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APPLICATION OF MICROFABRICATION TECHNOLOGY TO THERMIONIC ENERGY CONVERSION

Final Report for the Period April 1, 1979—March 31, 1981

By
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April 1981

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U. S. DEPARTMENT OF ENERGY

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**APPLICATION
OF MICROFABRICATION
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TO THERMIONIC
ENERGY CONVERSION**

FINAL REPORT
FOR THE PERIOD 1 APRIL 1979 TO 31 MARCH 1981

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ABSTRACT

The program reported here on the application of microfabrication technology to thermionic energy conversion was originally designed to cover a three-year period but was terminated at the end of the second year for budgetary reasons. The first-year effort emphasized study of the kind of microstructures that could improve the performance of thermionic converters. Two ideas considered to have a fair chance of success emerged from this study.

- Use of a very closely spaced diode to eliminate the space-charge limitation of electron flow from emitter to collector, cesium vapor being used to control the work function of the emitter.
- Use of field emission electrons, injected into a relatively large diode gap from microcathodes built into the collector, to produce ions to neutralize the space charge. The gas in the diode gap would be a mixture of cesium (to control the emitter work function) and xenon to optimize the ionization.

A number of schemes were attempted to build closely spaced diodes with spacing in the 1 to 5 μm range, which overcame the problems of lateral differential expansion, surface irregularities on the electrodes, and heat loss down the pillars holding the gap spacing.

Theoretical studies on using field emitter electrons to produce the space charge neutralizing ions showed that this approach was feasible. However, the program was terminated before any experimental work could be initiated in this area.

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I INTRODUCTION

This is the final report in a theoretical and experimental program to evaluate those areas where three-dimensional microfabrication techniques could be of value in improving methods of thermionic energy conversion. SRI International (SRI) conducted the program for the Division of Fossil Fuel Utilization, Department of Energy (DOE), under Contract DE-AC02-79ET15423. The program was originally intended as a three-year effort but was terminated at the end of the second year; hence the intended scope of work was not completed. The program was divided into three parts, each to have taken approximately one year:

- A general theoretical study of microstructures that could enhance the performance of thermionic energy converters.
- A specific study both theoretical and experimental, of the closely spaced diode system.
- A specific study both theoretical and experimental, of field emission for creating ions for space-charge neutralization.

Because of the early termination of the program, no experimental work was carried out on the field emission device.

In thermionic energy conversion (TEC), assuming the emitter and collector temperatures are specified by the application, we must simultaneously control several physical parameters to ensure a large power output at high efficiency:

- (1) The work function of the emitter surface, which must be uniform and optimized to some specific optimum value (ϕ_E).
- (2) The work function of the collector (ϕ_C) which should be as low as possible.
- (3) The impedance of the interelectrode gap, which must be as low as possible. This entails removing any space-charge limitation to current flow, and minimizing any energy loss mechanisms as electrons cross the gap.

- (4) The transfer of material from the hot emitter electrode to the cold collector, which will close the interelectrode gap during operation and must be very low particularly if small gaps are necessary.

In conventional TEC devices, a relatively wide gap filled with cesium vapor is used to control simultaneously Items 1, 2, and 3. For Item 4, refractory metals (tungsten, molybdenum) are used for the basic electrode materials in the form of single crystals or oriented polycrystals to avoid patches of differing work function. The material used to control the work function of the electrodes (cesium) is supplied from an external vapor source, such as a heated cesium reservoir, rather than from the interior of the electrode as in conventional dispenser cathodes. Cesium ions that form on contact with the hot emitter surface are adsorbed on the emitter surface for a certain time and are then injected into the gap, where they serve to neutralize the electron space charge. Cesium condensing on the collector surface forms an equilibrium layer of several monolayers thick which serves to form the low work function collector surface. The temperature of the collector must be above that of the cesium reservoir vapor so that cesium condenses on the colder collector surface. The vapor pressure over the adsorbed layer (a few monolayers of cesium) at the collector temperature is then in equilibrium with the vapor pressure over the cesium reservoir.

We see, therefore, that cesium is used to control three distinct functions but with only a single control variable: namely, the cesium vapor pressure. Nevertheless, with appropriate compromises the system works remarkably well. The major drawback is that in order to optimize the current flow, the cesium vapor pressure is sufficiently high that the energy lost by the electrons through collision processes in crossing the gap lowers the efficiency by a significant fraction. This loss is manifested as a voltage drop across the plasma called the "arc drop". Electrons elastically reflected at the collector surface and injected back into the plasma region may lose more of their energy to the plasma, making it unavailable for conversion and further increasing the effective arc drop.

It was therefore considered that microfabrication technologies might be useful in three general areas.

- Structuring the collector electrodes to reduce or eliminate the reflection of electrons at the collector surface.
- Structuring the emitter electrodes to increase their effective surface area, improve their thermionic emission characteristics, or provide a close third (gridded) electrode.
- Finding means to neutralize the space charge such that the energy loss is substantially less than in existing methods.

In the first year of this program, we considered a number of possible microstructure arrangements for achieving these ends and selected two for experimental fabrication: the very closely spaced diode and the production of neutralizing ions by the injection of field-emitted electrons injected from microstructures built into the collector. In the second year, we attempted to solve the problems associated with building very closely spaced structures.

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II PRELIMINARY SURVEY

Several types of microstructures suitable for thermionic energy converters were surveyed:

- Microstructured emitters
- Microstructured collectors
- Microstructuring for fabricating closely spaced diodes
- Microstructures for injecting ions into the interelectrode space.

A. Microstructured Emitters

Several ideas were considered that entailed forming reentrant structures on the surface of the emitter. Certain structuring with appropriately sized openings can be used to obtain an effective "A" value for the Richardson equation that is closer to the theoretical value of 120 and thus gives greater emitter currents at a given temperature. However, with the advent of patch-free surfaces of oriented polycrystals, the advantages of such structures appeared marginal.

Another possibility is to structure the surface area of the emitter so as to increase its emitting surface area over the projected electrode area. It appears, however, that in order to be effective the structuring must be large compared to the sheath thickness between the plasma and the emitter; otherwise the sheath will simply smooth-out the structured surface in regard to electron flow. Large scale structuring ($>10\text{ }\mu\text{m}$) was not considered in the realm of microfabrication.

Another scheme, suggested by F.N. Huffman of Thermo-Electron Corporation, is shown in Figure 1. The microstructures on the emitter consisted of an array of small refractory metal elements insulated from the emitter by a refractory oxide material. The array of metal elements

FIGURE 1 EMITTER-IONIZER ELECTRODE ARRAY ELEMENT CONFIGURATIONS
FOR SURFACE IONIZATION TRIODE

essentially forms an electrically floating grid spaced a small distance from the emitter. Since the temperature of the grid elements is close to that of the emitter, surface ionization of the cesium takes place at the surface and the tips are charged negative. Thus the ions are held in a region close to the tip, which, being close to the emitter, permits a large number of electrons to flow without space-charge interaction. Such a device is called a surface ionization triode (SIT). The SIT concept has great merit; but we regretfully concluded that development of the fabrication technology, although quite feasible, would require resources much larger than the program funding allowed for microfabrication services to other DOE contractors. A separate program to build such emitter structures might be considered for future work.

B. Microstructured Collectors

The electrons arriving at the collector have very low energies, of the order of 1 eV. Such electrons have a high probability of being elastically reflected from the emitter surface and returned to the interelectrode space. Thus an electron may strike the collector surface several times before being absorbed. This has the effect of increasing the electron density in the gap region, requiring more ions to neutralize the electron-space charge, and, as a result, possibly increasing the arc drop in a cesium neutralized plasma.

An array of tiny holes can be drilled in the collector so that electrons are absorbed in a manner analogous to black body holes absorbing light. Discussions with experts on the plasma diode revealed, however, that electron reflection at the collector is not now considered a major source of efficiency loss in thermionic converters, when compared with the energy used to create ions to neutralize the space charge and the energy dissipated in the plasma arc drop.

C. Microstructures for Fabricating Closely Spaced Diodes

Neutralization of the electron space charge by simply using a closely spaced diode is most attractive because no energy is lost in forming ions or in collision processes as the electrons cross the gap. Cesium vapor can be used to control the work function of emitters made from a refractory metal (such as tungsten or molybdenum) provided its vapor pressure is such that the mean free path for electron-cesium collisions is much greater than the gap spacing. The collector work function takes a value dependent on the material of which the collector is made and the collector temperature, and is always low. A detailed analysis of this type of diode was carried out using electrode temperatures compatible with a flame-generated heat source such as might be useful for a topping cycle in fossil-fuel power plants or in utilizing organic waste gases from petrochemical manufacturing plants. These results are reported in detail in Section III below. For $T_{\text{Emitter}} = 1650$ K, and $T_{\text{Collector}} = 700$ K, the theoretical analysis revealed several significant aspects of the microstructured diode. First, with a $1\text{-}\mu\text{m}$ spacing and with a cesium pressure (~ 3 torr) needed to attain the desired work function of about 2.4 eV, the atom/atom mean free path is greater than the electrode spacing. The same is true for the electron/atom mean free path. Thus, we expect the internal voltage drop caused by plasma resistance to be insignificant compared to the diode voltage. The second significant aspect can be related to space-charge conditions. Because of the small spacing, cesium ions are not needed in the gap for space-charge neutralization. In other words, the saturated thermionic emission current is not space-charge limited to any significant extent. Thus, by virtue of these two features of close electrode spacing, the cesium is required only to control the emitter work function and is relieved of its other role of providing space-charge neutralization in the gap, where it also contributed a negative effect of plasma resistance. A preliminary analysis yielded a maximum efficiency of 16 percent, at which the electrical power was about 11 W/cm^2 . We

showed that to be able to take advantage of this operational capacity, the electrode spacing must be in the range of 1 to 5 μm . Fabrication of such closely spaced diodes presents several severe problems:

- The insulating pillars must be able to hold the spacing at about 1 μm to be able to function at high temperatures, in a cesium atmosphere, and with a large temperature differential between its ends.
- Under the above conditions the pillars must also be sufficiently electrically and thermally insulating so that no significant power is lost down the pillars from these sources.
- The contours of the electrodes must follow each other to a precision of much less than the height of the pillars to prevent shorting between pillars. That is, they must be parallel within 1000 Å.
- A scheme must be developed whereby the stresses caused by differential lateral expansion between the electrodes as they are put into operation are relieved or made sufficiently small that the shearing forces applied to the ends of the insulating pillars do not cause their disruption.

The theoretical aspects of these problems are discussed in Section III below; several fabrication schemes that were generated are reported in Section IV.

D. Microstructures for Injecting Ions into the Interelectrode Space

The amount of cesium required to obtain the desired work function on the emitter surface is usually lower than that required to produce ions for space-charge neutralization. Thus a separate source of chemically inert ions for the latter purpose could prove of value in optimizing the ion concentration for space-charge neutralization while minimizing the arc drop. Injecting xenon ions from an independent field ionizer source was initially considered, since the field ionization process theoretically requires little energy. However, such schemes appeared impractical to implement without injecting the ions into the gap with intolerable losses or with initially high energies. A simpler scheme was considered whereby pulses of electrons from microfield emission

sources incorporated in the collector were injected into the gap region with sufficient energy to create ions. By incorporating the sources in the collector, all the injected electrons are used to create ions and none are lost to the system. An analysis of this scheme is given in Section V; about 3 percent of the output energy of the converter would be needed for ion generation for space-charge neutralization.

III THE THEORY OF CLOSELY SPACED DIODES

A. Basic Theory of Thermionic Energy Conversion

The theoretical analysis was designed to yield a quantitative evaluation of the operating parameters that might be assigned as design goals for a microfabricated diode. The analysis was performed in two steps: In the first step we determined the desirable electrical parameters for a diode; in the second step we determined the gap spacing that would be needed to ensure the attainment of those parameters.

We chose to analyze a diode in which both the emitter and collector were cesiated tungsten electrodes because data are available for cesiated tungsten over a wide range of operating conditions. Cesium tungsten has a very low evaporation rate and SRI is experienced in tungsten thin-film technology.

Low evaporation rate is an important criterion for thermionic diodes, where long operating lifetimes are difficult to attain. Shorting between the electrodes is relatively common failure mode that results from the migration of evaporated materials. Because this problem would be particularly noticeable with ultra-closely spaced diodes, we decided to analyze the very-low-evaporation-rate material. Choosing the same material for both electrodes has the advantage of preserving the integrity of the initial characteristics over long operating lifetimes: The coating of one electrode by evaporant material from the other electrode is much less likely to affect its characteristics when the materials are the same.

The other initial conditions selected for this analysis are the electrode operating temperatures. We used a collector temperature

$T_C = 700$ K and an emitter temperature $T_E = 1650$ K. These temperatures are compatible with a flame-fired converter diode clad with a silicon carbide protective shield.

The emission current is one of the most important parameters that governs the operation of a thermionic diode. If electron reflection at the solid vacuum interface is neglected, the governing relation is the Richardson-Dushman equation, given by

$$J_S = 120 T^2 \exp(-e\phi/k_B T)$$

where J_S is the saturated emission current density, T is the absolute temperature of the solid, e is the electronic charge, k_B is Boltzmann's constant, and ϕ is the effective work function.

In a converter analysis, both the emitter emission and the back emission from the collector must generally be considered. Although the collector temperature is much lower than the emitter temperature, its emission can be significant if the collector work function is very low. This is not the case in this analysis, however, where we have chosen a cesiated tungsten collector. At a temperature of 700 K, the collector surface is effectively coated with cesium and exhibits the work function of cesium, or $\phi_C = 1.7$ V. The saturated collector emission is thus $J_{CS} = 34 \mu A/cm^2$, which as demonstrated below is a negligible amount. At the chosen operating temperature, the saturated emitter emission is

$$J_{ES} = 3.267 \times 10^8 \exp(-7.032 \phi_E) \quad .$$

The efficiency η of an idealized converter is defined as the electrical power output divided by the total thermal power that must be delivered to the converter. The total thermal power includes emitter

heat losses caused by electron emission, cooling, radiation, and heat conduction loss through the electrical connection (Houston and Webster, 1962).^{*} When these factors are considered,

$$= \frac{J_E(\phi_E - \phi_C - V_W)}{J_E(\phi_E + 2k_B T_E/e) + R + H_W},$$

where R is the radiation heat loss, H_W is the heat conduction through the electrical lead, and V_W is the voltage drop in the electrical lead. If radiation from the lead is neglected, and the electrical and heat conductivities of the lead are assumed to be related by the Lorenz number L , the voltage drop V_W and the heat conduction per unit emitter area H_W of the optimum lead are given by:

$$V_W = \left[L\eta(T_E^2 - T_C^2)/(2 - \eta) \right]^{1/2}$$

$$H_W = J_E V_W (1 - \eta)/\eta$$

where L is 2.45×10^{-8} (W-ohm)/deg² and η is the converter efficiency.

The four equations above were solved simultaneously with the following input parameters: $T_E = 1650$ K, $T_C = 700$ K, and $\phi_C = 1.7$ V. We expressed the radiation loss as $R = \epsilon R_{bb}$, where R_{bb} is the black body radiation for the chosen emitter temperature ($R_{bb} = 5.62 \times 10^{-12} T_E^4$ in W/cm²). We used $\epsilon = 0.3$, as being representative of a reasonably obtainable surface emissivity. The solution of converter efficiency as a function of emitter work function is given in Figure 2. The peak efficiency of 16.3 percent occurs at a emitter work function of 2.38 V. The efficiency is fairly strongly peaked, being small above 3 V and below 1.8 V.

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^{*}References are listed in full at the end of this report.

FIGURE 2 EFFICIENCY OF THE IDEALIZED CONVERTER

The electrical power output, the thermal conduction to the connecting lead, and the total thermal power were also obtained in the solution and are plotted in Figure 3. The radiation loss is also shown as the dashed line. At the point of maximum efficiency, the electrical power output is about 11 W/cm^2 and the total thermal power required is 65 W/cm^2 . The saturated emission current at maximum efficiency is about 18 A/cm^2 . The results of this calculation show that the electrical power peaks at a considerably lower work function than the position of maximum electrical efficiency. At the maximum power point, the required emitter work function is very low and the thermal power is exceptionally high, as is the required saturated current density. It is quite conceivable that in this converter design the attainable electrical power output will be limited by the capability of supplying thermal energy to the emitter.

FIGURE 3 ELECTRICAL POWER OUTPUT AND THERMAL POWER DISSIPATION OF THE IDEALIZED CONVERTER

The second step of the analysis was to examine the conditions for attaining the desired emission current in the converter. As shown earlier, the collector emission in our design is negligible, so it is not necessary to reverse bias the converter to suppress collector emission. Also, as will be shown later, we expect negligible plasma resistivity because of the closely spaced gap. Therefore we can express the converter voltage V as the difference between the work functions of the electrodes, $\phi_E - \phi_C$, and can now examine Child's Law for space-charge

limited emission to determine gap spacing required to allow the saturated thermionic emission to pass without being space-charge limited. Child's Law is given by:

$$J = 233.45 V^{3/2}/d^2 ,$$

where J is in A/cm^2 , V is in volts, and d is in μm . This relationship is plotted in Figure 4, which expresses the electrode gap d as a function of emitter work function ϕ_E . At the maximum efficiency point, an electrode spacing of $2.7 \mu m$ or less would be sufficient; at the maximum power point a submicron electrode gap would be required to permit the saturated current to flow.

Because potential differences in a vacuum converter are relatively small, electron thermal velocities cannot be neglected in any analysis of electron space charge; thus, Child's Law gives only approximate results. Langmuir (1923) has calculated the potential distribution in a planar diode assuming the electrons issue from the emitter with a Maxwellian distribution of velocities. The current-voltage characteristics of the diode can be expressed in terms of the space-charge parameter R' , which is defined by the equation

$$R' = 8424 J_{ES} d^2 / T_E^{3/2} ,$$

where J_{ES} is in A/cm^2 and d is in μm (Houston and Webster, 1962).

When $R' = 0$, space-charge effects are negligible. Larger values of R' are indicative of increasing space-charge effects that reduce the emission current below the saturation value. We have plotted in Figure 4 a curve for the value $R' = 5$; this corresponds to an emission about 75 percent of the saturation value when the diode internal voltage is 0. Thus, in the figure, diode spacings below the curve are sufficient to provide at least 75 percent of saturated emission current. At the peak

FIGURE 4 INTERELECTRODE SPACING
OF THE IDEALIZED CONVERTER

efficiency point ($\phi_E = 2.38$ V), values below $1.5 \mu\text{m}$ are acceptable. Based upon these results, we chose a nominal gap spacing of $1 \mu\text{m}$ as a design target.

B. Effect on Efficiency of Other Energy Loss Mechanisms

To evaluate converter performance, the energy conversion efficiency must be studied. In computing this efficiency, several contributions to heat loss must be considered:

- Electron cooling rate of the emitter
- Heat conduction rate through electrical leads
- Joulean heat rate in leads

- Interelectrode thermal radiation
- Heat conduction through cesium vapor
- Heat conduction through structural components (i.e., the spacing pillars).

The ideal case for a lead-optimized vacuum converter was considered above taking into account the first four contributions. The energy conversion efficiency was maximized with respect to the emitter work function ϕ_E . At emitter and collector temperatures of 1650 K and 700 K, respectively, it was found that the maximum efficiency ϕ_E occurs at 2.38 eV for a collector work function ϕ_C of 1.7 eV. Under these conditions, the values of the first four heat loss contributions are approximately 48.3, 3.7, 0, and 12.3 W/cm², respectively.

When the interelectrode gap distance is less than the cesium atom mean free path, the pressure in the interelectrode space is in the Knudsen regime. In a steady-state situation, cesium atoms arrive and leave each electrode at the same rate (defined as the arrival rate μ_a in atoms/(cm²-s)). Because the atoms leaving the emitter and arriving at the collector are more energetic than those traveling the other way, there is a net flow of heat across the gap, independent of the gap distance. The heat loss contribution of the cesium atoms is given by

$$Q_{cs} = 2\mu_a k_B (T_E - T_C) \text{ W/cm}^2 \quad .$$

The cesium atom arrival rate is an inverse function of the emitter work function ϕ_E ; for $\phi_E \sim 2.4$ eV, $\mu_a = 8 \times 10^{20}$ atoms/(cm²-s), which corresponds to a heat loss of $Q_{cs} = 20.98$ W/cm².

The primary structural component heat loss is in the aluminum-oxide pillar configuration. At an average electrode temperature of 1175 K,

the thermal conductivity of aluminum oxide is $K \sim 590 \text{ W/(cm-K)}$. The heat loss through the pillars increases as the gap distance d decreases. It is given by:

$$Q_p = \frac{K}{d} (T_E - T_C) \text{ W/cm}^2 .$$

This heat loss is large for a gap distance of $1 \mu\text{m}$ and has a value of $Q_p = 5.57 \times 10^5 \text{ W/cm}^2$ or $5.57 \text{ mW}/\mu\text{m}^2$. This loss is comparable only to the other losses for pillar areas of about $2000 \mu\text{m}^2/\text{cm}^2$ of electrode area or a fractional coverage of about 2×10^{-5} . For our electrode area of 0.585 cm^2 , this corresponds to a maximum pillar area of about $1200 \mu\text{m}^2$. It is uncertain whether $1200 \mu\text{m}^2$ is sufficient to support the copper collector under operating conditions. If more support is needed, it may be necessary to increase the interelectrode gap spacing to get a practical efficiency.

The maximum obtainable energy conversion efficiency for small-spaced thermionic converters may occur at a gap spacing greater than $1 \mu\text{m}$ but less than about $10 \mu\text{m}$, which is the approximate electron-cesium atom mean free path; greater spacings would add detrimental collision losses in the interelectrode space.

Overall, several competing factors determine the efficiency. A particular set of conditions will yield the maximum obtainable efficiency for a given pillar support area.

1. Detailed Analysis of Closely Spaced Diode Performance

In order to determine the effect on the efficiency of the competing influences between relatively small ($\sim 1 \mu\text{m}$) interelectrode gap spacings and the heat loss through structural components, we have conducted a more detailed analysis of closely spaced diode performance. As the gap spacing is made smaller, the power loss due to space charge is decreased as the heat rate loss through the structural components (i.e. the

insulating pillar array) is increased. Depending on the magnitudes of the two losses, the efficiency may be maximum at a gap spacing greater than the proposed $1 \mu\text{m}$ spacing. In the following theory these two losses are taken into account, as is the heat loss through the cesium vapor, which was neglected in the basic theory of Section III-A. We continue to ignore collisional losses because interelectrode spacings exceed the mean free path of electron-cesium atom collisions.

In general, the energy conversion efficiency of the thermionic energy converter diode is given by

$$\eta = \frac{J(V - V_w)}{Q_E + Q_{cs} + Q_p + R + H_w}$$

where Q_E , R , H_w , V_w are the electron cooling rate of the emitter, the interelectrode thermal radiation, the heat rate conducted through the optimized leads, and the voltage drop across the optimized leads, respectively; all are given in Section III-A. The additional terms Q_{cs} , Q_p correspond to the heat loss through the cesium vapor and the heat loss through the pillar array as given above. J and V are the current density and voltage at which the efficiency is calculated. Substituting these terms gives an implicit function of the efficiency

$$\eta = \frac{B - \left(\frac{C\eta}{2-\eta} \right)^{1/2}}{A + \left(\frac{C\eta}{2-\eta} \right)^{1/2} \left(\frac{1-\eta}{\eta} \right)}$$

where:

$$A = Q_E + \frac{2k_B T_E}{e} + \frac{1}{J} (Q_{cs} + R + Q_p)$$

$$B = V$$

$$C = L (T_E^2 - T_C^2)$$

L = the Lorenz number.

Solving explicitly for η gives the following:

$$\eta = \frac{AB + C - \left\{ C \left[C + B(2A - B) \right] \right\}^{1/2}}{C + A^2} .$$

The efficiency of the converter was found at the operating point where the product of J and V (the output power) is maximum. Under ideal conditions, J equals the saturation current density J_{ES} , V equals the contact potential $V_0 = \phi_E - \phi_C$, and $W_{max} = J_{ES}V_0$. These were the assumed conditions in the basic theory, with the voltage drop across the lead, V_w , subtracted from the contact potential. Under actual operating conditions, the electrode output power is smaller than ideal because of space charge.

At the maximum electrode output power, the output current density $J = J_{maxW}$ and the electrode output voltage $V = V_{maxW}$ can be found. There exists a parameter called the critical output current-density, which corresponds to the minimum current density in the space-charge-limited mode of operation (the critical point) (Hatsopoulos and Gyftopoulos, 1973). This current density follows from Child's Law and is given by:

$$J_m = 7.729 \times 10^{-12} \left(\frac{T_E^{3/2}}{d^2} \right) .$$

As stated earlier, Child's Law gives only approximate results under certain conditions. The actual critical-output-current density is given by a correction factor Z^2 ($0 < Z < 1$), such that $J_R = Z^2 J_m$. The factor Z^2 is a complicated function of the ratio J_{ES}/J_m (Nottingham, 1956). The critical output voltage V_R at the critical point is given by

$$J_R = AT_E^2 \exp\left(\frac{-\phi_C + eV_R}{k_B T_E}\right) .$$

From the values of J_R and V_R we are able to find $J_{\max W}$ and $W_{\max}$ from the following relations (Hatsopoulos et al., 1960)

$$J_{\max W} = J_R \left[1 + 0.31 \left(\frac{eV_R}{k_B T_E} \right)^{4/3} \right]$$

$$W_{\max} = 0.383 \frac{J_R V_R^2}{V_T} .$$

At $V_{\max W}$ and $J_{\max W}$ corresponding to the maximum output power, the energy conversion efficiency is determined by the relations given earlier, letting $V = V_{\max W}$ and $J = J_{\max W}$ with $T_E = 1650$ K, $T_C = 700$ K, and ϕ_C assumed to be ~ 1.7 eV as before, the efficiency η depends only on the variables ϕ_E , d , and f (the fractional electrode area coverage of the aluminum-oxide pillar array). At a given spacing and a given coverage, the efficiency can be found as a function of the emitter work function. The work function (ϕ_E') at which the efficiency is maximum ($\eta_{\max}$) was found and was used to compare the converter performance for each set of operating conditions.

2. Sample Calculations

Some sample calculations using the above theory are summarized in Table 1. For gap spacings of 1 μm to 5 μm , the fractional pillar coverage f varies from 0 to 1.71×10^{-5} to 1.71×10^{-4} which corresponds to pillar areas of 0, $10^3 \mu\text{m}^2$, and $10^4 \mu\text{m}^2$. The efficiency is found to decrease as the pillar area is increased at fixed gap spacings. For fixed pillar areas, the efficiency also decreases as the gap spacing is increased. This illustrates that the space charge has a stronger effect in lowering the efficiency than does the heat loss through the pillar array.

Table 1

RESULTS OF DETAILED DIODE PERFORMANCE THEORY

d	f	Pillar Area (μm^2)	Q'_E (eV)	W_{max} (W/cm ^{2})	Q_p (W/cm ^{2})	η_{max} (%)
1 μm	0	0 ₃	2.40	15.92	0	16.53
	1.71×10^{-5}	10 ₄	2.25	27.54	9.58	14.41
	1.71×10^{-4}	10 ⁵	1.95	32.53	95.58	8.09
2 μm	0	0 ₃	2.45	9.30	0	14.56
	1.71×10^{-5}	10 ₄	2.35	11.16	4.79	12.39
	1.71×10^{-4}	10 ⁵	2.00	17.70	47.92	6.12
3 μm	0	0 ₃	2.50	6.03	0	12.12
	1.71×10^{-5}	10 ₄	2.50	6.03	3.19	10.30
	1.71×10^{-4}	10 ⁵	2.20	9.40	31.95	5.44
4 μm	0	0 ₃	2.60	3.85	0	10.10
	1.71×10^{-5}	10 ₄	2.50	4.59	2.40	8.66
	1.71×10^{-4}	10 ⁵	2.20	7.13	23.96	4.65
5 μm	0	0 ₃	2.65	2.87	0	8.55
	1.71×10^{-5}	10 ₄	2.55	3.41	1.92	7.40
	1.71×10^{-4}	10 ⁵	2.30	5.01	19.17	4.05

C. Management of Relative Lateral Expansion
Between Emitter and Collector

A straightforward approach to spacing the electrodes that avoids the problem of insulator strain is shown in Figure 5. The spacing is provided by a single insulator (or closely spaced array) located at the

FIGURE 5 CONCEPT OF CENTER INSULATOR

center of the diode and anchored to only one of the electrodes. The assembly is held together by axial force applied at the center of the diode. Additional short insulators that do not span the gap may also be included at various radii to prevent the electrodes from touching in the case of slight warping during heating and cooling. This design requires very smooth and flat electrode surfaces. Mechanical polishing of metal surfaces often produces a slight convex curvature of the surface; therefore, in this design, the interelectrode gap might increase gradually with increasing distance from the center of the diode.

A second approach that does not require such a flat surface is illustrated in Figure 6. An insulating film about $1\text{-}\mu\text{m}$ thick is vapor-deposited onto a solid polished electrode. The other electrode--also very thin--is a vapor-deposited metallic film. Lithographic techniques are then used to produce an array of small holes in the metal film; most of the insulating material is chemically etched away through these

FIGURE 6 CONCEPT OF DEPOSITED/ETCHED INSULATOR

holes, leaving an array of insulating posts in the gap. Finally, a heavier electrode for thermal and electrical connection is attached to the thin-film electrode.

One possible representation of the final arrangement is shown in Figure 7. The advantage of such an arrangement is that closely spaced holes in the metallic film provide means to accommodate the differential thermal expansion by slight deformation of the film between the posts. The following analysis shows that the posts must be on approximately 10- m centers to avoid film warping that might cause contact with the other electrode. In addition, the electrical and thermal connections must be on a 1-mm grid to avoid large thermal gradients and IR voltage drop in the thin film. Thus, Figure 7 depicts only a section of a much larger array.

If a thin film is used as the collector or the emitter in a diode, it must not only have sufficient strength to withstand the thermal expansion stresses, but must also be capable of transporting thermal power and electrical current from the free-standing film areas to the

FIGURE 7 PORTION OF AN ARRAY USING THE CONCEPT SHOWN IN FIGURE 6

thermal and electrical connections. Below we analyze these aspects to determine the spacing required for the support insulator posts and the thermal and electrical connections to the film.

1. Strain and Deformation

We assume here that the film electrode has a relatively large area and is supported on a large number of closely spaced insulator posts permanently attached to the other electrode. When the film is the collector electrode, it will be stretched during operation; if the film is the emitter electrode, it will tend to be under compression and buckle during operation at normal temperatures. In the stretched case, the yield point of the film must not be reached. The tensile stress P is given by $P = Y(\Delta L/L_0)$, where Y is the elastic modulus and

$\Delta L/L_0$ is the tensile strain. The tensile strain for tungsten due to differential thermal expansion is about 0.5 percent. For tungsten, $Y = 5 \times 10^7 \text{ lb/in}^2$. Thus the tensile stress $P = 2.5 \times 10^5 \text{ lb/in}^2$. This value may exceed the tensile strength of the film at 700 K.

2. Linear Film Expansion

Here we assume that the thin film is the emitter electrode. Thus, when the diode is heated, differential expansion causes the film to buckle because the emitter is hotter than the collector. We would like to know the maximum distance between insulating posts that can still accommodate a buckling resulting from a 0.5-percent differential expansion. With a simplifying assumption that the film bends in the middle and deforms toward the opposite electrode, we find that (to avoid shorting) the distance between the insulating supports must be less than 20 times the interelectrode spacing. Thus, for a $1\text{-}\mu\text{m}$ interelectrode spacing, the insulating posts must be on approximately $10\text{-}\mu\text{m}$ centers.

3. Thermal Conduction

A circular electrode that has heat supplied (or removed) at its periphery and removed (or supplied) uniformly over its surface area will have a temperature gradient across the surface caused by thermal conduction.

For a uniform heat flow through the surface, J_0 , and a thermal conduction coefficient λ the temperature differential between the center and edge of the film is given by $\Delta T = J_0 L_0^2 / 16 \lambda d$, where L_0 is the film diameter and d is the film thickness. This result shows that the thermal power cannot be transported over long distances through the film. For example, for $J_0 = 50 \text{ W/cm}^2$, $L_0 = 1 \text{ mm}$, $\lambda = 1 \text{ W/(cm-K)}$, and $d = 1 \mu\text{m}$, we obtain a temperature differential of about 300 K. Consequently, a device built using a film electrode must be supported on something like a honeycomb structure of the scale of a 1-mm grid to transport the heat adequately.

4. Electrical Conduction

It now remains to be determined whether the voltage drop resulting from electrical conduction through the film is significant. The voltage drop $\Delta V = J_0 L_0^2 / 16d$, where J_0 is the current density through the film surface in A/cm^2 , and ρ is the electrical resistivity of the film material. Using the same diode example with $J_0 = 18 A/cm^2$ and using $\rho = 16 \mu\Omega\text{-cm}$ for tungsten, we arrive at $\Delta V = 1.8 \text{ mV}$. Thus, the voltage drop is much less significant than the temperature gradients in the film, because the temperature gradient will have a significant effect upon the distribution of emission over the emitter surface. For this reason, it would be more desirable to have the film as the collector electrode, where thermal gradients would have much less effect on the work function of the surface.

A third approach is to use for the electrodes materials of different coefficients of linear expansion. In a practical realization of this scheme, the emitter would be made of pure tungsten or molybdenum, whose work function will be controlled by the cesium vapor pressure maintained in the gap. The collector would be made of a cesium-compatible material, whose expansion coefficient is such that there is no relative movement between it and the emitter when both are heated from room temperature to their respective temperatures of operation. For this we assume, as previously, $T_E = 1650 \text{ K}$, $T_C = 700 \text{ K}$, values compatible with the topping of a fossil-fuel power station. The insulator will be aluminum oxide, which is known to be cesium-compatible at these temperatures. Copper has proved to be an attractive collector material. Knowing the expansion characteristics of tungsten (or molybdenum) and copper, we have plotted (Figure 8) T_E versus T_C such that the relative expansion between the two electrodes is zero. Thus, for $T_E = 1650 \text{ K}$, T_C must be 745 K and 665 K for emitter electrodes of molybdenum and tungsten, respectively. These are close to the chosen value of 700 K . During warm-up as T_E is increased, T_C should be held at the

FIGURE 8 TEMPERATURES AT WHICH EMITTER AND COLLECTOR TEMPERATURES ARE SUCH THAT THE ELECTRODES HAVE SIMILAR EXPANSIONS WHEN HEATED FROM ROOM TEMPERATURE ($\sim 300\text{K}$)

corresponding values given by Figure 8 to maintain zero relative expansion between the electrodes. Copper also has the following necessary or desirable properties:

- Readily deposited by evaporation.
- Cesium-compatible at collector temperatures.
- Very low vapor pressure at the collector operating temperature ($\sim 10^{-14}$ torr).
- Physically soft and yielding; can accommodate shear stresses even when perfect expansion matching is not always obtained.
- High electrical and thermal conductivities.

Fabrication schemes can be visualized in which the copper collector electrode surface can be made to replicate exactly the surface of the emitter electrode, thus obviating the necessity for producing perfectly flat surfaces over large areas.

IV FABRICATION OF CLOSELY SPACED DIODES

The following fabrication schemes were investigated.

Spacers Between Flat Polished Surfaces--The concept of this method was shown in Figure 5. Both electrodes are polished flat. A large single insulator of the required thickness is formed at the center of one electrode. The assembly is held together by an axial force applied at the center of the diode. Additional small short insulators that do not quite span the gap are included at various radii to prevent the electrodes touching in the case of slight warping or slight off-axis force.

For our studies of this method of electrode fabrication, we obtained 1/2-inch diameter tungsten and molybdenum discs. The surfaces were ground flat and then polished with a polishing wheel. The discs were placed in a holder and rough polished with a Buehler nylon cloth and 6- μ m diamond polishing compound lubricated with kerosene. Ten to twelve hours polishing time was required to remove the ground surface on the specimen.

Next a 1- μ m diamond compound on a clean nylon cloth was used to remove any scratches made by the previous operation. Cleaning the surface usually took two to three hours. A final polish was then performed with a Buehler microcloth with Al_2O_3 polishing compound and distilled water for a clean scratch-free surface. The photograph of a polished molybdenum surface shown in Figure 9 was taken with interference contrast microscopy at a magnification of 162X. The dark sector in the right-hand portion of the picture is a 1- μ m thick aluminum-oxide (alumina) film deposited upon the molybdenum surface. The interference contrast technique greatly emphasizes the apparent vertical structure of the surface. The vertical relief in this picture is less than about 0.1 μ m.

SCALE: 4mm ON PHOTO = 25 μ m ON OBJECT

FIGURE 9 MECHANICALLY POLISHED MOLYBDENUM SURFACE

An equivalent photograph for a polished tungsten surface is shown in Figure 10. In this case, the vertical relief is somewhat greater than for the molybdenum sample; however, the most notable feature of our tungsten discs is the macroscale crack structure that covered the surface of most of these samples and that is evident in the figure. They are probably related to the technique used in manufacturing the discs and represent various bulk orientations.

To test the concept of separating two discs by small space, we deposited an array of aluminum-oxide film on one of the discs, as shown in Figure 11. We then placed another disc on top of this one, and determined that there was no shorting between the two discs. To determine the separation, we measured the capacitance of the assembly. In one trial the average disc spacing was 3.2 μ m, and in a second trial it was 4.6 μ m. Even though the alumina film that divided the spacing was only 1- μ m thick, we measured a much greater average disc spacing; this probably results because the discs are not perfectly flat, but rather are slightly convex in their surface shape.

SCALE: 4mm ON PHOTO = 25 μ m ON OBJECT

FIGURE 10 MECHANICALLY POLISHED TUNGSTEN SURFACE

SCALE: DIAMETER OF DISK = 0.5 INCH

FIGURE 11 ELECTRODE PAIR, SHOWING PATTERN OF VAPOR-DEPOSITED ALUMINA SPACERS

In another fabrication test, a disc was completely coated with a 1- μ m film of alumina, after which an array of 1/32-inch diameter aluminum discs was deposited as counterelectrodes. The purpose of this test was to determine whether the alumina film was pinhole free. (In films with pinholes, the counterelectrode deposition tends to short out the microcapacitor that has been formed.) The alumina discs were not shorted to the molybdenum. Capacitance measurements showed that the dielectric constant of the alumina film was within the expected range

for alumina ceramic for one of the samples that we made; for two of the other samples, the measured dielectric constant was greater than that for alumina. These results may indicate that some tungsten oxide is being deposited from the vaporization source along with the alumina.

In summary, we have produced highly polished molybdenum and tungsten surfaces and deposited upon them 1- μ m-thick films of alumina. We have also shown that counterelectrodes can be deposited on the alumina without shorting through to the opposite electrode. We have produced unshorted interelectrode spaces of 3 to 5 μ m, which could possibly be reduced by producing a flatter electrode surface.

However, this method was not considered satisfactory because of the expensive requirements of polishing essentially optical flats over large areas and the operational likelihood of surface movement during the heating process. The emitter, unless it is a single crystal, recrystallizes at operating temperature, causing movements of greater than one μ micron perpendicular to the surface. This effect is particularly significant in molybdenum.

Method Using Thin Film Technology--This approach, which does not require a high degree of surface flatness, was illustrated in Figure 6. An insulating film about 1- μ m thick is vapor-deposited onto a solid polished metallic film. The other electrode--also very thin--is a vapor-deposited metallic film. Lithographic techniques are then used to produce an array of small holes in the metal film, and most of the insulating material is chemically etched away through these holes leaving an array of insulating posts in the gap. Finally, a heavier electrode for thermal and electrical connection is attached to the thin-film electrode.

The original concept behind this type of arrangement was that the closely spaced holes in the metallic film provide means to accommodate the differential thermal expansion by a slight deformation of the film between the posts. The analysis in Section III shows that the posts

must be on approximate 10- μ m centers to avoid film warping that might cause contact with the other electrodes if both are made of the same refractory metal (tungsten or molybdenum). In addition, we note that the electrical and thermal connections must be on a 1-mm grid to avoid large thermal gradients and IR voltage drop in the thin film. However the use of copper as the collector film material and molybdenum as the solid emitter electrode, as shown in Section II, ensures that little lateral stress need exist if the temperatures of each electrode are held at specific values. Thus, relieving lateral stress is no longer critical in the spacing between the parts. We therefore proposed to fabricate the diode by the following sequence of operations (Figure 12):

- Step 1: A disc of molybdenum (or tungsten) 1/2-inch diameter is polished to a smoothness of substantially less than 1 μ m. Note that flatness is not so essential to this technique as is smoothness.
- Step 2: A film of aluminum oxide 1- μ m thick is evaporated on the smooth surface.
- Step 3: A film of copper a few micrometers thick is evaporated over the oxide film.
- Step 4: An electron beam resist is spun on the surface and holes produced in the resist by the usual methods. The copper is etched away, leaving a corresponding array of holes in the copper layer.
- Step 5: An etch that attacks aluminum oxide, but not copper or molybdenum, is used to etch the oxide layer. Etching is continued until only diamond-shaped pillars of oxide remain between the holes. The cross-sectional area of the pillar will be small compared with the exposed area of the electrodes.

(a) POLISH EMITTER

(b) EVAPORATE 1- μm LAYER OF Al_2O_3

(c) EVAPORATE 5- μm LAYER OF Cu

(d) SPIN ON e-BEAM RESIST. EXPOSE, DEVELOP, AND ETCH AN ARRAY OF 5- μm HOLES. REMOVE RESIST

(e) ETCH Al_2O_3 LEAVING SMALL PILLARS

FIGURE 12 FABRICATION PROCEDURE

We are left with the structure shown in Figure 13. Although the details of the hole sizes and spacing have yet to be fixed, clearly the area covered by the pillars and holes should be small compared to the total electrode area.

The completed structure is thermally tested. The holes in the copper allow cesium vapor to enter the interelectrode gap at a vapor pressure corresponding to the lowest temperature in the system. The work function of the emitter is controlled by the cesium pressure; the collector will always be cool enough that condensed cesium will determine the work function of the collector surface. Because all the current must travel through the collector, it may have to be made thicker by plating to reduce power loss by Joule heating and to maintain the good heat conduction necessary if the temperature over the copper electrode is to be uniform.

We proceeded to implement this approach using an emitter material consisting of 1/2-inch diameter molybdenum discs which were micropolished by techniques similar to those discussed previously. Initially we had difficulties eliminating small pits in the polished surface which can cause pinholes in the aluminum-oxide film to be subsequently deposited on this surface. The pits were found to be caused primarily by overpolishing the surface during the final step with the Al_2O_3 polishing compound. As a final preparation of the surface before deposition of a film, we preheated the molybdenum substrate (in vacuo) to accelerate any grain growth that might (undesirably) occur during converter operation and to thoroughly clean the surface. The discs were heated to a temperature slightly above the proposed emitter operating temperature of $T_E = 1650$ K. (We had chosen molybdenum rather than tungsten here because our tungsten discs showed large bulk orientation boundaries in addition to grain boundaries after heating. This problem might be avoided by using single-crystal materials or polycrystalline materials treated to inhibit grain growth or shifting, such as thoriated tungsten.)

SECTION VIEW

TOP VIEW

FIGURE 13 PROPOSED STRUCTURE

Expansion coefficient of the collector material is such that there is no net differential expansion relative to the emitter material between room temperature and the respective electrode operating temperatures.

We proceeded to evaporate a 1- μ m thick film of aluminum oxide (alumina) on the smooth surface. We still encountered problems with some pinholes in the film caused by the unavoidable imperfections in the molybdenum surface and by debris which had collected during and after the deposition and had broken loose. These pinholes are disastrous, as they could cause the copper film electrode evaporation that follows to short to the molybdenum electrode. We attempted to perform multiple evaporations of aluminum oxide after polishing-back the pinholed layer, but this was unsuccessful as the film could not be polished flat enough. Pinholes in the alumina film appeared to be unavoidable with such thin films and with the deposition technologies we had available.

Nevertheless, the next step--evaporating a thin film of copper--was carried out, with the hope that our best effort in polishing the molybdenum and in evaporating alumina would yield a diode structure free of shorts--or one with shorts over a small area that could potentially be etched away later when the array of aluminum-oxide pillars are formed. The resulting thin-film configuration consisted of copper on aluminum oxide on molybdenum (Figure 14).

In view of the difficulty of obtaining pinhole-free films of alumina on molybdenum and the anticipated difficulties of etching the pillar array to the required precision, this procedure was eventually abandoned as impractical.

To solve the problems of duplicating the electrode surfaces, pinholes in the alumina coating, and the possible difficulties of keeping the interelectrode gap clean and free of debris in the two-piece diode, two revised methods of fabricating a one-piece diode structure have been formulated.

FIGURE 14 THIN FILM CONFIGURATION

Magnification 35X; $\sim 1\text{-}\mu\text{m}$ thick copper on $1\text{-}\mu\text{m}$ thick aluminum oxide on a molybdenum substrate.

The first consists of the following steps (Figure 15).

- Step 1: A $1\text{-}\mu\text{m}$ aluminum-oxide film is evaporated onto a micropolished surface of a 1/2-inch diameter molybdenum (or tungsten) disc.
- Step 2: A negative resist is spun onto the oxide surface. The resist is exposed in the areas corresponding to the pillar configuration and is then developed by the usual method.
- Step 3: The unexposed area is etched away, leaving the $1\text{-}\mu\text{m}$ high pillar configuration covered with a thin layer of resist.
- Step 4: A filler material is evaporated onto the substrate to a thickness of $1\text{ }\mu\text{m}$ or slightly less. The remaining resist (which acts as a separation layer) is dissolved, eliminating the filler material that has collected on top of the pillars.

FIGURE 15 FABRICATION PROCEDURE USING FILLER MATERIAL

Step 5: The copper collector film is evaporated over the existing layer and then plated to the desired thickness.

Step 6: The filler material will either be dissolved by an etchant that does not attack molybdenum, copper, or aluminum oxide, or it will be heated and melted away.

We are left with a one-piece diode structure with pillars extending into the copper collector.

The advantage of this technique is that the copper collector can be made as thick as necessary to accommodate Joule heating. However, there may be some difficulty in completely filling-in the area around the pillars with the filler materials. In our experience with evaporation, we have noted the effects of undercutting and shadowing in the region immediately surrounding the pillars. The extent of the shadowing depends on the angle of evaporation, the size of the pillars, and the surface area of the source. It appears possible, however, to overcome this shadowing problem.

The second fabrication method consists of the following steps (Figure 16).

Step 1: A 1- μ m aluminum film is evaporated onto a 0.5-inch diameter micropolished molybdenum (or tungsten) surface.

Step 2: A positive resist is spun onto the aluminum surface and exposed through a mask that corresponds to the pillar arrangement. The resist is then developed, leaving the pillar locations exposed.

Step 3: These exposed areas of aluminum are then anodized using standard aluminum anodization techniques. The resist then removed, leaving the 1- μ m aluminum-oxide pillars surrounded by the original aluminum film.

FIGURE 16 FABRICATION PROCEDURE USING ANODIZATION

Step 4: The copper collector is then evaporated over the existing layer and plated to the required thickness.

Step 5: An etchant is used that will dissolve the aluminum while not attacking the copper, molybdenum, or aluminum oxide (anodized aluminum).

This will also leave a single-piece 1- μ m diode structure with a sufficiently thick copper collector. This method eliminates the potential problems of using an organic filler material.

A suitable aluminum etchant, consisting of a 25-percent (by volume) solution of concentrated hydrochloric acid in water, has already been found. This solution does not attack aluminum oxide or copper and attacks molybdenum only slightly. We anticipate a possible problem of insufficient penetration of the acid into the interelectrode gap, which is only 1- μ m wide.

Method of Conformal Matching of Emitter and Collector Surfaces--In this technique, we proposed a two-piece diode structure consisting of separate electrodes (molybdenum or tungsten and copper, as before) between which an insulator configuration will be evaporated directly through a mask. By this scheme, the collector will continue to yield the advantages presented in Section III, but the copper can be made thicker to accommodate the Joule heating and to maintain good heat conduction necessary for uniform temperature distribution throughout the collector. The soft and yielding nature of the copper is also utilized in this diode fabrication technique. Etching through the copper and alumina films is thus avoided, and pinholes in the alumina pillars will not cause shorting as there is no evaporation step.

The planned diode configuration was to consist of a "top-hat" shaped emitter (Figure 17) with three (or more) equilaterally spaced holes in the rim to accommodate sapphire/ruby spheres. These spheres act to support the copper collector in order to help maintain the micron spacing and to facilitate future realignments of the collector.

FIGURE 17 EMITTER CONFIGURATION

The ruby spheres act to support and align the copper collector.

We initially planned to fabricate a diode by the following procedure (Figure 18):

- Step 1: A disc of molybdenum (or tungsten) 1/2-inch in diameter is micropolished to smoothness and machined into the proposed emitter configuration.
- Step 2: A film of aluminum oxide 1- μ m thick is evaporated on the polished surface. Then, sapphire/ruby spheres (~1/16-inch diameter) are placed in the emitter structure holes.
- Step 3: A disc of polished copper 1/2-inch in diameter is aligned and hydraulically pressed onto the emitter structure until it yields and forms itself over the inherently convex polished emitter surface and the ruby spheres.
- Step 4: The emitter structure and the collector is separated and the aluminum-oxide film removed from the emitter surface.
- Step 5: A 1- μ m thick aluminum-oxide pillar array is evaporated on the emitter surface; then, the copper collector is realigned on the emitter and its supports and held in place by some manner.

The completed structure is a diode with a uniform 1- μ m spacing over the entire area. In this approach, because it is the copper collector electrode that yields when the discs are pressed, we decided to machine the copper disc into the "top-hat" configuration while keeping the ruby sphere support holes in the molybdenum emitter electrode.

The pressing operation was carried out at room temperature, with a hydraulic press calibrated from 0 to 12 tons. The idea was to increase the pressure beyond the yield point for the copper (~7,900 psi for OFHC copper at room temperature) while keeping the pressure below the molybdenum's room temperature yield point (~43,000 psi for arc-cast molybdenum).

(a) POLISH AND MACHINE EMITTER CONFIGURATION

(b) EVAPORATE Al_2O_3 FILM AND PLACE SAPPHIRE/RUBY SPHERES

(c) HYDRAULICALLY PRESS COPPER COLLECTOR ONTO EMITTER STRUCTURE

(d) SEPARATE ELECTRODES AND REMOVE Al_2O_3 FILM

(e) EVAPORATE PILLAR ARRAY AND REPLACE COLLECTOR ON EMITTER

FIGURE 18 FABRICATION PROCEDURE
USING SURFACE REPLICATION

Several problems were encountered during the disc pressing. First, the brittle molybdenum tended to crack near the ruby sphere support holes. The cracking occurred along grain boundaries from the stresses that the spheres caused during pressing. To solve this problem, it was decided to make spherical cups in which to seat the balls instead of drilling support holes completely through the molybdenum. In addition, a yoke was built to confine the molybdenum (and copper) disc during pressing.

Second, the copper did not always press evenly against the molybdenum, thus causing a nonuniform pressure on the molybdenum surface. To overcome this problem, the faces of the molybdenum and copper discs were paralleled with precision before polishing. Great care was taken to polish the molybdenum disc face flat and to keep the front and back faces parallel by mounting the disc in epoxy during the polishing process. To further ensure parallel pressing, a pressing setup was constructed with a die-making set.

It was originally proposed that an aluminum-oxide film 1- μ m thick would be evaporated to keep a uniform spacing during the pressing; however, the film usually shattered, and it was decided to do the pressing before the film deposition.

Several successful pressings were made. After the approximate load required for pressing had been determined, it was observed that as the pressure was slowly increased, the copper yielded and at first duplicated the molybdenum surface around the outer edge of the copper surface at first. At greater pressures, this area of duplication moved toward the center of the surface. At a sufficient applied pressure, the entire copper surface duplicated the molybdenum surface. This effect appears to occur because the molybdenum disc surface deforms elastically to a greater extent in the center, where more pressure is thus required to shape the copper. It was also found that the diameter of the copper surface increased at heavier loads as the copper flowed radially outward, causing additional problems in surface duplication.

An aluminum-oxide pillar array (Figure 19) was evaporated onto the molybdenum surface after pressing and separating the electrodes. The film was evaporated at a slight angle through a screen mask with square ($\sim 25\text{-}\mu\text{m}$ on a side) holes, spaced $100\text{-}\mu\text{m}$ center to center. Because the mask holes slowly closed during the evaporation, the resulting pillars were in the shape of truncated pyramids $1\text{-}\mu\text{m}$ high, covering about 6.25 percent of the electrode area.

SCALE: 17cm = $100\text{ }\mu\text{m}$

FIGURE 19 PILLAR ARRAY CONFIGURATION

Aluminum oxide pillars evaporated through a screen mask onto the molybdenum substrate.

The copper disc was then replaced on the molybdenum disc, using the ruby spheres for realignment. The completed diode structure (Figure 20) was placed in a test fixture with the threaded screw mechanism for exerting pressure on the diode and electrical contact was made to each electrode. The capacitance of the diode was measured in this test fixture. Because of the dielectric aluminum-oxide pillars, the net capacitance is increased from its free-space value by a factor $[\epsilon f + (1 - f)]$, where ϵ is the dielectric constant of the aluminum oxide and f is the

FIGURE 20 THE COMPLETED DIODE STRUCTURE

fractional volume of the interelectrode space taken up by the aluminum oxide. The electrode spacing is given by:

$$d = \frac{\epsilon_0 A}{C} [\epsilon f + (1 - f)]$$

where

$$\epsilon = 8.85 \times 10^{-12} \text{ F/m}$$

$$A = \text{electrode area (m}^2\text{)}$$

$$C = \text{capacitance (F).}$$

Four diode structures were made. A different load, ranging from 4500 to 10,000 lb, was applied to each during the pressing, and the capacitance of each diode was measured as the pressure in the test fixture was varied. In calculating the diode gap spacing, it was assumed that the aluminum-oxide pillar array was in complete contact with the copper surface so that the fractional volume taken up would be equivalent to the 6.25 percent fractional area, at all pressures. This was assumed even though some pillars sank into the copper at higher pressures, causing eventual shorting of the electrodes. At lower applied pressures in the test fixture an interelectrode spacing of 10.13 μm was estimated for the diode pressed at a 10,000-lb load and a spacing of 2.98 μm was estimated for the diode pressed at a 4500-lb load. The minimum spacing measured for each before shorting was 5.81 μm and 1.50 μm , respectively. After the measurement, it was noticed that the copper pillars had sunk deeper in certain surface regions, and the diode had shorted in the area where the pillars had sunk to a depth of 1 μm . These measured values are an average for the entire electrode area, because the copper did not perfectly match the molybdenum's surface.

Because of the difficulty in duplicating the electrode surfaces by pressing techniques, another method of surface duplication was proposed. In this technique a thick copper film is evaporated directly onto the emitter surface and then removed, leaving a duplicate of the emitter surface in the copper. Before evaporating the copper, a minute film of salt, which acts as a separation layer to help remove the copper film, is evaporated over the surface. Within a defined temperature range that corresponds to a particular source-to-substrate distance, the copper adheres well and does not buckle. A realignment scheme has yet to be worked out for this technique, but it appears to be promising, because the duplication is done "atom-by-atom" by evaporation.

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V THE THEORY OF THE FIELD EMISSION ION GENERATION SCHEME

The principle of operation of this scheme is shown in Figure 21. The spacing between the emitter and collector is made comfortably large (~ 1 mm) so that the problems of close spacing are avoided (i.e., no support structure is needed). Ions to neutralize the space charge are produced by the injection pulses of energetic field-emitted electrons into the gap from holes in the collector as shown. The gas in the gap is cesium at the partial pressure necessary to maintain the desired work function on the emitter, and xenon maintained at a pressure such that the injected electrons will have many ionizing collisions with gas molecules before reaching the emitter.

Field emitting arrays of this type have been developed by C.A. Spindt of SRI. By making the cones extremely small (~ 1 μm tall, 500-Å tip radius), and by bringing the gate very very close to the tip (~ 0.6 μm) electrons can be field emitted into the gap with very low voltage (25 to 50 V) between the cones and the gate electrode (which also serves in this application, as the collector electrode for the thermionic energy converter).

In operation the field emitting cones would be pulsed negative for a short time, t_0 , with long intervals between pulses of time τ . The injected electrons would collide with the vapor molecules in the gap, forming positive ions which would serve to neutralize the space charge generated by the electron current flow. To the cesium vapor, at a pressure necessary to optimize the emitter work function, would be added xenon gas, if necessary, to optimize the number of ionizing collisions a field emitter electron would have in the gap.

Since the fabrication problems of building such arrays have been solved for other applications, the reduction to practice of this scheme should be relatively straightforward, although other practical

(a) SCHEMATIC DESIGN

(b) TIMING

FIGURE 21 IONIZATION OF GAS IN INTERELECTRODE REGION BY FIELD EMISSION

The substrate is switched from ground (or collector potential) to $-V$ volts such that a current density J (averaged over the array) is injected into the inter-electrode region for a time t_0 .

difficulties may become apparent. (These would include the necessity of thickening the gate/collector film so that the large currents associated with thermionic conversion may be carried in the film without excessive Joule heating losses, and possible gas breakdown phenomena on applying the voltage pulses at these cesium pressures.) We show below on a theoretical basis that the energy cost of operating this scheme is not excessive.

The cesium ion current density J_i A/cm² required to neutralize an electron current flow of J_e A/cm² is given by

$$J_i = \frac{m}{\sqrt{M}} J_e$$

where m = electron mass and M = ion mass = 133 amu for cesium.

Hence,

$$J_i = 2 \times 10^{-3} J_e = 36 \times 10^{-3} \text{ A/cm}^2 \text{ for } J_e = 18 \text{ A/cm}^2 .$$

The field emission current density J_F to be injected into the gap to create this ion current is given by $J_i = K(V)(J_F)$, where $K(V)$ is the number of ions produced by an electron with initial energy V . The mean free path of an electron of energy V is given by

$$\lambda = \frac{T}{273p[P_C(V)]}$$

where

T = absolute temperature,

p = gas pressure in torr,

$P_C(V)$ = average number of collisions that occurs when an electron travels 1 cm at a pressure of 1 mm Hg (1 torr) at 0°C (273 K).

Figures 22 and 23 show plots of $P_C(V)$ for cesium and xenon. If we assume that the field emission can be obtained with 50 V, then $P_C(50) \sim 300$. Therefore,

$$\lambda_p \lesssim 6.7 \times 10^{-3} \text{ cm} .$$

SOURCE: Brode, 1933

FIGURE 22 PROBABILITY OF ELECTRON COLLISIONS IN CESIUM

Thus with a spacing of 1 mm (or greater than 15 mean free paths) we may reasonably assume that at least half of the electron energy would be used in forming ions. Since the ionization potential of cesium is 3.89 eV, a 50-V electron would produce at least 6 cesium ions, i.e., $K(50) \geq 6$. Hence, to produce an ion current density of 36 mA/cm^2 (needed to neutralize a diode electron current density of 18 A/cm^2) an injected 50-V average field emission current density of 6 mA/cm^2 would be required. This average current would be injected in the form of pulses with a small duty cycle. If a duty cycle $t_0/(t_0 + \tau)$ of 10^{-3} is chosen, then the field emission cathodes would have to project 6 A/cm^2 during

SOURCE: Brode, 1933

FIGURE 23 PROBABILITY OF ELECTRON COLLISIONS IN XENON

the pulse which is a comfortable range for the field emission arrays to operate with 50 V applied. Very short voltage pulses may be necessary (say 1 microsecond duration repeated every millisecond) so that gas breakdown processes were not initiated. The power used by the ionizing electrons would average $50 \times 6 \times 10^{-3} \text{ W/cm}^2 = 0.3 \text{ W/cm}^2$, which is about 3 percent of the optimum output from the converter under the chosen conditions ($T_E = 1650 \text{ K}$, $T_C = 700 \text{ K}$, $p_{CS} = 3 \text{ torr}$): that is, 11 W/cm^2 , from the basic theory in Section III.

The addition of xenon is not required because of the short mean free path of electrons in cesium and its high collision cross section. Cesium ions are also formed by contact ionization at the emitter surface, but for $p_{CS} = 3 \text{ torr}$, which is necessary to obtain $\phi_E = 2.4 \text{ eV}$ at $T_E = 1650 \text{ K}$, the rate of formation of ions is too small to add significantly to the ion current.

Because the electron current in a converter of this type would be flowing in a much lower vapor pressure of cesium than in the ignited type of diode, energy loss from the arc drop would be avoided.

We conclude from this analysis that experimental investigation of cesium ion formation from micro-field-emission arrays would be extremely valuable for application in thermionic energy converters.

VI SUMMARY AND CONCLUSIONS

This report has presented the results of a three-year research project which was terminated after the second year for budgetary reasons. During the two-year research period, efforts were directed towards the study and fabrication of microstructures that could improve methods of thermionic energy conversion. A study of various types of microstructures was carried out, and a detailed analysis of thermionic energy converter performance was completed to determine a thermionic diode design that might be practical.

Two diode designs and applications of microfabrication technology appeared promising and were theoretically investigated. The first uses a very closely spaced diode, which has the high performance of a vacuum diode and utilizes cesium vapor to control the electrode work functions. At emitter and collector temperatures of 1650 K and 700 K respectively, and for a $1\text{-}\mu\text{m}$ interelectrode spacing with less than 0.002-percent electrode coverage of aluminum-oxide support structures, an output power density of over 27 W/cm^2 at an energy conversion efficiency of about 14.4 percent is obtainable, with a cesiated emitter work function of 2.25 eV. The second design uses low-voltage field-emission sources to create ions, in a relatively large interelectrode gap, for space-charge neutralization. In a diode with a 1-mm spacing and a cesium pressure of ~ 3 torr, a set of field-emission cathodes, pulsed with a duty cycle of 10^{-3} at an average current density of 6 mA/cm^2 , will neutralize the interelectrode space-charge, while using only about 3 percent of the total converter output power. The theoretical results for both these approaches were highly encouraging.

The experimental results were, in general, inconclusive (because of the early termination date). Of the various fabrication schemes attempted, none were entirely successful. Electrode surface parallelism

and flatness were difficult problems in the close-spaced diode design. Surface replication was shown to be a possible solution, but more work is needed. The etching techniques proposed also appear feasible with additional work. The field-emission cathode arrays are working well in other programs, and have the potential of operating well in a thermionic converter. In theory, both diode designs are practical, but more extensive engineering efforts will be required if they are to become functional.

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