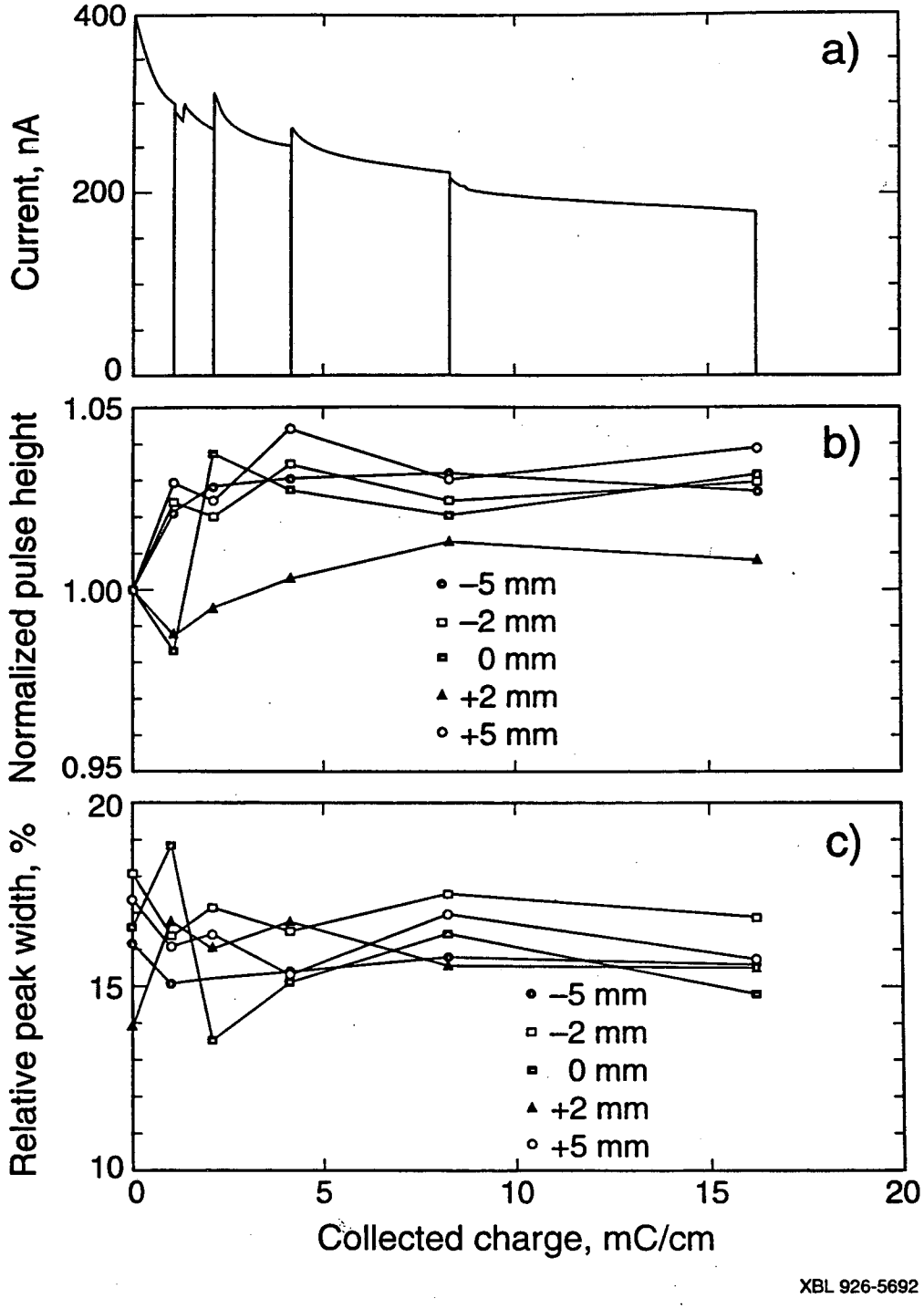


Fig. 3. Aging parameters as a function of collected charge for an Au/W wire aged in CF_4: (a) current, (b) pulse height, (c) energy resolution. Distances are relative to the center of irradiation. The current overshoot in (a) is observed when an aging test with CF_4 is interrupted and exposed to Ar/C_2H_6 (see text).

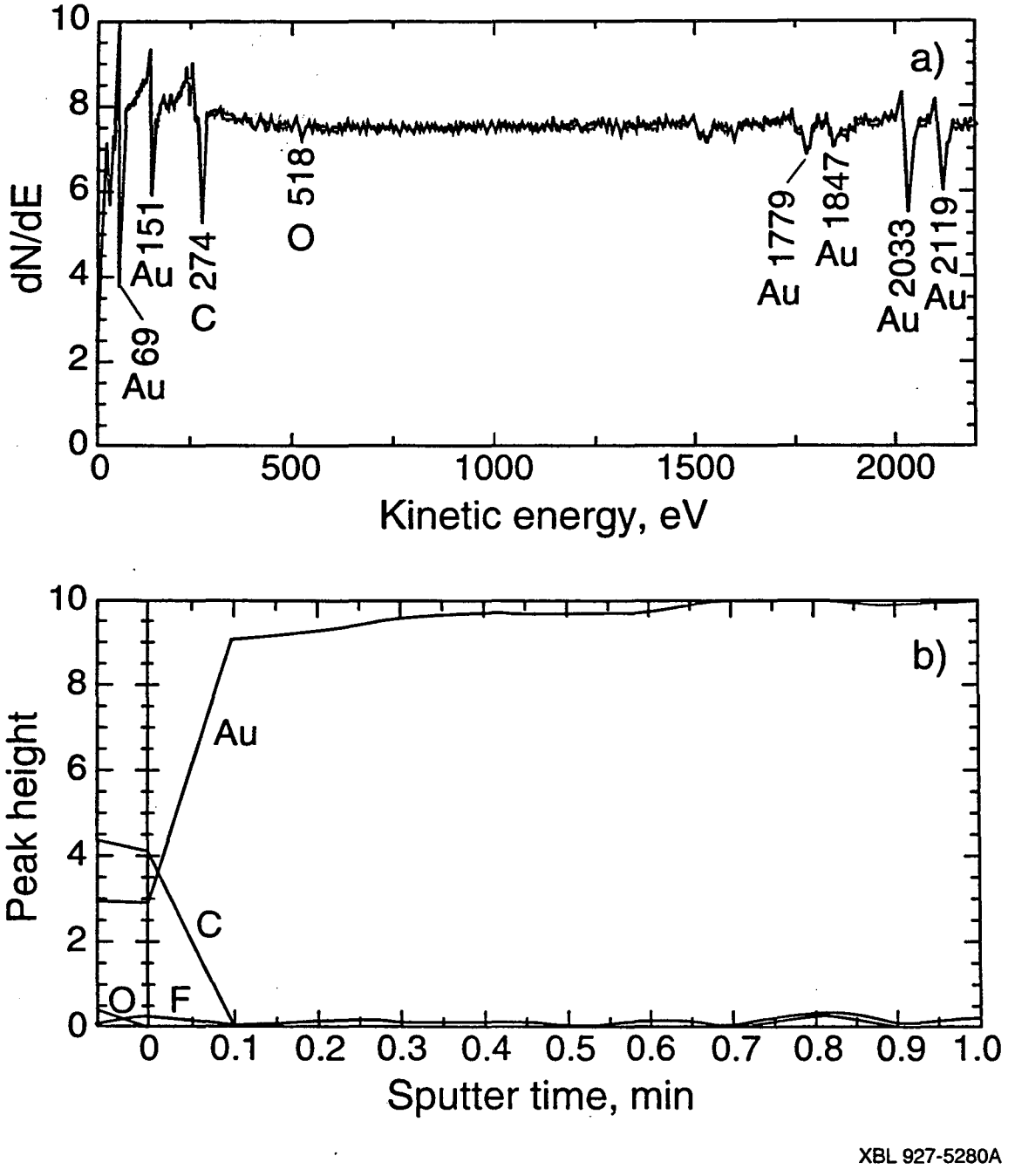
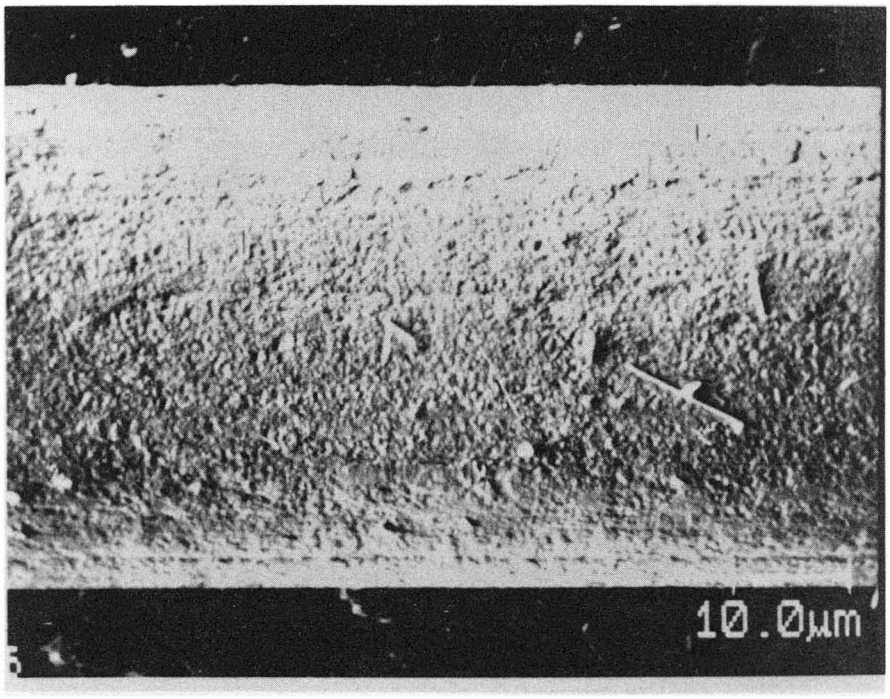


Fig. 4. (a) AES spectrum and (b) depth profile of Au/W wire aged in CF_4.



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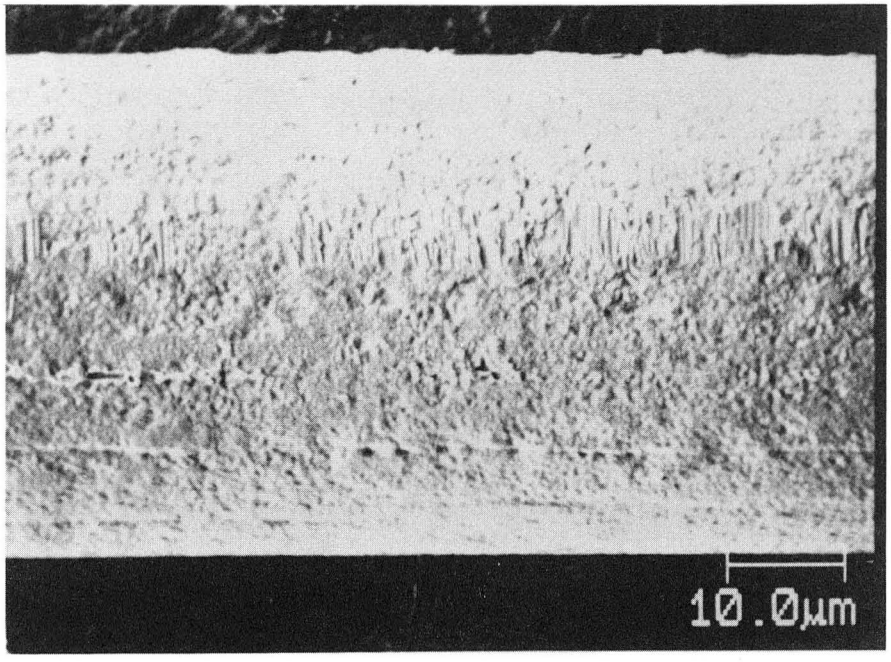

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Fig. 5. Photos of Au/W wires: (a) new, (b) aged in CF_4.

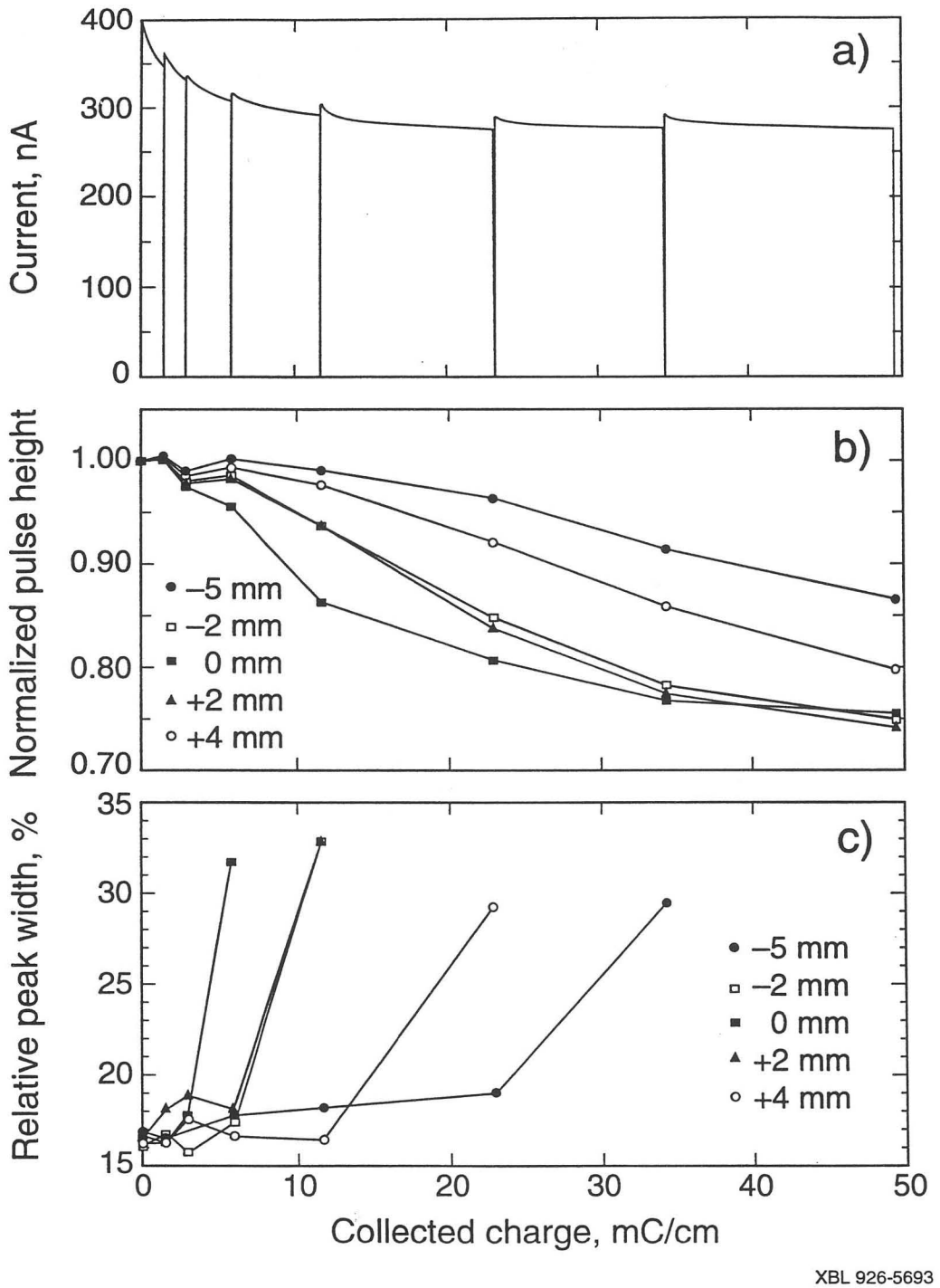


Fig. 6. Aging parameters as a function of collected charge for a Cu wire aged in CF_4: (a) current, (b) pulse height, (c) energy resolution. Distances are relative to the center of irradiation. The maximum measurable value of the energy resolution (relative peak width) is ~33%, a limit imposed by splitting of the principal ^{55}Fe peak.

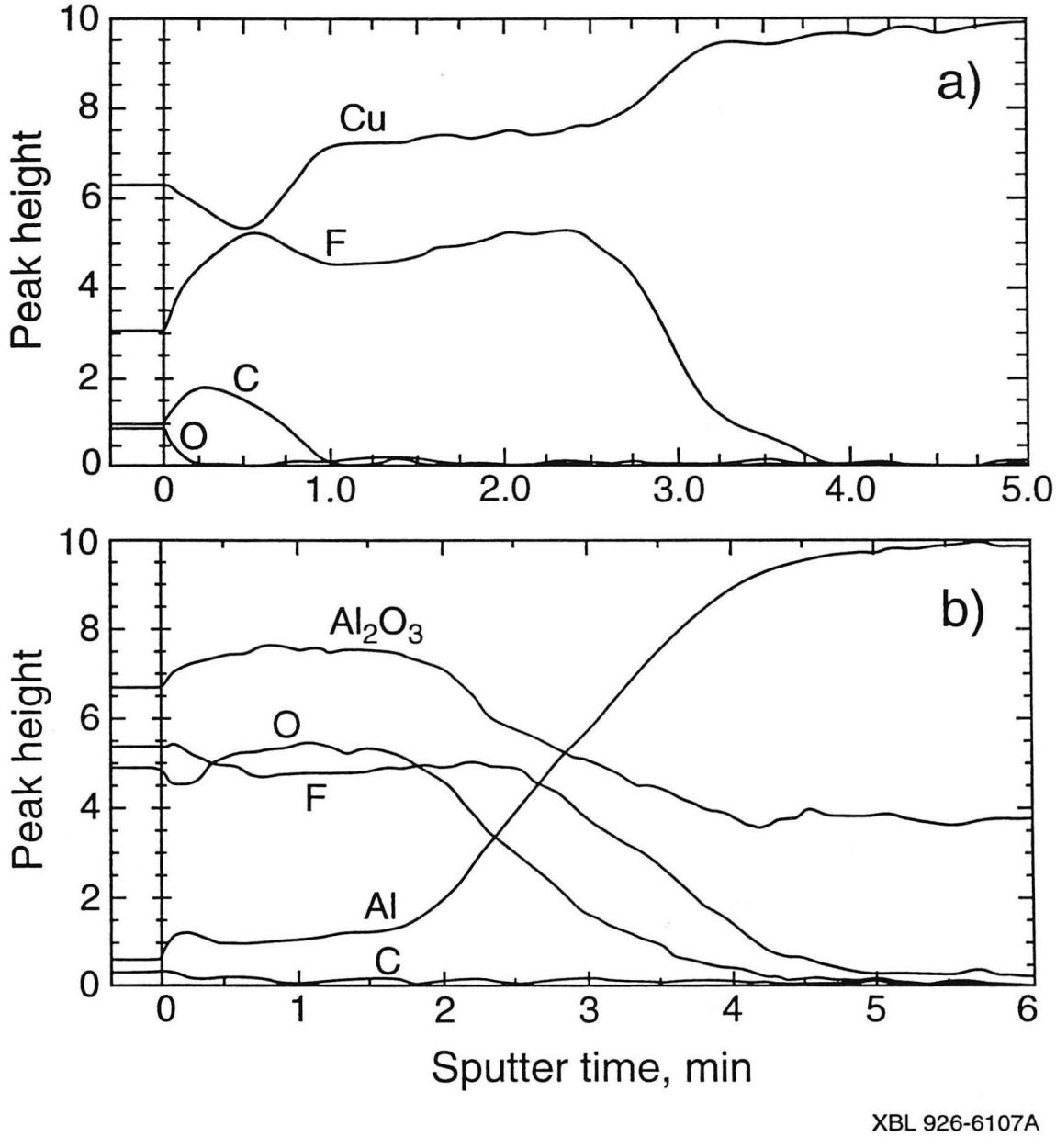
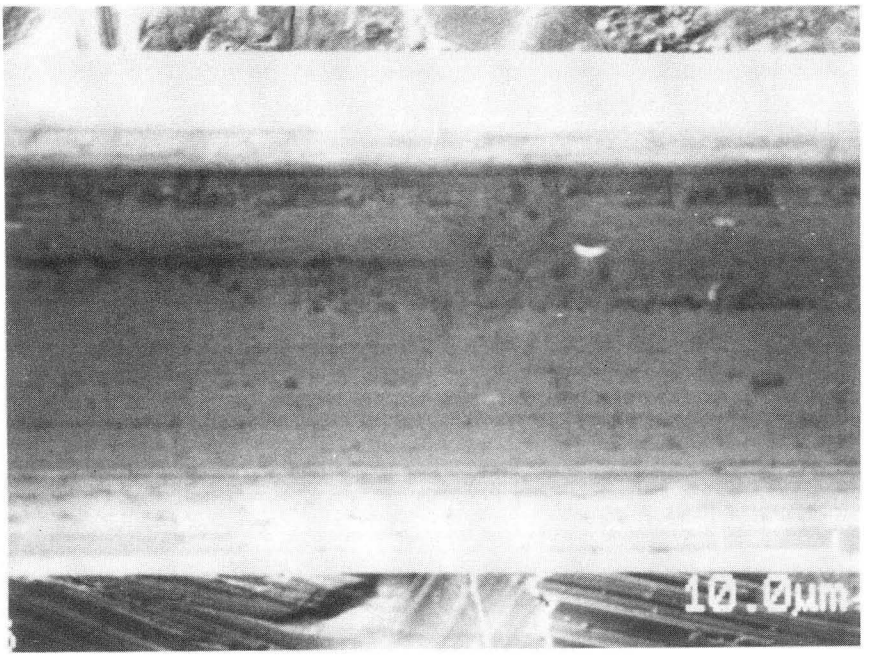


Fig. 7. AES depth profiles of (a) Cu wire and (b) Al wire aged in CF_4 showing metal fluoride films. The Al_2O_3 curve stabilizes at a nonzero value as a result of an artifact in the data acquisition process, which does not differentiate the 1378 eV peak (binding energy of Al in Al_2O_3) from the tail of the 1396 eV peak (binding energy of Al metal).



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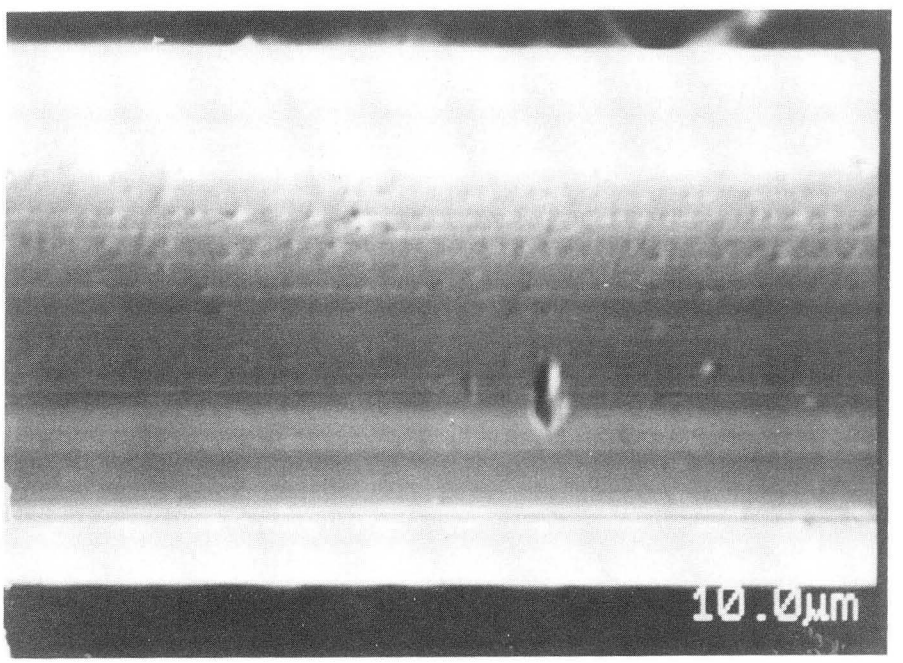

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Fig. 8. Photos of Ni wires: (a) new, (b) aged in CF_4. Note the smooth surfaces. The small dark spots on the new wire are native contamination. Other non-gold wires have similar appearances.

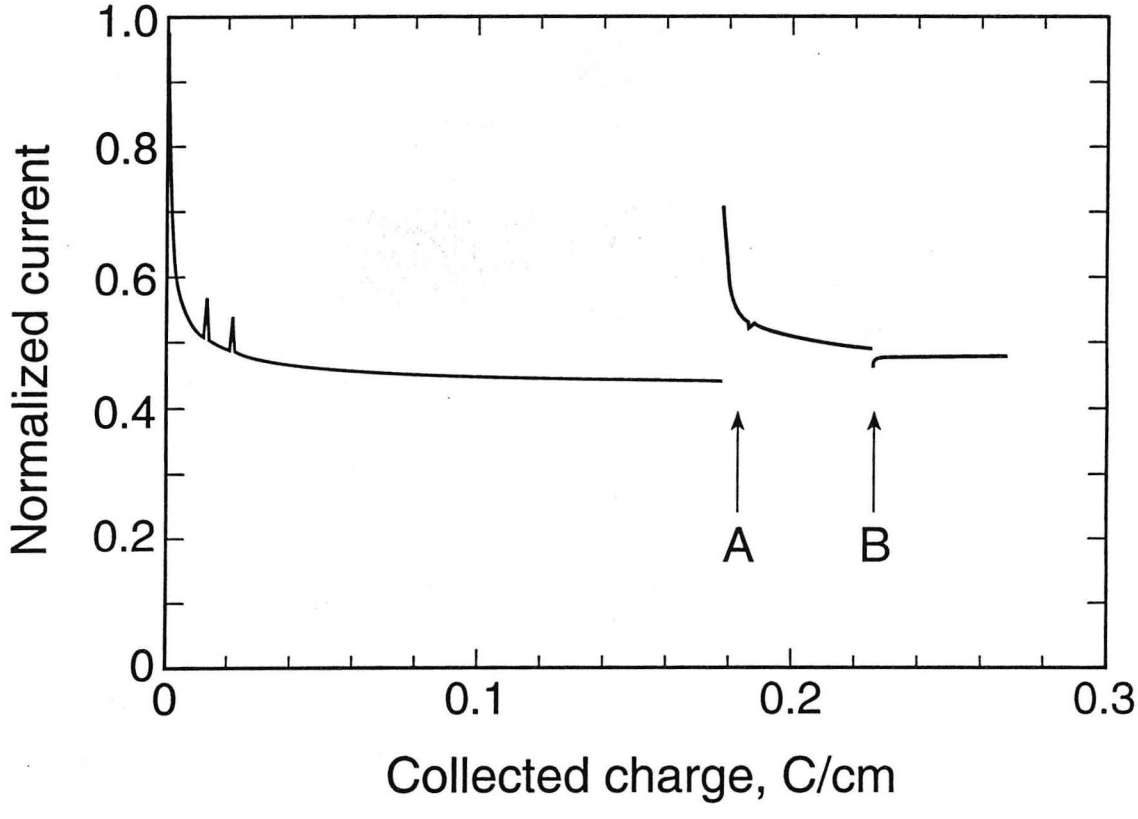

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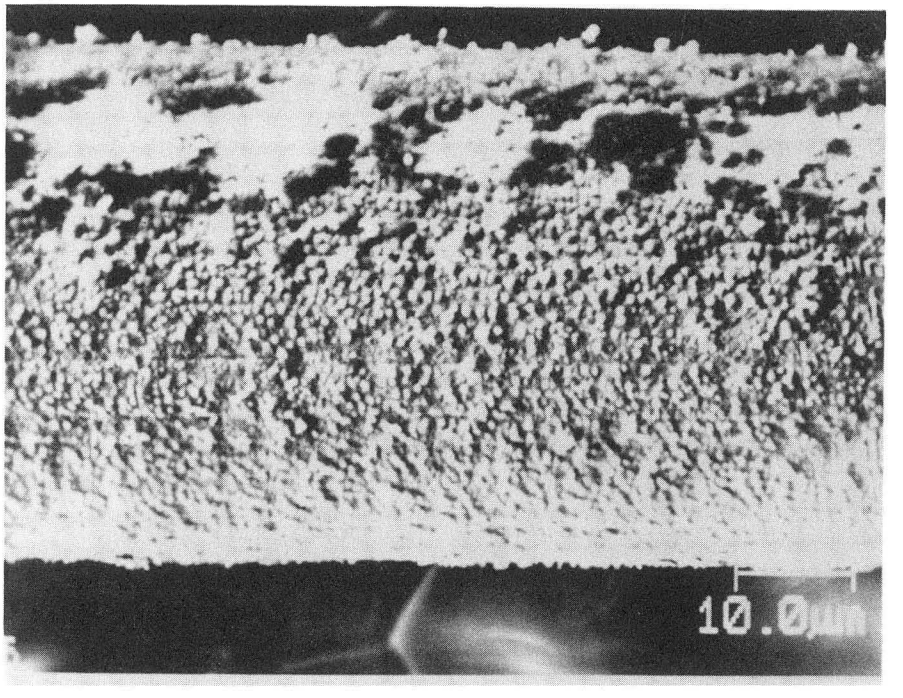
Fig. 9. Effect of new Au/W anode wires in a cathode shell aged with CF_4. The initial current was 408 nA. New anode wires were installed at points A and B. The time intervals were 55 days and 2.15 hr, respectively.



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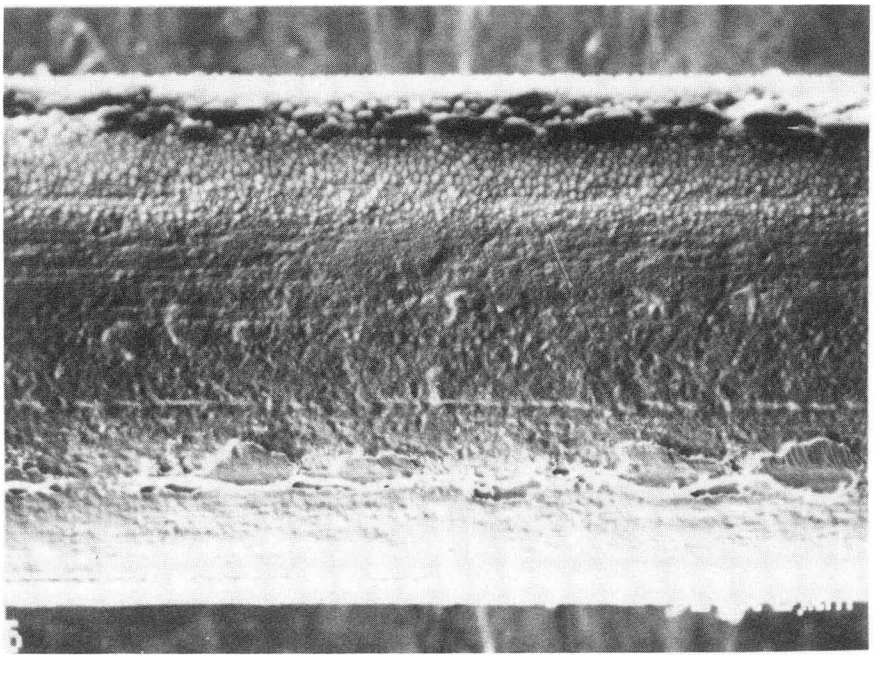

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Fig. 10. Photos of Au/W wires aged in CF_4/iC_4H_{10} mixtures: (a) 95/5, (b) 90/10, (c) 80/20.

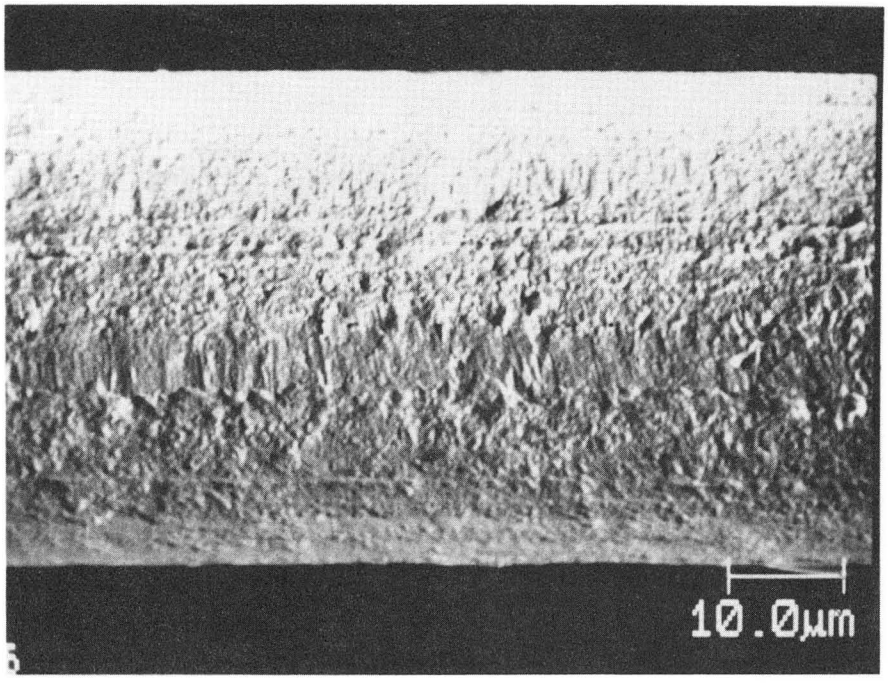

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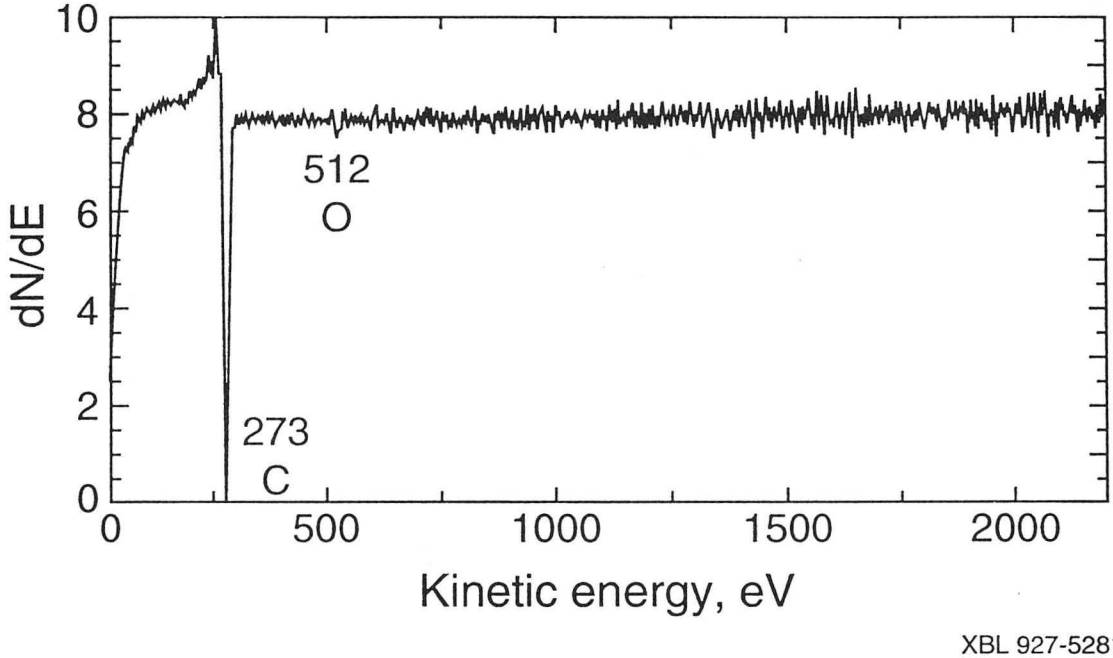
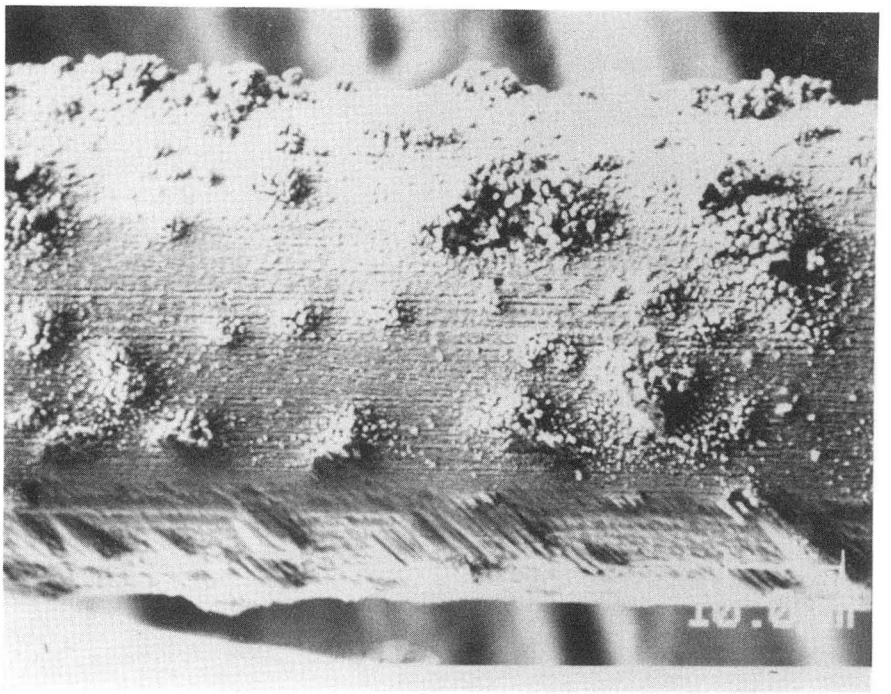
Fig. 10c. Photo of Au/W wire aged in CF_4/iC_4H_{10} (80/20).



XBL 927-5281

Fig. 11. AES spectrum of Au/W wire aged in CF_4/iC_4H_{10} (95/5). An intense C peak masks the underlying metal.



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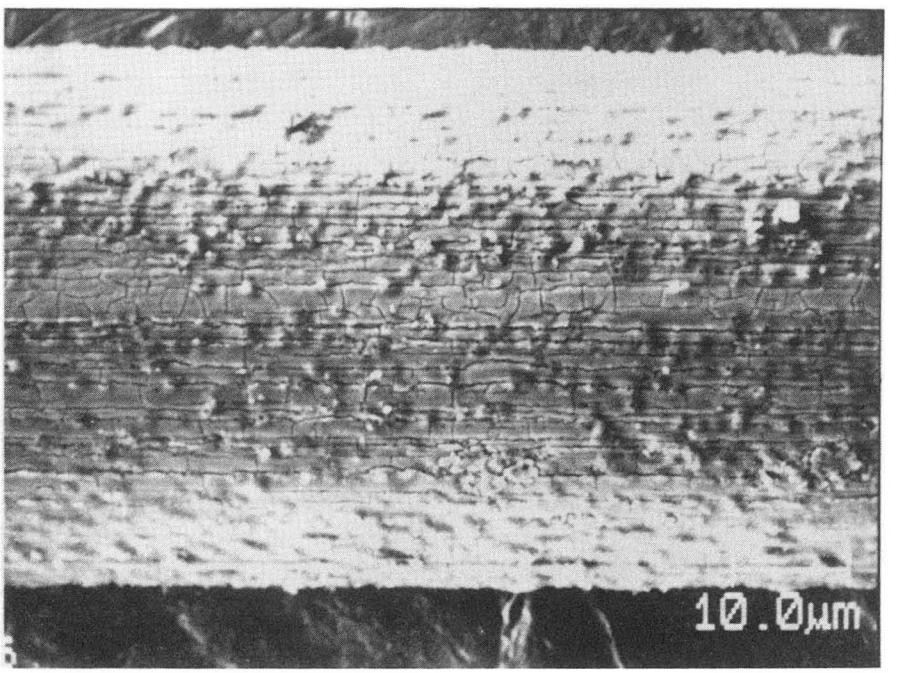

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Fig. 12. Photos of non-gold wires aged in CF_4/iC_4H_{10} mixtures: (a) Al wire, 95/5, (b) Ni wire, 80/20.

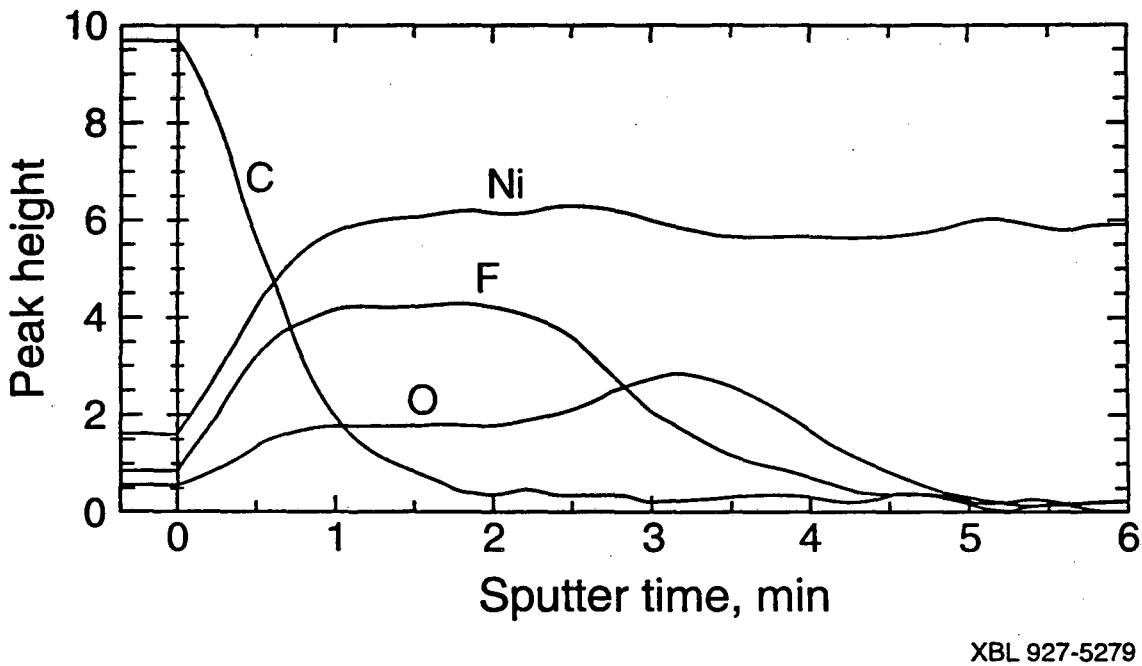

Fig. 13. AES depth profile of Ni wire aged in CF_4/iC_4H_{10} (95/5). A stratified deposit structure with a carbonaceous layer on top of a metal fluoride layer is evident.

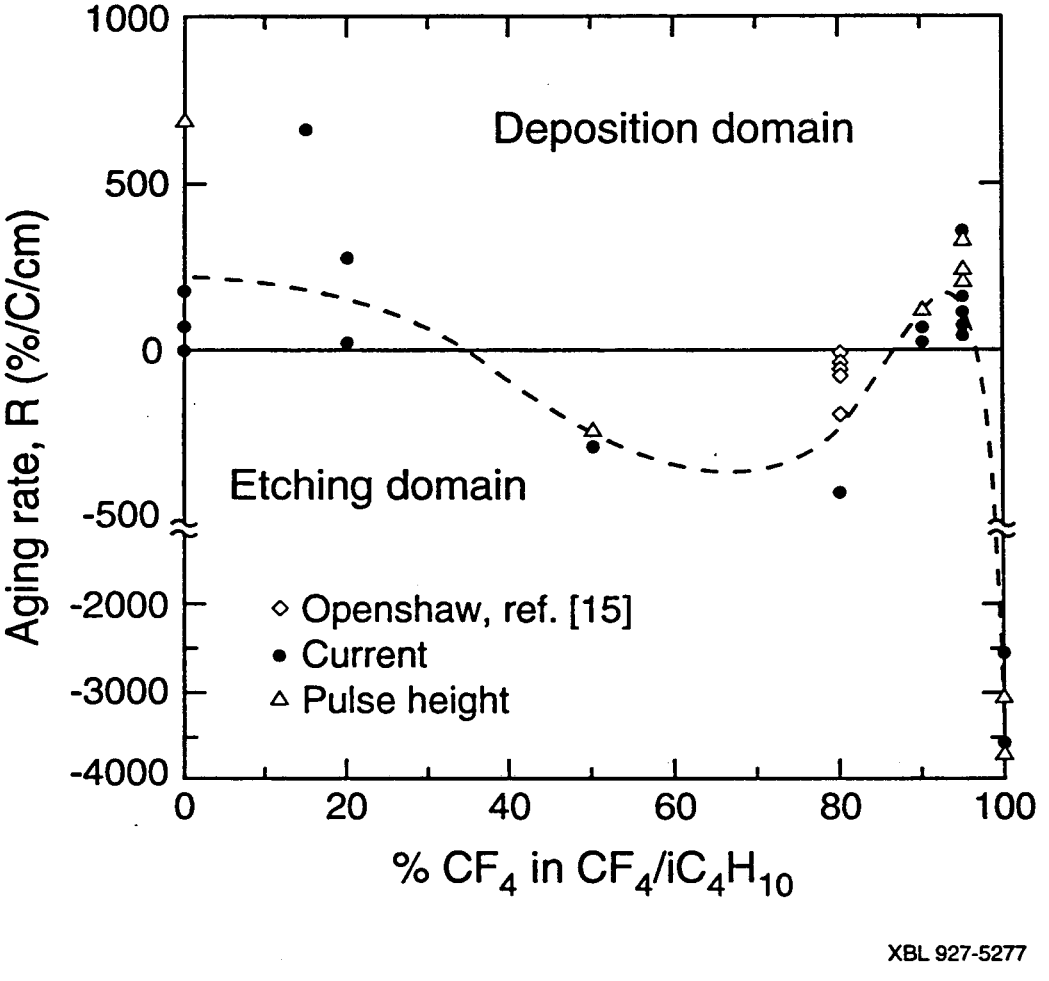

Fig. 14. Aging (recovery) rates for Au/W wires as a function of gas composition in CF_4/iC_4H_{10} mixtures. The dashed line is for eye guidance.

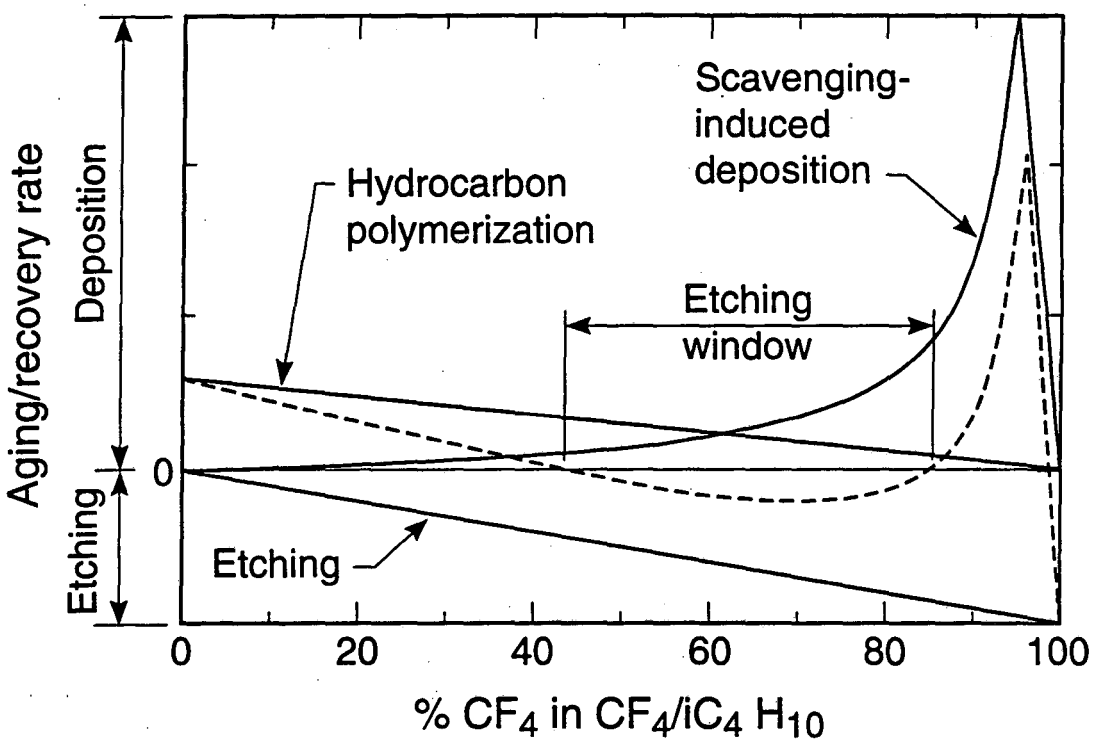

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Fig. 15. Model of anode aging in CF_4/hydrocarbon gases showing relation between polymerization, etching, and scavenging-induced deposition and overall result.

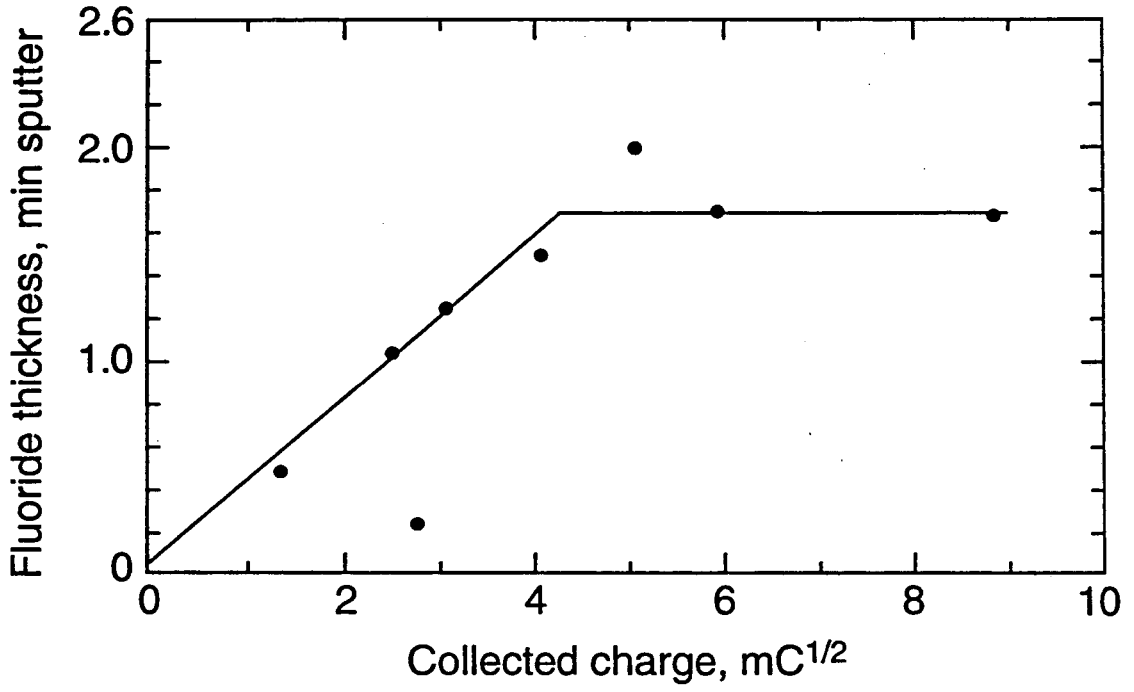

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Fig. 16. Thickness of the copper fluoride film, measured by AES depth profiling, as a function of collected charge.

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