EFFECT OF FLUORINE AND OXYGEN ON THE WORK FUNCTION OF POLYCRYSTALLINE TUNGSTEN*

Pages 6
Code 1
CR-85160
Cat 26

[redacted]

CFSTI, H.C 3.00
M.F. .65

N68-27389

J. G. Bergman and R. E. Stickney
Department of Mechanical Engineering
and
Research Laboratory of Electronics
Massachusetts Institute of Technology, Cambridge, Massachusetts

I. Introduction

Recent indications that fluorine additives may be used to improve the performance of thermionic energy converters[1-4] have led to a number of experimental[1-7] and theoretical[8-10] investigations of the effect of these additives on the work function of various electrode materials. In these experimental studies, the fluorine has generally been introduced into the system as CsF rather than as pure F_2 gas because the latter is extremely reactive and, therefore, presents many practical problems. The results of the CsF studies are difficult to interpret because of the complex nature of binary adsorption, and they are questionable because the data often are not reproducible.[3,11] The existing data are not sufficient for formulating a detailed physical model of fluorine-electrode interactions or for making an accurate comparison of this additive with other possible additives (e.g., O_2).

The purpose of the present investigation is (a) to determine the dependence of the work function of tungsten on F_2 pressure and on emitter temperature, (b) to measure the desorption energy of F_2 on tungsten, and (c) to compare these data for F_2 with corresponding data obtained for O_2. Although we realized that it would be extremely difficult to work with gaseous F_2, this approach appeared to be necessary in order to obtain results that are not complicated by the presence of cesium or unknown contaminants.

Although the results presented here are not entirely satisfactory with respect to accuracy and reproducibility, we believe that they illustrate the general trends as well as some of the problems and anomalous effects that may be associated with fluorine additives. The mass spectrometer measurements suggest possible explanations for the fact that our results do not agree with the existing data discussed in Section II.

[redacted]

II. Discussion of Existing Data

[redacted]

A. Gaseous F_2 Studies

To the best of our knowledge, the only published data on the effect of gaseous F_2 on the work function of W is that of Metlay and Kimball.[12] The main conclusions of their study are:

---

*Work supported by the National Aeronautics and Space Administration (Grant NGR-22-009-091).

(This paper was presented at the Twenty-sixth Annual Conference on Physical Electronics, M.I.T., March 20-22 1966.)

1. Fluorine adsorbs so tenaciously on tungsten that temperatures as high as 2600°K are not sufficient to cause complete desorption (i.e., to clean the specimen).

2. The work function of fluorinated tungsten is $\sim$5.6 eV. (The data were not sufficiently reproducible to allow accurate determination of the work function.)

3. Fluorine reacts with tungsten to form a compound which evaporates at a rate of 1×10^{16} tungsten atoms per cm^2 per sec for temperatures of 2000-2400°K and F_2 pressures of 1×10^{-3} to 6×10^{-3} Torr.

B. Surface Ionization Studies

The first point listed above is in agreement with results reported by Dukel'skii and Ionov[13] in connection with their study of the negative surface ionization of KF. (A similar effect was observed to a small extent with NaCl, NaBr, and NaI by Johnson and Phipps.[14]) It is important to note, however, that this inability to desorb F from W at high temperatures <u>has not</u> been reported by other investigators who have performed similar experiments with KF and RbF (e.g., see Bailey[15]).

C. Thermionic Sudies Using CsF

The most detailed investigation of the additive CsF is that performed by Aamodt, Brown, and Nichols[5] for molybdenum emitters. Their results, together with those obtained by other investigators,[1-7] suggest that CsF molecules dissociate on the emitter surface to form an adsorbed layer of Cs and F atoms. Since Cs desorbs more rapidly than F because of its lower energy of adsorption, the net effect of CsF on a high temperature emitter is to coat the surface with F which, due to its high electro-negativity, results in a higher work function. (This increase in the emitter work function is often desirable in thermionic energy converters because it causes Cs to adsorb more tenaciously to the substrate, the result being that a lower Cs pressure is required to obtain a specific work function.)

III. Experimental Apparatus

The major components of the experimental apparatus are shown schematically in Fig. 1. The ultrahigh vacuum system is constructed primarily from 50 mm pyrex tubing and is evacuated by a Hg diffusion pump. Pressures in the range of 10^{-9} Torr are attained after thorough outgassing and several bakeouts at 300°C.

The pumping speed is controlled by a magnetically-operated valve. O_2 and H_2 are introduced into the system through diffusion-type leaks (K-B Glass Apparatus Co.). The pressures of F_2 and He are controlled by Granville-Phillips valves. A General Electric Monopole Partial Pressure Analyzer is used to determine the composition of the gas in the system.

Since we were unable to purchase F_2 gas in one-liter pyrex flasks which are so convenient for vacuum studies, we purchased a 0.5 pound tank of 98% pure F_2 gas from the Matheson Company. This tank is then used to fill a small container consisting of a stainless steel tube, 15 cm long

[redacted]

IV. Thermionic Emission Measurements

The cylindrical thermionic diode shown schematically in Fig. 1 was used in an attempt to determine the dependence of the work function of tungsten on temperature and on O_2 and F_2 pressure. A polycrystalline tungsten filament is located along the axis of a cylindrical anode which is divided into three separate sections. The end sections serve as guard rings, and only the emission current reaching the center section is recorded.

The emission current is measured as a function of filament temperature, O_2 pressure, and F_2 pressure. Although these measurements indicate that at equal pressures and temperatures a higher work function results for F_2 than for O_2, we are uncertain of the reliability of the data because (1) the reproducibility is poor, (2) a large amount of O_2 is included in the F_2 gas, (3) the accuracy of the pressure measurements is questionable because of the existence of F^+ desorption (Section III), and the unknown ionization efficiency of F_2, (4) the filament resistance varies with time. (The effect of halogens on metals is discussed by van Arkel.[18])

Another reason for questioning the validity of the data is that the F ions produced by electron bombardment of the collector may cause the flux of fluorine upon the filament to be substantially higher than the value calculated from the pressure. The applied potential is such that these ions are attracted to the filament. For example, consider the case where the yield is 1×10^{-3} ions per incident electron. If the electron current density is 1×10^{-3} amps per cm^2 (e.g., the work function is 4.6 eV and the temperature is $2000^\circ K$), then the resulting ion current density of 1×10^{-6} amps per cm^2 is equivalent to an F_2 pressure of $\sim 1 \times 10^{-8}$ Torr.

V. Contact Potential Measurements*

Because of the difficulties encountered in the thermionic experiments, we decided to change to the contact potential method. The advantages of this method are: (1) the change in filament resistance is reduced because prolonged exposure of the hot filament to F_2 are no longer required, (2) the effects of F ions desorbed by electron bombardment are minimized by omitting the extensive anode surfaces and by reducing the applied potentials, and (3) both the desorption energy and the work function may be measured.

Since the contact potential techniques employed here are similar to those discussed by Bosworth,[19] a brief description will suffice. Two tungsten filaments, 5 cm long and 1.27×10^{-2} cm in diameter, are placed perpendicular to one another with a gap of ~ 1 mm between their center sections. After aging the filaments, the I-V curve labelled "clean tungsten" in Fig. 3 is obtained in vacuum with filament #1 at $\sim 2400^\circ K$ and filament #2 at room temperature. With both filaments at room temperature, O_2 or F_2 is admitted until a pressure of $\sim 5 \times 10^{-5}$ Torr is attained.

---

*Since these measurements were performed after the Conference, the results were not discussed in our verbal presentation or in the abstract which was submitted to the A.P.S. Bulletin. In light of these new results, we now believe that some of the conclusions stated in the abstract are invalid.

At this pressure, filament #2 is heated to 2200°K for several seconds and then cooled slowly back to room temperature. The gases are evacuated from the system and I-V curves are again recorded with filament #1 at ~2400°K and filament #2 at room temperature. The horizontal shift of the O_2 and F_2 curves (Fig. 3) with respect to the "clean tungsten" curve represents the change in work function of filament #2 caused by the adsorbed gases. Each curve is constructed from the average data of at least three separate tests.

As shown in Fig. 3, the work function of filament #2 increases by ~1.7 eV when O_2 is allowed to adsorb upon the surface. Since this value agrees well with the expected value,[20] we are confident that the apparatus is functioning properly. The fact that the curve for F_2 indicates a work function change of 2.0 eV is not of particular interest because we are concerned primarily with the effect of F_2 on tungsten at temperatures above 1800°K. To investigate this point, we performed the desorption experiment described below.

If the current collected by filament #2 is held constant by varying the voltage between the filaments, then the work function change is equal to the voltage change. Hence, we may compare the desorption energies of O_2 and F_2 by measuring the change in voltage resulting from heating filament #2 to various temperatures for one minute. The data shown in Fig. 4 are the average of three separate runs at temperatures ranging from 1500°K to 2300°K in steps of 200°. Notice that the data for O_2 and F_2 are essentially the same except at 1500°K.

VI. Conclusions

The three possible explanations of the desorption data shown in Fig. 4 may be stated in the following manner. The desorption energy and the work function changes of F_2 on tungsten are (1) essentially the same as those of O_2, (2) greater than those of O_2 but are not observed in the present experiment because the O_2 impurities prevent adsorption of F_2 on the surface, (3) less than those of O_2 and therefore the F_2 data actually respresent the effects of the O_2 impurities. We do not favor the first explanation because it is extremely improbable that the behavior of two different gases would be almost identical at high temperatures. The second explanation is discarded because it is unlikely that O_2 can completely exclude the adsorption of F_2. We believe, therefore, that the third explanation is the most logical one. The two indications that F_2 actually adsorbs to some extent on the filament are the increased contact potential at room temperature (Fig. 3) and the lower contact potential at 1500°K (Fig. 4). The mass spectrum shown in Fig. 2 proves that we were successful in introducing F_2 into the system.

Although our results are far from being conclusive, they do serve as an indication that, contrary to the results reported by other investigators (Section II), F_2 does desorb completely from tungsten at temperatures below 2600°K. In both the thermionic and the contact potential studies, we were able to return the filament to its initial (i.e., clean) state after exposures to F_2. We conclude that the existing experimental results described in Section II may have been influenced by the problems which we also encountered in our thermionic experiment (Section IV).

and 2.5 cm in diameter. Bakeable metal valves are welded on both ends of the tube, and the outlet of one valve is joined to the vacuum system by a Kovar-to-pyrex connection. Before making this connection, the container is placed under a hood where it is thoroughly purged with F_2 and then filled to a pressure of approximately one atmosphere.

Our observations of the behavior of F_2 in the vacuum system will be described in considerable detail because they illustrate the difficulties which are encountered when working with this gas. As indicated in Fig. 1, the F_2 container is located outside the bakeout oven so that it will not be exposed to elevated temperatures. Before opening valve B (see Fig. 1), valve A is held open so that the pyrex tube between A and B may be evacuated. (Tube AB is heated slightly during the evacuation process because this accelerates the removal of adsorbed gases.) Valve A is then closed and B is opened momentarily, thereby allowing F_2 to fill tube AB. We may now introduce F_2 into the system by adjusting valve A.

The mass spectrum shown in Fig. 2 is typical of those observed when valve A is opened sufficiently to increase the system pressure to $\sim 5 \times 10^{-5}$ Torr. Although the largest peak is that of F_2, the O_2 and N_2 peaks are more than two orders of magnitude greater than their corresponding values measured with valve A closed. It appears, therefore, that O_2 and N_2 are impurities in the F_2 container. The detrimental effect of the presence of O_2 is discussed in Sections IV and V. Various attempts to reduce these impurities were unsuccessful.

Since F_2 may decrease the efficiency of the electron multiplier of the partial pressure analyzer, we have established the He peak as a reference. This is done by setting the He valve to obtain a constant pressure of 5×10^{-6} Torr (measured by the G.E. Ion Gauge with valve A closed). All pressures are reported here as equivalent N_2 pressures because the ionization efficiency of F_2 is not known.

Although the F_2 , O_2 , and N_2 peaks decrease rapidly when valve A is closed, the F peak decreases very slowly with time. In fact, F is often the largest peak when the gas inlet valves are closed; this condition persists even after subjecting the system to repeated bakeout and outgassing procedures. (We should note, however, that the F peak was extremely small initially, i.e., before F_2 was introduced into the system for the first time.) This observation is consistent with results reported by Moore[16] and by Robbins.[17] It appears that F ions are produced by electron bombardment of fluorinated surfaces. We shall return to this point in Section IV.

The HF peak is, most likely, the result of catalytic reactions occurring on the surfaces of the system. The magnitude of this peak increases when H_2 is introduced into the system and when the temperature of a tungsten filament is increased. Although HF resides in the system longer than F_2, O_2, and N_2, it is much less persistent than F.

Exposure of the system to F_2 results in the formation of a yellowish compound (most probably Hg_2F_2) on the walls of tube AB, the liquid nitrogen trap, and the diffusion pump. It appears, however, that these compounds do not affect the efficiency of the pump.

REFERENCES

1. W. A. Ranken, R. L. Aamodt, L. J. Brown, and B. D. Nichols, Adv. Energy Conversion 3,235 (1963).
2. C. H. Skeen, J. Appl. Phys. 36, 84 (1965).
3. D. Lieb, Thermionic Conversion Specialist Conference, 281 (1965).
4. A. A. Jester, Thermionic Conversion Specialist Conf., 93 (1964).
5. R. L. Aamodt, R. J. Brown, and B. D. Nichols, J. Appl. Phys. 33, 2080 (1962).
6. R. Langpape and A. Minor, Thermionic Conversion Specialist Conference, 87 (1964).
7. E. D. Wolf, Report on the 25th Annual Conference on Physical Electronics, 57 (1965).
8. E. N. Carabateas, Report on the 24th Annual Conference on Physical Electronics, 185 (1964).
9. M. Kaplit and G. L. Schrenk, Thermionic Conversion Specialist Conference, 195 (1965).
10. L. K. Tower, Thermionic Conversion Specialist Conference, 206 (1965).
11. R. L. Aamodt (Private communication).
12. M. Metlay and G. E. Kimball, J. Chem. Phys. 16, 779 (1948).
13. V. M. Dukel'skii and N. I. Ionov, J. Expt. Theoret. Phys. (U.S.S.R.) 17, 272 (1940).
14. A. A. Johnson and T. E. Phipps, J. Chem. Phys. 7, 1039 (1939).
15. T. L. Bailey, J. Chem. Phys. 28, 792 (1958).
16. G. E. Moore, J. Appl. Phys. 32, 1241 (1961).
17. J. L. Robbins, Can. J. Phys. 41, 1385 (1963).
18. A. E. van Arkel, in *Reine Metalle*, Springer Co., Berlin (1939), p. 35.
19. R. C. L. Bosworth, Proc. Roy. Soc. (New S. Wales) 79, 53 (1945).
20. R. V. Culver and F. C. Tompkins, in *Advances in Catalysis*, Vol. 11, Academic Press, New York (1959); see Table III on page 103.

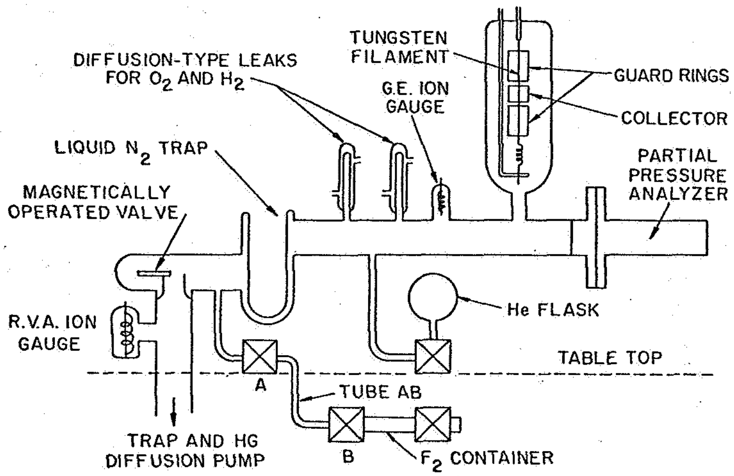

Fig. 1. Experimental Apparatus.

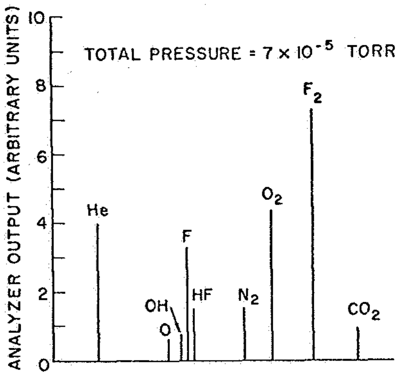

Fig. 2. Mass Spectrum (Traced from actual recording).

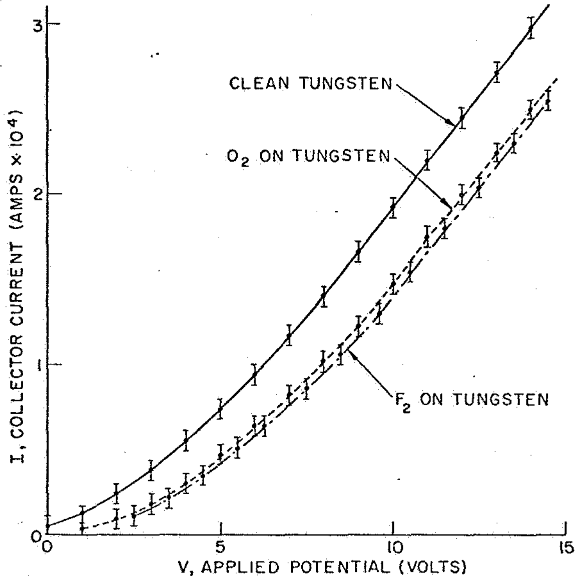

Fig. 3. Contact Potential Data.

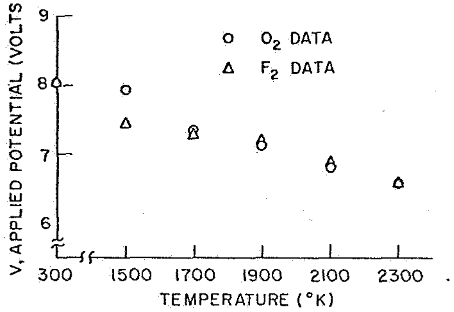

Fig. 4. Desorption Data.