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J. Wise, J.A. Kadyk and D.W. Hess

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J. WISE and J.A. KADYK
Lawrence Berkeley Laboratory, University of California, Berkeley, CA 94720

and

D.W. HESS
Department of Chemical Engineering, University of California, Berkeley, CA 94720
UC, Berkeley, Chem. Eng. Dept.

ABSTRACT

We are investigating the chemistry that leads to wire aging transients that we have observed in various CF_4/isobutane gas mixtures including the well-studied 80% CF_4 + 20% isobutane mixture. Aging tests using such mixtures exhibit transients resulting in loss of gain. The magnitude and duration of these transients are dependent on the CF_4/isobutane ratio and the wire material, and are sufficiently large to affect the gain stability during the early operation of an experiment. Film formation on the wire may explain these observations.

1. Introduction

The very good aging properties of the CF_4/isobutane (80/20) mixture have been known for some time,[1,2] and there has recently been a report that hydrocarbon deposits were etched away by using this mixture.[3] However, in aging tests using the 80/20 as well as other mixtures of CF_4/isobutane, we observe transients in which the wire current changes (almost) exponentially towards a nonzero steady-state value, a result that may be interpreted as a competitive ablation and polymerization process.[4]

This investigation is along three lines: 1) monitoring of the aging of the wire, 2) analysis of the aged wire surface, and 3) analysis of condensible species in the proportional tube effluent, presumed to be associated with the gas-phase chemical reactions that may have led to the aging. Only the first two parts are discussed in this report.

2. Experimental

In this series of experiments, wire aging has been investigated as a function of gas composition and wire material. Gases used were CF_4 and isobutane, both individually and in mixtures with each other. Wire materials used were gold-plated tungsten,

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Table 1: Decay constants and gain changes for some wires and gases.

Gas	*Wire*	τ, *mC*	I_∞/I_0
CF_4	Au/W	1.9 ± 0.5	0.6 ± 0.1
CF_4	Stablohm	1.1 ± 0.1	0.75 ± 0.06
CF_4	Nickel	0.9 ± 0.2	0.4 ± 0.1
CF_4	Copper	1.2 ± 0.2	0.7 ± 0.1
CF_4	Carbon	1.2 ± 0.2	0.75 ± 0.1
80/20	Au/W	7.7 ± 2.3	0.96 ± 0.04
80/20	Stablohm	25 ± 5	0.59 ± 0.14

Stablohm, nickel, copper, and carbon. The techniques used to collect aging data have already been described.[2]

3. Exponential Curve Fits

In aging tests using different mixtures of CF_4/isobutane, we observe transients in which the wire current approaches a nonzero value. We model these transients a a constant plus an exponential. The two parameters used are the gain change (I_∞/I_0) and the decay constant. Although not always a good fit ($\chi^2/n \sim 100$), this procedure nevertheless gives a consistent basis for comparison of different aging tests.

Although the experiments are still in progress and little data is presently available for gas mixtures containing more than 20% isobutane, indications are that the decay constant increases with increasing isobutane content, but that the gain change shows no distinct trend. For CF_4 alone, the decay constant is independent of the wire material. For CF_4/isobutane mixtures, however, the decay constants for Stablohm wires are much longer than those for gold-plated wires, suggesting that the two types of wires age by different mechanisms. The decay constant for CF_4 alone is also much smaller than for CF_4/isobutane mixtures. Gain changes and decay constants for some of the aging tests in this study are summarized in Table 1.

4. Surface Analysis

Wire surfaces are analyzed using secondary electron microscopy (SEM) and Auger spectroscopy combined with argon ion milling of the surface so that a composition-depth profile can be obtained. Hydrogen is not detectable with the Auger technique, so hydrocarbons appear only as carbon. This technique has been used previously by Williams,[5] and an example of an Auger depth profile is illustrated in that work.

4.1. Aged Gold-Plated Wires

Aging deposits on gold-plated wires are predominantly carbonaceous: little or no fluorine is observed, suggesting that the gold surface is not significantly chemically attacked. This is so even for wires aged in CF_4 without admixture of isobutane, in which

case the source of the hydrogen presumed to be in the deposits is unclear. There is, however, evidence from other investigations that we have done on CF_4 indicating that significant hydrocarbon contamination exists in this gas. The carbonaceous deposits appear to be an agglomeration of spheres with diameters typically $1\mu m$.

4.2. Aged Stablohm, Nickel, and Copper Wires

In contrast to gold-plated wires, aged Stablohm, nickel, and copper wires show deposits containing significant amounts of fluorine. These deposits are thinner than the carbonaceous deposits, and are not always easily seen at 1500x magnification. Heavy carbonaceous deposits, which are readily identified by Auger analysis and by their distinctive appearance under SEM observation, are sometimes present in addition to the fluorinated deposits.

5. Discussion

The fact that fluorine is a major component of deposits on non-gold-plated wires while carbon is the major component of deposits on gold-plated wires suggests that different aging mechanisms are in effect and that the surface plays a role in the determination of which mechanism dominates. This interpretation is supported by the observation that different wire materials have different aging decay constants.

A possible explanation for these observations is that metals more active than gold react with the $F\bullet$ and/or $CF_3\bullet$ radicals expected to be produced in the avalanche to form an insulating metal fluoride. After the wire surface is passivated by this fluoride, hydrocarbon or fluorocarbon deposits may also form, at a rate dependent on the CF_4/isobutane ratio of the counter gas.

In the avalanche environment, we expect that fluorine radicals will react with carbon on the wire surface to form volatile species (e.g., CF_4). However, fluorine radicals will also react with hydrogen to form HF, leaving behind carbon-rich species that will tend to polymerize and deposit onto the wire. The necessary factors for a competitive ablation and polymerization process are thus present, and the fact that the aging curves approach nonzero asymptotes suggests that this process indeed occurs: a steady-state film thickness results from the two competing processes.

Unresolved questions about this work that remain under investigation include 1) How does isobutane affect CF_4 so that the CF_4/isobutane mixture ages less rapidly than CF_4 alone, and 2) Why is the decay constant for aging of CF_4 essentially independent of the wire surface material.

References

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