Simple pressure gauge for uranium hexafluoride

Patricia M. George, Mark N. Swanson, and J. L. Beauchamp

Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91125

(Received 18 September 1978; accepted for publication 6 July 1979)

A sensitive detector and pressure gauge for uranium hexafluoride in high-vacuum systems is described. Negative surface ionization of UF_6 occurs on ribbon filaments operated at temperatures too low for electron emission to be significant. The ion current measured on a cylindrical collector surrounding the filament assembly varies regularly with UF_6 pressure below 10^{-3} Torr. Different filament materials are considered, including rhenium, thoriated tungsten, and platinum. Rhenium is found to be the most satisfactory material for operation of diode emitters as a pressure gauge. Gauge constants (in $A\,Torr^{-1}$) are derived from comparing negative surface ionization currents with the response of a capacitance manometer and are shown to be independent of temperature within a reasonable operating range. The effects of exposing the rhenium filament to various gases is considered, and it is shown that brief exposure to acetylene substantially improves the operating characteristics of the gauge.

INTRODUCTION

Recent experimental studies of the behavior of uranium hexafluoride in ionized gases in our laboratory[1,2] led to the observation that ionization gauges of conventional design experience difficulties when exposed to this species. Although inverted Bayard–Alpert ionization gauges appear to respond properly to UF_6, the thoria-coated iridium filaments commonly used in these gauges have short lifetimes even at relatively low pressures of UF_6 (10^{-6} Torr). Schulz–Phelps-type gauges, using rhenium wire filaments, behave erratically when exposed to UF_6.[1] Deposits of thermally decomposed UF_6 accumulate on heated surfaces of both gauges and further interfere with their proper operation.

The electron affinity of UF_6 is exceptionally high (5.2 eV[2,3]) and is comparable to the work functions of many metals. The resulting efficient negative surface ionization of UF_6 on metal surfaces formed the basis of a UF_6^- ion beam source in our earlier experiments,[2] and it was suggested that this phenomenon could be further exploited in the design of a detector for uranium hexafluoride. Subsequent results of Compton *et al.*[4] have shown that large amounts of UF_6^- are formed when fluorine gas is passed over heated uranium wire. The temperature dependence of UF_6^-, formed in this way, was found to be approximately the same as that formed by passing UF_6 over a hot uranium wire. Recently, the formation of UF_6^- from UF_6 on a carbon-coated platinum surface[5] has been reported. This proceeds with an absolute efficiency of ~99%, the heat of adsorption of UF_6^- being 33.6 ± 1.1 kcal mol^{-1}.

This paper reports additional studies of the negative surface ionization of UF_6 on various metals and the design, operation and calibration of a simple detector and pressure gauge for UF_6.

I. EXPERIMENTAL

An all stainless-steel vacuum system pumped with a liquid nitrogen trapped 2-in. diffusion pump was assembled. After bakeout at 200 °C the base pressure was 5×10^{-8} Torr. A stainless-steel sample reservoir containing 60 g of UF_6 was attached to the vacuum system through a Granville Phillips variable leak valve. The sample reservoir was maintained at 0 °C in an ice bath to reduce the vapor pressure of UF_6 and prevent distillation into other parts of the apparatus. Pressures below 10^{-4} Torr were monitored using a Bayard–Alpert ionization gauge (Veeco type RG75K). In the presence of UF_6, excessive currents were required to maintain regulated electron emission, leading to eventual failure of the filament. The gauge was replaced several times during the course of this investigation. At higher pressures (above 10^{-4} Torr) a capacitance manometer was employed (MKS Instruments, model 221).

A filament holder with cylindrical collector (Fig. 1) was assembled on a 2.75-in. flange and mounted in the vacuum system such that the filament could be viewed with an optical pyrometer through a small aperture in the cylindrical collector. Optical access to the assembly was provided by a quartz window. Rhenium, thoriated tungsten, and platinum ribbon filaments of length 1.3 cm and various widths were used. The collector was operated at ground and a variable negative bias was applied to the filament to extract negative ions. A negative bias of 300 V was maintained for calibration of the system as a pressure gauge.

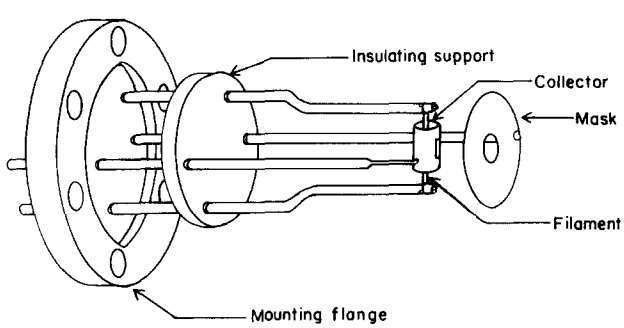

FIG. 1. Apparatus for investigation of UF_6 negative surface ionization on filaments on various materials.

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For a given filament, the thermionic emission current was measured as a function of the apparent filament temperature (T_i), determined with an optical pyrometer (Leeds and Northrup model 8622-C), and the true temperature (T) was found from the equation[6]

$$T^{-1} = T_i^{-1} + (\lambda_i/c_2)\ \ln[q\epsilon(\lambda_i)], \qquad (1)$$

where $\epsilon(\lambda_i)$ is the emissivity of the filament at wavelength λ_i, 650 nm, and temperature T, c_2 is the second radiation constant, and q is the transmission of the quartz window.

The electronic work function of the filament ϕ was obtained by applying the Richardson–Dushman equation[7]

$$J = AT^2 \exp(\phi/kT), \qquad (2)$$

where J is the saturation electron current density emitted from the surface at absolute temperature T, A is a constant, and k is the Boltzmann constant. Work functions can vary with both temperature and exposure to various gases (especially UF_6). Optically determined work functions have the advantage that they can be measured at a fixed temperature. In the present study these were simply determined by varying the wavelength of the incident light and observing the threshold for photoelectron emission.[8] The filament was illuminated with a 150-W xenon light source, dispersed by a monochromator (Bausch and Lomb, 0.25 m). A mask allowed the light to strike the filament but not the collector.

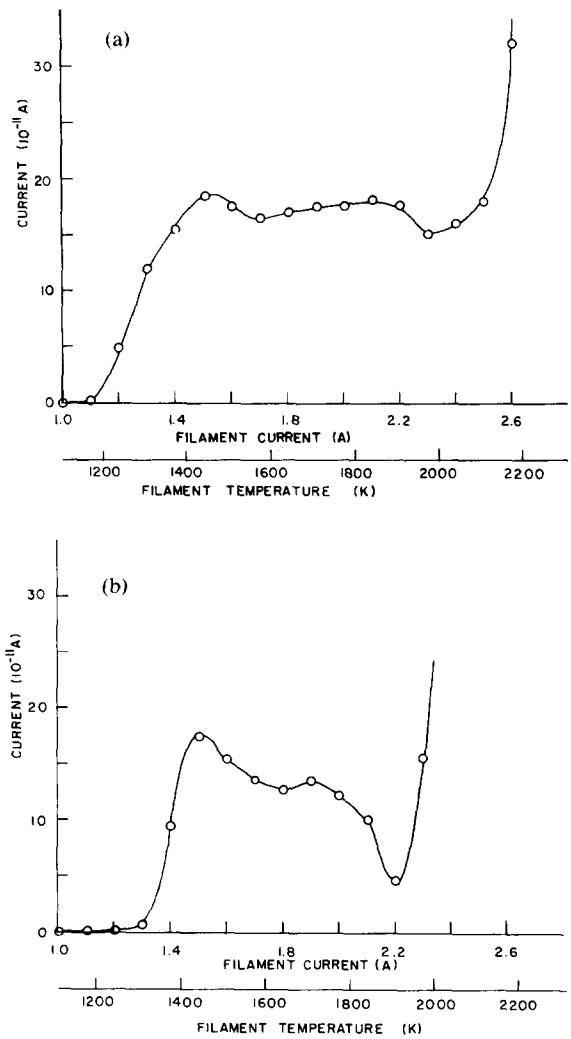

FIG. 2. (a) and (b). Representative data showing variation of negative collector current with rhenium filament current and temperature, in the presence of 2×10^{-5} Torr of UF_6.

TABLE I. Average electronic work functions of filament materials.

Filament	$\epsilon_{0.65}$[b]	Electronic work function (eV) Thermionic	Photo-electric	Liter-ature[d]	MP K[c]
Re	0.42	4.7	4.5	4.96	3453
W(Th)[a]	0.43	4.4	~4.5	4.55	3683
Pt	0.33	3.2	—	5.65	2042

[a] Thorium depleted by strong heating.
[b] W. H. Kohl, *Materials and Techniques for Electron Tubes* (Reinhold, New York, 1960).
[c] *Handbook of Chemistry and Physics*, 53rd ed. (Chemical Rubber Company, Cleveland, 1972).
[d] H. B. Michaelson, J. Appl. Phys. **48**, 4729 (1977).

Pressure-gauge calibrations were carried out using a 0.0012 × 0.030 in. rhenium ribbon. Gauge constants were determined for treated and untreated rhenium filaments. Treatment involved passing acetylene at 5×10^{-5} Torr over the heated filament (~1400 K) for ~10 min before allowing UF_6 into the system. This forms a surface carbide on the filament and typically enhances formation of UF_6^- by $\sim 10^3$ over that of untreated filaments. The rhenium filaments were degassed and cleaned by heating to ~2300 K for several minutes before use.

Rhenium filaments subjected to different operating conditions were examined with a scanning electron microscope to identify changes in surface characteristics.

II. RESULTS

A. Rhenium

In an earlier study in this laboratory,[2] it was observed that UF_6^- was formed on a rhenium filament at filament temperatures too low for electron emission to be significant. Detection and characterization of UF_6^- was accomplished by ion cyclotron resonance spectroscopy. The mass spectrum showed no other major negative ions produced on the filament. Small amounts of rhenium hexafluoride were, however, detected in the positive-ion mass spectrum. At a UF_6 pressure (measured on an ionization gauge) of 1×10^{-6} Torr, the onset for UF_6^- emission occurred at a filament temperature of about 1100 K, while electron emission did not occur until ~2000 K. This behavior has been confirmed in this study; the variation of negative-ion current with filament temperature for a 0.0012 × 0.030 in. rhenium ribbon is shown in Fig. 2. UF_6^- is initially observed in the temperature range 1000–1200 K. The negative-ion current steadily increases with temperature until it reaches a maximum. Thereafter, it either remains at a maximum, Fig. 2(a), or decreases, Fig. 2(b), until electron emission is observed at higher temperatures. Location of this maximum and subsequent behavior of the UF_6^- current depends on individual filaments and the condition of that filament, but in all

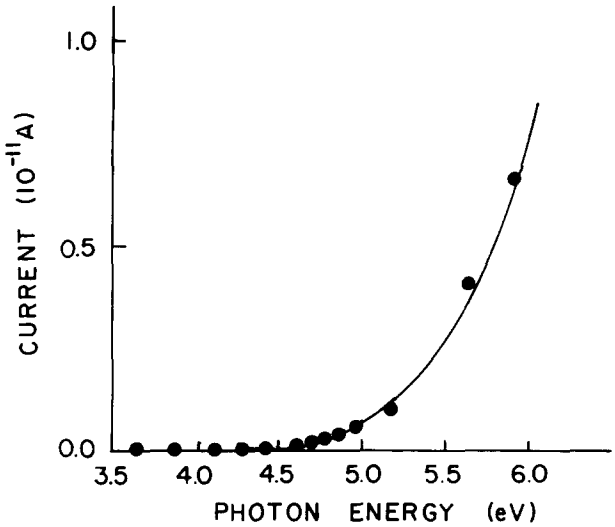

FIG. 3. Variation of electron current with frequency of light impinging on rhenium surface. Threshold extrapolation of work function yields a value of 4.5 eV.

cases maximum emission is readily located. At this point the negative ion current is flux dependent and varies linearly with pressure (see below). Operating range for the detector and the pressure gauge is in the vicinity of this maximum (1200–1600 K).

With a new rhenium filament mounted, analysis of the electron emission as a function of temperature yielded an average work function of 4.7 eV (a summary of work functions obtained is given in Table I). The filament was then exposed briefly to UF_6 and UF_6^- emission was observed with an apparent low negative surface ionization efficiency of 1.3×10^{-7}. Upon removal of UF_6 vapor, thermionic emission measurements indicated that the work function had increased to 5.5 eV. This increase in work function was also demonstrated using photoelectric techniques. Figure 3 shows the observed photocurrent before contact with UF_6, threshold extrapolation of which yields a value of 4.45 eV for the work function. Irradiation of the rhenium ribbon with 200 nm (6.2 eV) light yielded a photoelectric current of 1×10^{-11} A. Exposure to UF_6 immediately quenched the current, which could only be restored by pumping away the UF_6 and strongly heating the filament. This suggests that the work function at ambient temperature (295 K) increases by over 1.6 eV upon exposure to UF_6, since the photoelectric threshold is now greater than 6.2 eV.

Electron micrographs show that initially the rhenium surface is devoid of any distinctive features. Deposits which appear to be UF_4 are formed after exposure to UF_6 at elevated temperatures. In addition to the deposits, surface striations are clearly visible. The filament operates in this condition but with low efficiency.

B. Thoriated tungsten

Thoriated tungsten was chosen since it is extensively used as filament material. However, prior heating to 2850 K of the 0.002×0.040 in. filament caused substantial depletion of thorium, so that the properties of the filament were essentially those of tungsten.[9] At a UF_6 pressure of 4×10^{-5} Torr, the variation of negative-ion current with filament temperature produced a curve similar to that for rhenium, with a maximum UF_6^- current of 5.6×10^{-8} A at 1100 K. The ionization efficiency for these filaments is 1×10^{-3}, but prolonged exposure to UF_6 lead to erosion and failure of the filament.

The thermionic work function of the clean filament was found to be 4.4 eV, while the photoelectric work function yielded a value of 4.5 eV. As was the case for rhenium, UF_6 caused an increase in the work function of the metal. Allowing UF_6 into the system eliminated the photoelectron current due to a 200-nm light impinging on the filament surface, and the work function remained high (5.3 eV in one measurement) for some time even after removal of UF_6 vapor.

C. Platinum

The 0.005×0.029 in. platinum filament was heated to 1250 K for ~2 h in order for the filament to outgas, after which the thermionic work function was found to be 3.2 eV. Consistent results were difficult to obtain, however, probably due to contamination by hydrocarbons, although this platinum is the material used for filaments in several applications. Of the untreated filaments investigated, platinum proved the most efficient in producing UF_6^-. Again, at a UF_6 pressure of 4×10^{-5} Torr a curve similar to that in Fig. 2(b) was obtained; the maximum UF_6^- current being 2.2×10^{-5} A. The ionization efficiency is ~0.5, much greater than that of the metals considered above. In spite of this high surface ionization efficiency, platinum was regarded as unsuitable as a filament material due to the repeated failure of the ribbon in a short period of time. Failure is attributed to surface reactions which erode the filament and lead to the development of hot spots. Another major drawback to the use of platinum is that it begins to volatize at ~1570 K and melts at 2042 K.

D. Calibration of pressure gauge using rhenium filament

On the basis of the above results, rhenium was chosen for use in the pressure gauge. The maximum UF_6^- current produced in this filament varies regularly with UF_6 pressure up to 10^{-3} Torr. The extraction bias is fixed at 300 V, which is above the value where the diode emitter is space-charge limited.[10]

Calibration of the pressure gauge was accomplished by recording UF_6^- current versus UF_6 pressure, measured by the capacitance manometer. Figure 4 shows the results of these measurements for the clean rhenium filament at temperatures varying from 1403–1583 K. The linearity is excellent in the range 10^{-4}–10^{-3} Torr, where the capacitance manometer provides reliable readings. Although not directly substantiated by our experiments, it is expected that the linearity extends to much lower pressures where the UF_6 gauge still responds. Consistent with this expectation is the observed extrapolation of the

data in Fig. 4 to zero pressure on both axes. The gauge constant (in A $Torr^{-1}$ is given by the slope of the line and it can be seen that this does not vary within the operating temperature range. Similar results were obtained for filaments treated with acetylene. Pressure gauge constants for treated and untreated rhenium filaments are $1.7 \pm 0.1 \times 10^{-7}$ A $Torr^{-1}$ and $1.1 \pm 0.3 \times 10^{-4}$ A $Torr^{-1}$, where the error limits are the standard deviations from the respective means. Acetylene treatment does increase the ion current by a factor of ~1000. However, it has the disadvantage that the characteristic UF_6^- emission in Fig. 2 often disappears after a few hours of UF_6 exposure and electron emission alone is observable at higher temperatures. Repeated use of acetylene, on the other hand, can revive the filament for short periods.

III. DISCUSSION

This study demonstrates that the simple device of Fig. 1 is very sensitive to UF_6, producing currents which vary rapidly and in a reproducible fashion with UF_6 pressures below 10^{-3} Torr.

The effect of UF_6 on the rhenium filaments has not been fully characterized. However, it appears that UF_6 is chemisorbed on the rhenium in two forms, the first being UF_6^- and the second being decomposed UF_6. If one assumes that the heat of adsorption for UF_6^- on rhenium is similar to that on carburized platinum[11] given by Dittner and Datz[5] it can be calculated from simple chemisorption theory[12] that the radius of the adsorbed ion is approximately 3.5 Å. Assuming point charges, a Re–UF_6 dipole moment of 23.5 D is calculated, from which the contact potential at complete coverage is estimated to be 4.4 eV. This suggests ~20% coverage for the observed 0.8 eV increase in work function. Similar calculations for decomposed UF_6, in the form of UF_n and F (the fluorine being chemisorbed while the UF_n is physisorbed) yields a contact potential of 0.5 eV at 20% coverage. Some of the UF_6 leaves the surface as negative ions, but it would appear that the work function increase is due to both chemisorbed UF_6^- and chemisorbed fluorine, the physisorbed material being removed when the filament is heated. It has been suggested previously that a layer of halogen atoms on a metal surface produces a dielectric layer that effectively increases work function of the metal.[7]

Ionization efficiencies obtained in these experiments are much lower than those calculated from the Saha–Langmuir equation. This is in agreement with the findings of Dittner and Datz[5] for the formation of UF_6^- on clean platinum. The temperature dependence of the UF_6^- current exhibited in Fig. 2 can be understood in qualitative terms by the covering effect of UF_6.[7] When the rhenium is exposed to UF_6 the work function increases due to development of an adsorption layer on the surface as noted above. The temperature dependence of the UF_6^- yield at low temperature is consistent with this increase in work function, provided that it exceeds the electron affinity of UF_6 (5.2 eV).[2] At higher temperatures (1600–2000 K) decomposition of UF_6 on the filament surface competes with UF_6^- formation. Decomposition may react with the rhenium to further modify the work function. Hence the UF_6^- emission current may decrease or remain constant depending on the condition of the filament.

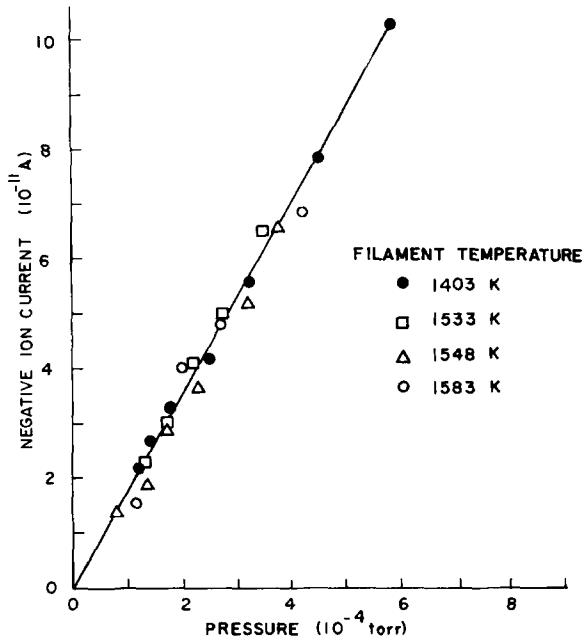

FIG. 4. Variation of UF_6^- current with pressure of UF_6 for a clean rhenium filament.

Conventional ionization gauges exposed to UF_6 are afflicted by an increase in work function which necessitates that they be operated at higher temperatures. One possible way of increasing the lifetime of an ionization gauge which is regularly exposed to UF_6 would be to replace the commonly used thoria-coated iridium filament with rhenium ribbon, which has a higher melting point and which appears to be fairly well behaved in the presence of UF_6. Schulz–Phelps gauges are unsuitable for UF_6 pressure measurements because both negative ions and electrons are registered as the emission current. Since emission currents in such gauges are typically 10^{-5}–10^{-6} A, ion emission can be a substantial fraction of the total. A problem which occurs with all filaments, however, is that the products of thermal decomposition of UF_6 can react with and erode the surface. In the case of rhenium, rhenium hexafluoride was detected by its positive-ion electron-impact mass spectrum.

As a UF_6 detector and pressure gauge, the device can be used for pressures below 10^{-3} Torr. Disadvantages of the device arise if a high pressure of UF_6 is sustained for too long a period of time. These are manifested by filament poisoning which may or may not be reversible with acetylene treatment. However, the simplicity of design and use of the gauge seems to adequately compensate for such difficulties which can be minimized by operating at the lowest possible temperature. Initially, it is advisable to calibrate the negative-ion current against an absolute gauge for the particular filament used. On the basis of this study, rhenium is the filament material suggested. There is no need to read filament temperatures since,

after exposure to UF_6, the maximum emission of UF_6^- at low filament currents can be located. Operation at this maximum guarantees that the gauge response will not change markedly with filament current.

ACKNOWLEDGMENT

This work was supported in part by the United States Department of Energy under Grant No. E(04-3)767-8.

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[8] This method does not lead to a precise value for the work function. It does, however, facilitate investigation of changes in work functions at fixed temperatures (see Ref. 7, pp. 20–24 for a complete discussion).
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[11] The heat of adsorption depends only on the work function of the surface, the $EA(UF_6)$, and the interaction energy between the ion and its electrical image. Since the last two terms are independent of the metal surface and the work function of Re (4.7 eV) is similar to the carbon-coated Pt surface (4.4 eV) it is felt this assumption is justified.
[12] For a complete discussion of simple chemisorption theory see, for example, (a) A. Clark, *The Theory of Adsorption and Catalysis* (Academic, New York, 1970), p. 169; or (b) Ref. 7, p. 52.