A WF6-CVD tungsten film as an emitter for a thermionic energy converter: II. Electron and Cs⁺-ion emission from WF6-CVD tungsten films

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A WF₆-CVD TUNGSTEN FILM AS AN EMITTER FOR A THERMIonic ENERGY CONVERTER II. Electron and Cs⁺-ion emission from WF₆-CVD tungsten films

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The workfunction of as-deposited WF₆-CVD tungsten films in vacuum is found to be $\phi_e = 4.3$ eV. This value corresponds with the workfunction of the (111) tungsten crystal faces. From the cesiated workfunction a bare workfunction of $\phi_e = 4.3$ eV is deduced as well. The power density produced by a thermionic energy converter using a WF₆-CVD emitter at a temperature of 1673 K is found to be 1.9 W/cm². The barrier index at 1673 K is $V_b = 2.06$ V. For the plasma drop a value of $V_d = 0.6$ V is found.

1. Introduction

As indicated in part I of this paper [1], using the WF₆ chemical vapour deposition (CVD) process, it is possible to deposit a textured tungsten film. The surface of the as-deposited film is composed of (111) crystal faces. The film has a (100) fiber texture. The electron emission of the as-deposited film in vacuum and in a cesium atmosphere will be described in sections 3 and 5 respectively. The Cs⁺-ion emission is described in section 5. The properties of an as-deposited WF₆ CVD tungsten film as an emitter in a thermionic energy converter (TEC) will be described in section 4. Before the start of the emission measurements, the emitter surface was characterized and the results were presented in part I of this paper [1]. Figs. 4a and 4b of part I show the microstructure prior to the emission experiments. After all emission experiments were carried out the emitter had.
been at 1673 K for about 2000 h. The surface and a cross section of the emitter film after these experiments are shown in fig. 1.

2. A research diode with an as-deposited WF₆-CVD tungsten emitter

The tungsten substrate coated with an as-deposited WF₆-CVD tungsten film, was brazed to a molybdenum emitter substructure using tantalum-40%cobalt as a filler material. The molybdenum substructure was built into a research diode in such a way that the CVD tungsten emitter faced a molybdenum collector. A schematic view of the diode is given in fig. 2. The TEC principles were described in part I of this paper. The various parts of the research diode are interconnected using stainless steel flanges joined by copper gaskets. The diode is situated in an evacuated bell jar in order to protect it against high temperature corrosion in air. The active area of the collector is 1.3 cm². The emitter also has a cross section of 1.3 cm², but due to the rough surface with its pyramidal morphology, the actual emitter surface is enhanced (maximum active area: 2.3 cm²). Emitter, collector and cesium reservoir temperature are automatically measured and controlled using Pt/Pt-10%Rh thermocouples. The emitter temperature can be maintained constant within 5 K, the collector temperature within 3 K and the cesium reservoir temperature within 1 K. The emitter thermocouple reading has been compared to the temperature measured by optical pyrometry via the sapphire window. The thermocouple readings are considered to be the most reliable. In order to achieve a sufficiently high emitter temperature (up to 1823 K) a 0.5 mm diameter tungsten electron gun is used. The interelectrode distance can be varied continuously, even during operation, in the range of 0.01 to 1 mm. The bell jar protecting the diode is evacuated by an oil diffusion pump. The diode itself is evacuated by a separate pumping system using a turbo-molecular pump and for the ultimate vacuum an AEI triode ion-getter pump (120 l/s). Before the diode is assembled all parts are thoroughly cleaned with freon, alcohol and distilled water.

3. Electron emission in vacuum

The diode was outgassed over a period of 16 days. The emitter temperature was gradually raised to an ultimate value of 1823 K and the ultimate pressure at this high temperature was 10⁻⁸ mbar. During outgassing the electron emission from the CVD tungsten film was monitored. The electron emission did not change during the last three days of the outgassing period. The electron emission measured at a small interelectrode distance (d = 0.01 mm) in the retarding and in the Schottky range is given in fig. 3. In fig. 3a, apart from the measured current density, also the Boltzmann line is indicated. This line represents the theoretical maximum of the electron current density at voltage $V_0$, at the specified emitter temperature ($T_e$); in formula:

$$I = 120T_e^2 \exp \left( \frac{V_0}{kT} \right).$$  

This means that the barrier index ($V_b$, see eq. (1) in part I) is zero at the Boltzmann line. In fig. 3a the Boltzmann line is shifted 4.45 V in order to get the line in the depicted voltage range. At a high external electrical load the current through the diode is low. As the interelectrode distance is small (d = 0.01 mm) there is no space charge during the electron emission measurement be-
Fig. 3. Electron emission current density ($I$ in A/cm$^2$; the emitter area is 1.3 cm$^2$) at 1788 K emitter temperature in a vacuum of $10^{-8}$ mbar. The collector temperature was 833 K and the interelectrode distance was 0.01 mm. The emitter is an as-deposited WF$_6$-CVD tungsten film, the collector is made of polycrystalline molybdenum. In (a) the current density in the retarding range is shown. The straight line is the Boltzmann line ($V + 4.45$ V). In (b) a Schottky plot is shown.

The measurement is done in vacuum, so there is no plasma present. Thus, the plasma drop is zero: $V_d = 0$, thus the barrier index at the conditions where the voltage–current characteristics are measured, is equal to the collector workfunction: $V_h = \phi_c$. The current density through the diode is thus governed by the sum of the voltage across the load $V_0$ and the workfunction of the collector $\phi_c$, see fig. 2, part I. In this case the current density is an exponential function of the output voltage ($V_0$). The potential difference between this measured line and the calculated Boltzmann line is the value of the workfunction of the collector $\phi_c$. So from the emission in the retarding range, the workfunction of the polycrystalline molybdenum collector is found to be $\phi_c = 4.5$ eV.

In fig. 3b the logarithm of the current density is plotted as a function of the square root of the applied accelerating electric field. At high electric field the current density becomes saturated. Extrapolation from the saturation region to zero field strength. Using this saturated current density $I_s$, the workfunction of the emitter can be calculated from a rearranged Richardson equation (eq. (2), part I):

$$\phi_e = kT_e \ln\left(\frac{120T_e^2}{I_s}\right),$$  

(2)

where $k$ is the Boltzmann constant and $T_e$ is the emitter temperature. The emitter area is taken to be 1.3 cm$^2$. Thus the workfunction of the WF$_6$-CVD tungsten is found to be $\phi_e = 4.3$ eV.

4. As-deposited WF$_6$-CVD tungsten as emitter in an energy converter

At temperatures of 1573 and 1673 K voltage–current characteristics at various cesium reservoir temperatures were determined [3], see fig. 4. A Tektronix 577D2 curve tracer with sense connection, applying an alternating voltage (50 Hz) to the diode was used. In order to avoid the effects of the electrical resistance of the leads, a four-point method is utilized [4]. The cross section of emitter
Fig. 4. Voltage–current characteristics at various cesium reservoir temperatures (indicated in K, steps of 10 K). The emitter is an as-deposited WF₆-CVD tungsten film, the collector is made of polycrystalline molybdenum. In (a) the emitter temperature is 1573 K, the collector temperature is 903 K and the interelectrode distance is 0.6 mm. (---) Boltzmann line \((V + 2.2 \text{ V})\). In (b) the emitter temperature is 1673 K, the collector temperature is 956 K and the interelectrode distance is 0.6 mm. (---) Boltzmann line \((V + 2.2 \text{ V})\).

Fig. 5. Power density \(P\) (in W/cm²; the emitter area is 1.3 cm²) as a function of the load voltage and as a function of the interelectrode distance. In (a) the emitter temperature is 1673 K, the collector temperature is 956 K and the cesium reservoir temperature is 573 K. The interelectrode distance is 0.6 mm. In (b) the emitter temperature is 1573 K, the collector temperature is 903 K and the cesium reservoir temperature is 653 K. The load voltage is 0.2 V.

Table 1
Experimental conditions at which the maximum power density was measured

<table>
<thead>
<tr>
<th>(T_e) (K)</th>
<th>(T_c) (K)</th>
<th>(T_{cs}) (K)</th>
<th>(d) (mm)</th>
<th>(V_0) (V)</th>
<th>(P) (W/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1473</td>
<td>848</td>
<td>503</td>
<td>0.5</td>
<td>-0.20</td>
<td>0.6</td>
</tr>
<tr>
<td>1573</td>
<td>903</td>
<td>563</td>
<td>0.6</td>
<td>-0.27</td>
<td>1.0</td>
</tr>
<tr>
<td>1673</td>
<td>956</td>
<td>573</td>
<td>0.6</td>
<td>-0.50</td>
<td>1.9</td>
</tr>
</tbody>
</table>

and collector is taken to be the active electrode area (1.3 cm²). At each emitter temperature the calculated Boltzmann line (eq. (1)) is indicated. From the difference between the measured voltage–current characteristic and the calculated Boltzmann line the barrier index \(V_b\) is calculated. The power density produced by the diode can be calculated from the voltage–current characteristics. The power density \((P)\) is obtained by multiplying the load voltage \((V_0)\) with the current density \((I)\): \(P = I \left| V_0 \right|\). In fig. 5a the power density is shown as a function of the load voltage. The influence of emitter, collector and cesium reservoir temperatures as well as the interelectrode distance are investigated [3]. The influence of the interelectrode distance (at a constant load voltage) is shown in fig. 5b. An optimal interelectrode distance is found at 0.4 mm. At operating conditions for...
practical applications the optimum interelectrode gap does not vary much (±0.15 mm) when the emitter and/or the collector temperature are varied. The optimum collector temperature depends on the emitter temperature. The characteristics in fig. 4 are taken at the optimal collector temperature. In achieving a high power density, the emitter temperature is the limiting factor. The maximum power density as a function of the emitter temperature is indicated in fig. 6. The experimental conditions at which this power density is measured are indicated in table 1.

5. Electron and Cs⁺-ion emission in a cesium atmosphere

The electron emission from the as-deposited tungsten films is measured in a cesium atmosphere. At the chosen emitter and cesium reservoir temperatures there are more Cs⁺-ions than electrons in the interelectrode space, in other words we have ion-rich conditions [2]. An example is shown in fig. 7a. It is obvious that saturation occurs, even when a deaccelerating load voltage is applied. Workfunctions are calculated from the rearranged Richardson equation (see eq. (2)) using the saturation current density I₆. In fig. 8 workfunctions calculated this way are depicted in a Rasor plot. The workfunctions are given as a function of the reduced temperature, that is the ratio of emitter temperature and cesium reservoir temperature. Workfunctions of the emitter can also be obtained in an alternative way. It is frequently assumed that the current density at the knee of the voltage–current characteristic (see fig. 4) corresponds to the saturated current density at zero field strength, I₆ [5]. From this current density at the knee and the rearranged Richardson equation (see eq. (2)) the workfunction can be calculated. Values obtained this way are presented in a Rasor plot, see fig. 8.

At electron-rich conditions, the Cs⁺-ion current from the as-deposited tungsten film is measured, see fig. 7b. A very high negative voltage is applied...
to this end. As a result the electric current through the diode changes sign. If this current is caused by electron emission from the collector, this current is expected to increase with increasing cesium reservoir temperature, while keeping the other temperatures fixed. However, the measured current is found to decrease when the cesium reservoir temperature is raised, so it is not caused by the electron emission from the collector. Clearly, the collector temperature is low enough and the collector workfunction high enough to produce only a negligible electron emission. The decreasing current at increasing cesium reservoir temperature can be explained by the fact that at a constant emitter temperature, when the cesium reservoir temperature is raised, the workfunction of the emitter is reduced. An emitter with a lower workfunction will ionize less Cs atoms, thus the Cs\(^{+}\)-ion current will decrease. The Cs\(^{+}\)-ion current is considered not to be influenced by the absence of guard-rings [2], because the Cs\(^{+}\)-ion current is the highest at regions where the workfunction is high. This implies it is the highest at regions with the highest temperature. The workfunction of the emitter can be calculated from the measured Cs\(^{+}\)-ion current density and the Saha–Langmuir equation [2]. Workfunctions calculated in this way are depicted in the Rasor plot shown in fig. 8.

### 6. Discussion

The electric power density of the TEC at 1673 K is found to be 1.9 W/cm\(^2\). This corresponds to an efficiency of about 14% [3]. Of the various methods used to measure the workfunction of the emitter, the workfunction calculated from the the Cs\(^{+}\)-ion current, is considered to be the most reliable. However, the Cs\(^{+}\)-ion current was measured at conditions where the ignited mode condition was not yet established. Under ignited mode conditions the emitter surface is cleaned by Cs\(^{+}\)-ion bombardment. During the Cs\(^{+}\)-ion current measurement, prior to this ignited mode operation, the emitter surface may still have been contaminated. For this reason the real emitter workfunction will probably be a little higher (about 0.2 eV) than indicated in fig. 8. The electron emission current measurements (see fig. 7a) are carried out immediately after operation of the diode in the ignited mode. For that reason the emitter surface is assumed to have been very clean during the electron emission current measurement. However, the electron emission current measurement may have been affected by the absence of guard-rings. Without guard-rings the emission from emitter substructure parts at lower temperature than the emitter temperature may not be negligible. Taking both effects into account, a bare workfunction of \(\phi_0 = 4.3\) eV is determined [3,5] from the cesiated workfunctions depicted in fig. 8. The barrier index (see eq. (1), part I) at 1673 K is deduced from the voltage–current characteristics and the Boltzmann line in fig. 4. Its value is found to be \(\phi_b = 2.06\) V.

The workfunction found for the cesiated polycrystalline molybdenum collector corresponds well to that found by other investigators [2,3]. At the conditions given in fig. 4b the workfunction of the collector is found to be \(\phi_c = 1.46\) eV. From the
barrier index and the collector workfunction a plasma voltage drop of \( V_d = 0.60 \) V is deduced.
This value is considered to be rather high compared to the value of \( V_d = 0.4 \) eV which is desired for practical applications of a thermionic energy converter.

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References