The High-Temperature Effective Work Function of Chemically Vapor Deposited Rhenium on a Polycrystalline Molybdenum Substrate

D.R. Bosch and D.L. Jacobson

The work function of chemically vapor deposited rhenium, with a (0001) preferred orientation, on a molybdenum substrate was determined using the thermionic emission method. Data were collected as a function of time and temperature on temperature ramps from 1800 to 2600 K in 100-K increments. The effect of pressure on effective work function was demonstrated by introducing oxygen, nitrogen, and carbon dioxide through a precision leak valve into the vacuum emission vehicle. The effect of introducing various gasses was negligible. Also, no significant time or temperature dependence was observed. The sample yielded the maximum average effective work function, 5.08 eV, at 2100 K. The overall average effective work function was determined to be 5.02 eV.

Keywords:
molybdenum, polycrystal, rhenium, substrate, chemical vapor deposition

1. Introduction

THE thermionic energy converter has emerged as a leading candidate for generating electrical power for space-based applications. The effective work function of a potential emitter material is a critical parameter in this method of energy conversion. A material with desirable physical properties is one that exhibits a high bare (*i.e.*, clean uncessiated surface) work function. This article presents the effective work function data from a molybdenum-rhenium composite. This material combination takes advantage of the favorable electron emission characteristics of rhenium while using molybdenum for base emitter support, thus minimizing the required quantity of the more expensive rhenium. The effects of time, temperature, and various gasses on the effective work function of this composite were determined.

2. Sample Fabrication and Preparation

The molybdenum substrate/chemically vapor deposited (CVD) rhenium sample was provided by LORAL Electro-Optical Systems (300 North Halstead Street, Pasadena, California). A thick film of rhenium approximately 0.2 mm thick was deposited by Ultramet from the decomposition of rhenium chloride vapor on the molybdenum substrate. The diameter and length of the sample were 9.3 and 5.5 mm, respectively. A hohlraum (*i.e.*, black body hole) with a depth-to-diameter ratio of at least ten was electron discharge machined radially into the sample for accurate temperature measurements with a micro-optical disappearing filament pyrometer. The pyrometer was calibrated routinely to a National Institute of Standards and Technology standard tungsten strip lamp to ensure precise temperature measurements. The sample was tested in the as-deposited condition following a light grinding to remove excessive surface roughness. The CVD rhenium was assumed to approximate a (0001) preferred orientation.[1,2]

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3. Experimental Procedure

The bare work function was obtained from high-temperature electron emission measurements taken with a guard-

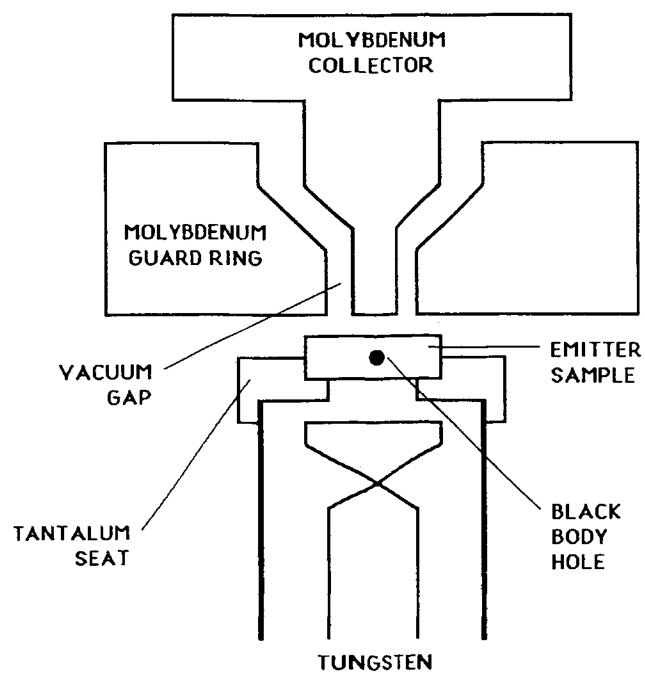

Fig. 1 Schematic of vacuum emission vehicle.[3]

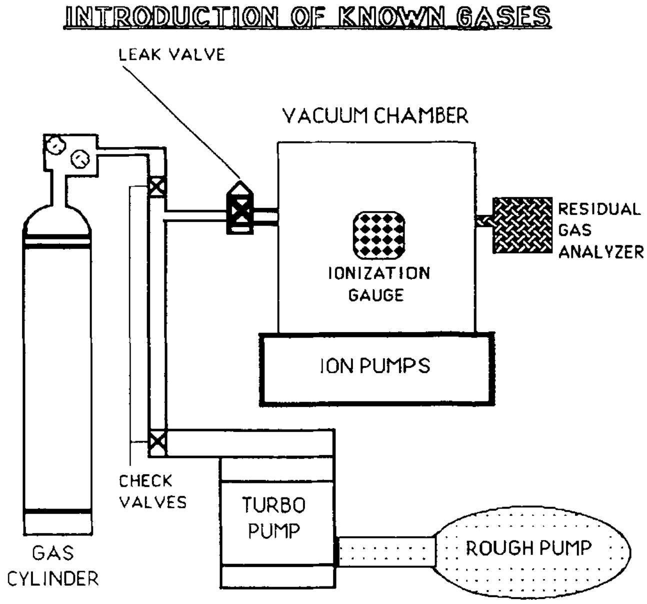

Fig. 2 Experimental configuration for leaking a known gas into the vacuum emission vehicle.[3]

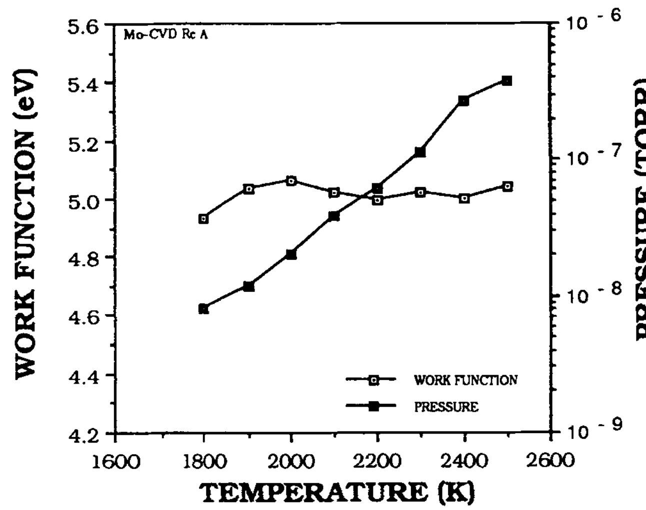

Fig. 3 Effective work function of molybdenum/CVD rhenium A and the total pressure during data acquisition.

Table 1 Effective Work Function of Two Tests on a Molybdenum/CVD Rhenium Composite (±0.05 eV)

	Experiment A		Experiment B	
Temperature, K	φ_E, eV	Pressure, torr	φ_E, eV	Pressure, torr
1800	4.93	8.04×10^{-9}	4.95	4.03×10^{-9}
1900	5.03	1.19×10^{-9}	5.04	5.83×10^{-9}
2000	5.06	2.04×10^{-9}	5.07	9.30×10^{-9}
2100	5.02	3.80×10^{-8}	5.08	1.59×10^{-8}
2200	4.99	6.06×10^{-8}	5.01	3.29×10^{-8}
2300	5.02	1.12×10^{-7}	4.98	7.09×10^{-8}
2400	5.00	2.68×10^{-7}	5.01	1.51×10^{-7}
2500	5.04	3.78×10^{-7}	5.03	2.25×10^{-7}

ringed vacuum emission vehicle (VEV), as shown in Fig. 1. The collector diameter was 3.5 mm with a 0.15-mm gap between it and the guard ring. The guard ring diameter was approximately 25 cm. The effective collector area was taken as the actual collector area plus one half of the area of the collector-guard ring gap.

The Richardson, Dushman equation was used to calculate the effective work function:

$$J_o = AT^2 \exp\left(\frac{-\varphi_E}{kT}\right) \qquad [1]$$

where J_o is the zero-field saturation current density (A/cm^2); A is a constant (120.4 A/cm^{2}K^2); T is the temperature (K); φ_E is the effective work function (eV); and K is the Boltzmann constant (0.861×10^{-4} eV/K). However, the current J_s that was measured with the vacuum emission vehicle was not the zero-field current density, J_o. To obtain J_o, the well-known Schottky equation was applied to compensate for the applied field effect:

$$\ln J_s = \ln J_o + 4.403\left(\frac{E^{0.5}}{T}\right) \qquad [2]$$

where J_s is the electron saturation current density (A/cm^2), and E is the applied field (V/cm). Equation 1 and 2 were combined to yield:

$$\varphi_E = kT \ln\left(\frac{A\,T^2}{J_s}\right) + 3.79 \times 10^{-4}\,E^{0.5} \qquad [3]$$

The effective work function as a function of time and temperature was calculated from Eq 3.

The effect of residual gasses was ascertained by precision leaking individual gasses into the vacuum emission vehicle with the apparatus shown in Fig. 2. The work function was determined in the presence of oxygen, nitrogen, and carbon dioxide at partial pressures between 10^{-7} to 10^{-9} torr.

A polycrystalline rhenium sample that was fabricated from a 0.5-in. rhenium rod acquired from Sandvick Rhenium Alloys, Elyria, Ohio. It served as a standard to establish the accuracy of the vacuum emission vehicle measurements.

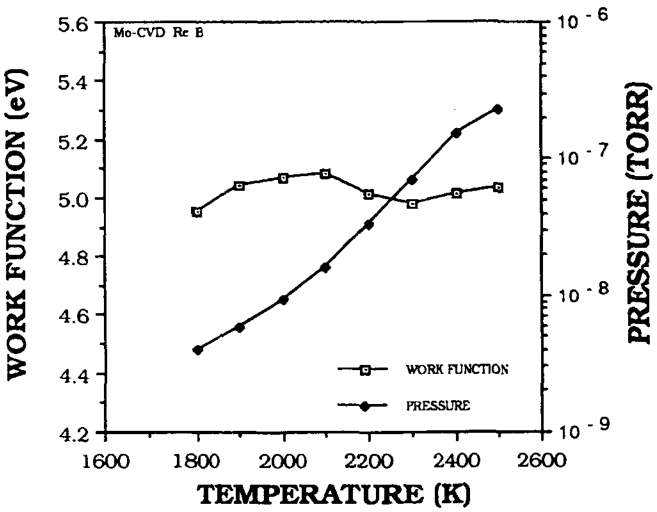

Fig. 4 Effective work function of molybdenum/CVD rhenium B and the total pressure during data acquisition.

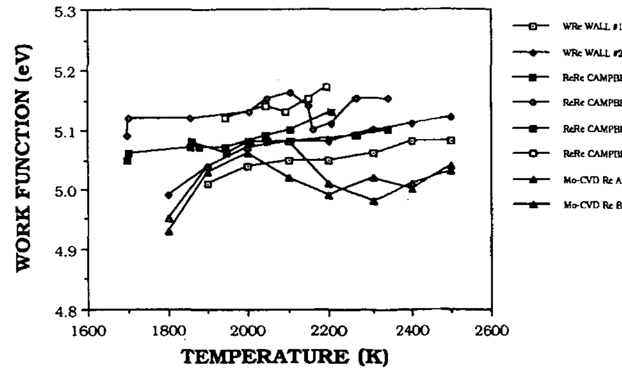

Fig. 5 Effective work function of molybdenum/CVD rhenium compared to experimental data.

4. Error Analysis

Temperature was the most critical of the measurements made in this high-temperature electron emission study. A small error in the measured temperature will result in a substantial error in the calculated effective work function. It was estimated that with careful control the temperature measurement was accurate within ±5 K. The pyrometer and viewport combination was calibrated before every fourth experiment to ensure accuracy. The ±5 K uncertainty in the temperature measurement resulted in an error of approximately ±0.03 eV.

Uncertainty in collector current and collector area measurements added about ±0.02 eV to the overall error. Thus, the reported effective work functions are estimated to be accurate within ±0.05 eV. An uncertainty analysis of this experimental apparatus is presented. The data reported in this work were reproducible to less than ±0.01 eV. Thus, the precision of the experiment was much higher than the estimated accuracy.

5. Results

The results for the molybdenum/chemically vapor deposited rhenium sample are listed in Table 1 and plotted in Fig. 3. The first experiment on the molybdenum/chemically vapor deposited rhenium sample, signified as Mo-CVD Re A in Fig. 3, yielded effective work functions that were mostly constant throughout the temperature range. However, the total pressure was considered rather high compared to some earlier studies. It is known that high gas pressures can significantly effect the high-temperature work function behavior of some materials.[1] Consequently, another experiment was conducted following a more extensive bake-out procedure. The results of the second experiment, signified as Mo-CVD Re B, are shown in Fig. 4.

Oxygen, nitrogen, and carbon dioxide were introduced through a precision leak valve to explore and understand the effects of residual gasses. None of these gasses had an effect on the measured effective work function during either of the experiments.

6. Discussion

The work function values obtained in Experiment 1 (Fig. 3) and Experiment 2 (Fig. 4) were identical. Pressure data obtained during the two experiments indicated that there was a slight reduction in total pressure throughout the temperature range. Furthermore, inputting gasses did not affect the effective work function measurements in these experiments.

Evidence of molybdenum substrate sublimation was observed. A thin film of molybdenum was noted on the observation viewport and on the internal stainless steel surfaces of the vacuum containment chamber. This sublimation was attributed to the sample having been operated at excessive temperature with respect to the level of vacuum within the vacuum emission vehicle. The sublimation most certainly occurred during the extensive high-temperature, long-term bake-out procedure implemented prior to the experiments. The vapor pressure versus temperature graph indicates that limiting the temperature to approximately 2000 K would have been required to circumvent significant molybdenum sublimation at the vacuum level produced within the vacuum emission vehicle.[2] It should be noted that the work done on pure polycrystalline molybdenum by Wall resulted in no noticeable molybdenum sublimation even though the samples were tested at a maximum temperature of 2500 K.[3] This was attributed to the significantly reduced high-temperature annealing time.

Figure 5 presents a comparison between the data that were obtained during these two experiments and tests by Campbell[4] of chemically vapor deposited rhenium on a rhenium substrate and tests by Wall[5] of chemically vapor deposited rhenium on a tungsten substrate. The differences between the two sets of data were attributed by Wall to greater total residual gas pressures. It was assumed that the differences in bare work functions in this study and in Campbell's were also at least partially attributable to residual gas pressure. Additionally, the differences in experimental error between the two experimental configurations may have been a contributing factor in the observed dissimilarities.

7. Conclusion

The effective work function of chemically vapor deposited rhenium on a substrate of polycrystalline molybdenum was studied. The work function results were reported for two experiments over a temperature range from 1800 to 2600 K. The reported bare work functions were greater than the values for polycrystalline rhenium.[6] Also, the work function values for chemically vapor deposited rhenium on a polycrystalline molybdenum substrate were observed to be similar to the reported values for chemically vapor deposited rhenium on substrates of rhenium and tungsten.

An extensive bake-out procedure was followed to minimize residual gas effects during testing. The effect of pressure on effective work function was established by introducing oxygen, nitrogen, and carbon dioxide through a precision leak valve into the vacuum emission vehicle. No effect was observed for any of the samples at partial pressures between 10^{-9} and 10^{-7} torr. No significant time or temperature dependence was observed for any of the tests.[7]

Acknowledgments

This work was funded by the Wright Research and Development Center under contract number (AFAPL) F33615-87-C-2706, which was awarded to LORAL Electro-Optical Systems of Pasadena, California. The authors thank Dr. Ralph N. Wall for his review of this manuscript.

References

1. R.N. Wall and D.L. Jacobson, *Metall. Trans.*, Aug 1991.
2. G. Wahl and P. Batzies, in IEEE Conference Record of the Thermionic Conversion Specialist Conference, Miami, Oct 26-29, 1970.
3. R.N. Wall, "High Temperature Electron Emission and Vaporization of Selected Refractory Materials," Ph.D. dissertation, Arizona State University, Tempe, 1989.
4. A.E. Campbell, Jr., R.W. Hammerdinger, and D.G. Worden, in IEEE Conference Record of the Thermionic Conversion Specialist Conference, Palo Alto, Oct 30-Nov 1, 1967.
5. R.N. Wall and D.L. Jacobson, *J. Mater. Eng.*, Vol 11, 1989, p 197.
6. V.S. Fomenko, *Handbook of Thermionic Properties*, Plenum Press, 1966.
7. R.N. Wall, D.L. Jacobson, and D.R. Bosch, *High Temp. Sci.*, Vol 30, 1991, p 95.