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# Results from the Microminiature Thermionic ~~RE~~ Converter Demonstration Testing Program

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**Abstract.** Research is in progress to develop microminiature thermionic converters (MTCs) with high energy conversion efficiencies and variable operating temperatures using semiconductor integrated circuit (IC) fabrication methods. The use of IC techniques allows the fabrication of MTCs with cathode to anode spacing of several microns or less and with anode and cathode materials that will have work functions ranging from 1 eV to 3 eV. The small cathode to anode spacing and variable electrode work functions should allow the conversion of heat energy to relatively large current densities (up to tens of Amps/cm<sup>2</sup>) at relatively high conversion efficiencies (15-25%).

## INTRODUCTION

The Defense Special Weapons Agency's (DSWA's) Advanced Thermionics Program (ATP) seeks to advance the state of the art of thermionic power conversion in the United States. One aspect of this program is to enable revolutionary advances in thermionic converter performance by dramatically reducing the gap size of the converter and incorporating low work function materials into the converter electrodes. Sandia National Laboratories (SNL) has started a program to develop the microminiature thermionic converter (MTC), a new generation of thermionic converters. The MTC is a planar, two-electrode thermionic diode. Several technological developments have enabled the development of the MTC. Commercial electronic fabrication techniques allow the MTCs to be fabricated as one unit with micron-sized features (a micron-sized gap between the electrodes plays a key role in obtaining the higher energy conversion efficiencies). Also, thousands of MTCs can be fabricated as one large conversion unit using these electronic fabrication techniques. This scale of fabrication may allow various MTC units to be fabricated (1) with power outputs ranging from milliwatts to hundreds of watts and (2) at very low cost. Emitter materials with low work functions that are compatible with the electronic fabrication techniques have been developed. Work is also in progress to produce materials with low but variable work functions. The use of variable work function electrodes will allow the creation of MTCs tailored to function efficiently for the different heat sources and their temperature regimes; these low work functions allow the MTC to operate at modest temperatures (800-1300 K).

The MTC program has several parallel development paths. Thermal modeling of the diode structure is performed to understand the structure types necessary to operate the MTC at desired electrode temperatures with a minimum of heat input to the diode. Electrical modeling of the diode is performed to understand the optimal diode operating conditions in terms of power output and conversion efficiency of heat to electricity. Material studies are necessary to identify the appropriate materials with which to fabricate the MTC diode structure and fabricate low work function electrode materials. The diode structure materials must maintain diode integrity at high operational temperatures, and the low work function materials must have appropriate electron emission characteristics at desired operational temperatures. Low work function materials with electron high emission properties have been identified in the open literature but have not been optimized for use in MTCs. Research must continue in the materials and deposition processes to enable fabrication of low work function electrodes with the proper emission characteristics at the desired structure sizes. The low work function electrodes will be part of the MTC structure, which will be made of ceramics (such as quartz, sapphire, and glassy carbon), metals (such as tungsten, nickel, platinum,

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and molybdenum), and semiconductors (such as silicon and silicon carbide). The metal/ceramic/semiconductor interfaces will have to be studied and characterized at high temperatures to determine the reliability of the MTC devices during high-temperature operation. Adhesion between materials and stresses due to thermal expansion mismatches must be carefully controlled. The susceptibility of MTCs to shock and vibration as well as the effects of combined radiation and temperature must also be studied and measured.

Both material types must demonstrate long lifetime and reliability at the diode operational temperatures. Various fabrication techniques have also been studied to identify the most feasible method to construct the MTC. Finally, tests must be performed to confirm the low work function material emission characteristics, the compatibility of diode materials at high temperatures, and the performance of the diode itself.

## PHYSICAL PROCESSES IN MTCs

Thermionic emission depends on emission of electrons from a hot surface. Valence electrons at room temperature within a metal are free to move within the atomic lattice, but very few can escape from the metal surface. The electrons are prevented from escaping by the electrostatic image force between the electron and the metal surface. The heat of the emitting surface gives the electrons sufficient energy to overcome the electrostatic image force. The energy required to leave the metal surface is referred to as the material work function,  $\phi$ . The rate at which electrons leave the metal surface is given by the Richardson-Dushman equation (Hatsopoulos, 1973):

$$J = AT^2 \exp(-[\psi - \mu_E]/kT_E), \quad (1)$$

where  $A$  is the Richardson constant (in  $A/m^2/K^2$ ),  $T_E$  is the emitter temperature (in K),  $k$  is the Boltzmann constant (in eV/K),  $\mu_E$  is the emitter Fermi energy level (in eV), and  $\psi$  is the maximum motive (in eV) experienced by an electron in transit. Figure 1 illustrates the energy levels that an emitted electron must overcome as required by equation (1) in a two-electrode thermionic converter. Electrons leave the emitter surface and travel to the collector surface. Operating the collector at lower temperatures minimizes electron emission from the collector to emitter. The maximum motive depends on (1) the sum of the emitter work function ( $\phi_E$ ) and the electron induced space charge,  $\Delta V_{sc}$ , or (2) the sum of the diode operating voltage ( $V_d$ ), the collector work function ( $\phi_c$ ), and  $\Delta V_{sc}$ .

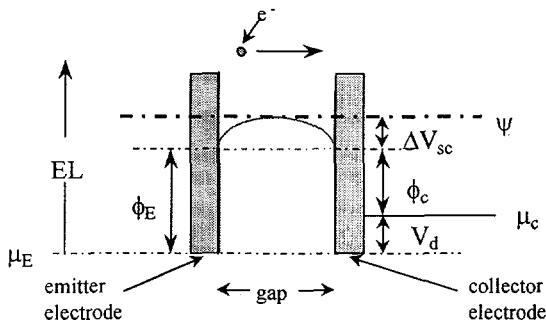


FIGURE 1. Energy Levels Experienced by Electrons During Transition.

Large emission current densities are achieved by coating the emitter surface with a low work function material and operating that emitter at as high a temperature as possible with the following limitations: 1) very high temperature operation may cause any material to evaporate rapidly and limit emitter lifetime and 2) low work function materials can have relatively high evaporation rates and must be operated at lower temperatures. Materials with low evaporation rates usually have high work functions.

Choosing the correct electrode coating is half the battle in designing thermionic converters. Once the electrons are successfully emitted, their continued travel to the collector must be ensured. Electrons emitted from the emitter

produce a space charge in the interelectrode gap (IEG). For large currents, the buildup of charge will act to repel further emission of electrons and limit the efficiency of the converter. Two options have been considered to limit space charge effects in the IEG: thermionic converters with small IEG spacing (the close-spaced vacuum converter) and thermionic converters filled with ionized gas.

Thermionic converters with gas in the IEG are designed to operate with ionized species of the gas. Cesium vapor is the gas most commonly used. Cesium has a dual role in thermionic converters: (1) space charge neutralization and (2) electrode work function modification. In the latter case, cesium atoms adsorb onto the emitter and collector surfaces. The adsorption of the atoms onto the electrode surfaces results in a decrease of the emitter and collector work functions, allowing greater electron emission from the hot emitter. Space charge neutralization occurs via two mechanisms: (1) surface ionization and (2) volumetric ionization. Surface ionization occurs when a cesium atom comes into contact with the emitter. Volumetric ionization occurs when an emitted electron inelastically collides with a Cs atom in the IEG. The work function and space charge minimization increases the converter power output. However, at the cesium pressures necessary to substantially affect the electrode work functions, an excessive amount of collisions (more than that needed for ionization) occurs between the emitted electrons and cesium atoms, resulting in a loss in conversion efficiency. Therefore, the cesium vapor pressure must be controlled so that the work function reduction and space charge reduction effects outweigh the electron-cesium collision effect. An example of an operational thermionic converter is found on the Russian TOPAZ-II space reactor. These converters operate at emitter temperatures of 1700 K and collector temperatures of 600 K with a cesium pressure in the IEG of just under one torr. Typical current densities achieved are  $< 4 \text{ A/cm}^2$  at output voltages of approximately 0.5 V. These converters operate at an efficiency of approximately 6%. The control of cesium pressure in the IEG is critical to operating these thermionic converters at their optimum efficiency. MTCs offer the simplest solution to thermionic energy conversion. A gas need not be introduced into the IEG to reduce the space charge effects resulting from the large current flow from the emitter to the collector. The small IEG size itself reduces the density of electrons in the gap (and their resulting current-limiting space charge). Historically, the close-spaced converter has been difficult to manufacture for large-scale operation due to the close tolerances (several microns or even submicron interelectrode gap size) needed for efficient operation. Large-scale production and operation of these close-spaced converters is now possible using IC fabrication techniques. Spacing on the order of 0.25 to 1 microns can now be produced and maintained over relatively large emission areas.

## MODELING

The MTC diode electrical characteristics were calculated using a computer code (MTCP) developed at Sandia that simulates the electrical performance of a vacuum diode. This code determines a range of possible current and voltage operational regimes for given diode operational temperatures and geometry specifications. Figures 2 and 3 illustrate potential unit diode current density output and power output versus the voltage range through which a diode is typically operated as calculated by MTCP. Figure 2 shows how the diode current density changes with the diode operating voltage as well as the diode gap size. The ideal diode represents a fictional diode with a gap size of zero. As the gap size increases, the diode current decreases due to the space charge effect of electrons transiting the gap from one electrode to the other (electrons already in the gap tend to retard further electron emission). The diodes must be fabricated with as small a gap size as possible. The calculations were performed with the emitter and collector electrodes at 1200 K and 700 K, respectively. Figure 3 shows how the diode power density changes with the diode operating voltage as well as the diode gap size.

The heat load required by the MTC diode to operate at desired electrode temperatures must be calculated to determine the MTC conversion efficiencies. The conversion efficiency is defined as the electrical power output from the diode divided by the total heat input to the diode. The values for the input heat flux through the diode were obtained from thermal analyses using PATRAN, a commercial, finite element thermal solver that calculates radiative, convective, and conductive heat transfer modes. The calculated conversion efficiencies and electrical power output are shown in Table 1. The electrical power output (in Watts) is shown in parentheses. The calculations were made for a circular diode with an outer radius of 5 mm. The emitter and collector electrode radii were varied from 0.625 to 4.95 mm. The emitter and collector electrode temperatures modeled were 1200 K and 700 K, respectively. Increasing the emitter radius resulted in an increase of diode efficiency for emitter radii up through 4.5 mm. As the emitter electrode radius is increased, electrical power output and thermal power input increase. The electrical power increase is greater than the thermal input power through the radius of 4.5 mm. Increasing the gap

size dramatically reduces the efficiency and output power because of current drop due to the increase in space charge.

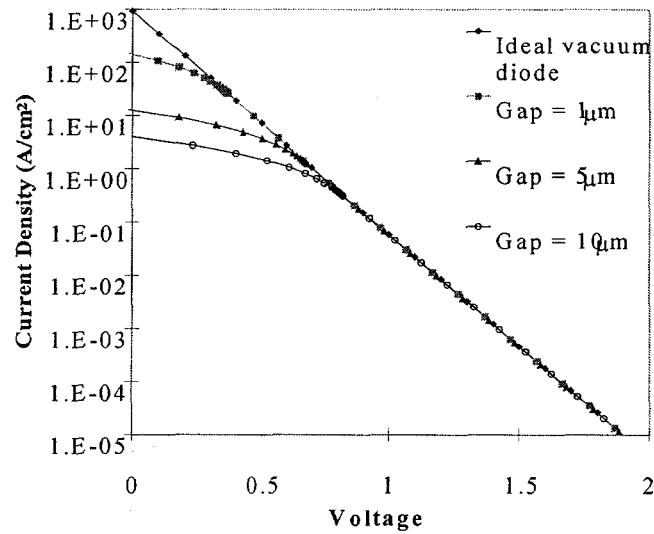


FIGURE 2. Calculated Current-Voltage Characteristics.

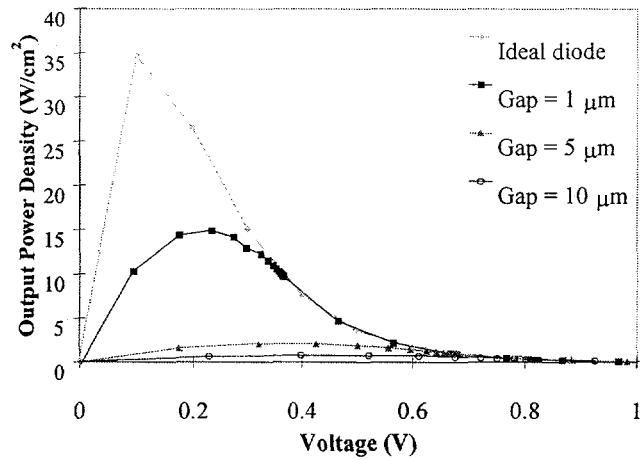


FIGURE 3. Calculated Power Output versus Diode Voltage.

Table 1. Estimated Conversion Efficiency of a Microminiature Thermionic Converter

	Emitter Radius (mm)	0.625	1.25	2.5	3.75	4.0	4.5	4.95
Gap Size (μm)								
1	5.80% (0.0524)	11.98% (0.2097)	18.32% (0.8382)	20.61% (1.8865)	20.73% (2.1465)	21.00% (2.7166)	--	--
5	2.44% (0.0198)	6.05% (0.0791)	11.65% (0.316)	14.46% (0.7113)	14.63% (0.8093)	15.01% (1.0243)	14.75% (1.2394)	
10	1.14% (0.0088)	3.03% (0.0354)	6.54% (0.1413)	8.64% (0.3181)	8.77% (0.3619)	9.07% (0.4581)	8.87% (0.5543)	
50	0.10% (7.36E-4)	0.29% (2.9E-3)	0.71% (0.0118)	1.02% (0.0265)	1.04% (0.0302)	1.09% (0.0382)	1.05% (0.0462)	

## FABRICATION

Vacuum field emission diodes have been fabricated using conventional integrated circuit (IC) fabrication techniques (King, 1995). The IC technique can also be used for MTCs. All elements of the diode (emitter, collector, and insulating spacer between the electrodes) are made with standard chemical vapor deposition (CVD) techniques and etch techniques used by the semiconductor industry. The CVD techniques allow us to reliably, reproducibly, and accurately grow extremely thin layers of metals (for the electrodes) and oxides (for the spacers). The fabrication procedure occurs roughly as illustrated in Figure 4 and described below:

1. The emitter material is first deposited onto a suitable substrate material. Emitter materials with different work functions are then deposited to optimize emission temperature to each application.
2. An oxide layer is deposited over the emitter material. This layer serves as the spacer between the emitter and collector. The oxide layer can be varied from several microns to several thousand angstroms.
3. The collector material is deposited onto the oxide spacer material. Collector materials with different work functions can be deposited to optimize the output voltage at which emission occurs.
4. Several holes (or vias) are etched through the collector material to the oxide spacer.
5. The oxide spacer is etched to form the vacuum space between the emitter and collector.

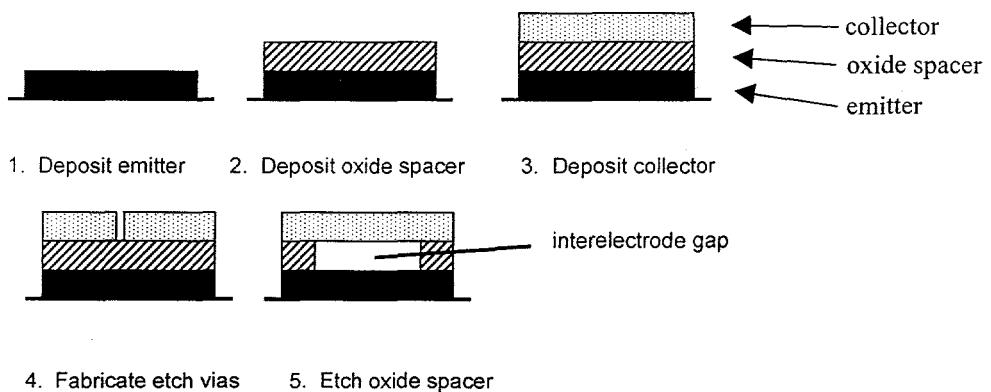


FIGURE 4. MTC Fabrication Sequence.

## TESTING

Two sets of emission tests have been completed. The emission test objective is to calculate the work function and effective Richardson constant of the low work function electrode coatings. The low work function material was a mixture of barium, calcium, and strontium oxides. The performance measurements are accomplished by sweeping a positive and negative voltage across the diode terminals and measuring the resulting output current at three or more operating temperatures. The emission test is performed in a prototype diode structure. One electrode, the emitter, is coated with the low work function material, and the collector is a bare metal electrode with no low work function coating.

Prior to testing, the low work function oxide coating on the emitter surfaces was heated to condition and activate the coating. The coating is delivered as a mixture of barium, calcium, and strontium carbonate ( $\text{BaCO}_3$ ,  $\text{CaCO}_3$ , and  $\text{SrCO}_3$ ) with some water content. During heating, carbon dioxide and water vapor must be driven from the carbonate mixture to form a mixture of barium, calcium, and strontium oxide. The conditioning profile was a bake-out temperature of 770 K for at least two hours followed by a two-hour activation bake at 1120 K.

Figure 5 illustrates a typical current emission profile caused by the voltage sweep during the emission test. For this test, the collector was grounded while the emitter electrode voltage was swept from 40 V to  $-40$  V. For vacuum diode behavior, current emission occurs while the emitter is negatively biased. Although the data are uncertain due to the small number of sample points, the measured emitter work function was between 1.0 and 1.6 eV. This range of values for the work function is typical of the published values for this type of oxide coating. The measured effective Richardson constant was approximately  $10^{-4}$  Acm $^{-2}$ K $^{-2}$ , somewhat low compared to about  $10^{-3}$  in the literature.

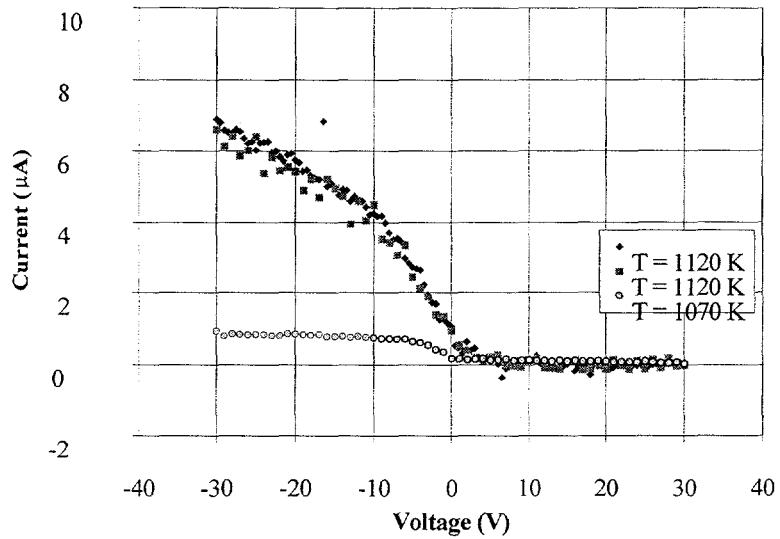


FIGURE 5. Emission Test Current Voltage Characteristic

## CONCLUSION

SNL is investigating the feasibility of fabricating MTCs using IC fabrication techniques. These techniques allow MTCs to be fabricated with micron-sized spacing between electrodes and low work function electrodes. Modeling has shown that thermionic diodes with these features have the potential to convert heat to electricity with relatively high efficiencies. SNL has fabricated prototype diode structures and has used those structures to test a first set of low work function materials. Preliminary test results have shown the materials thermionically emit electrons. Work to optimize the low work function material continues.

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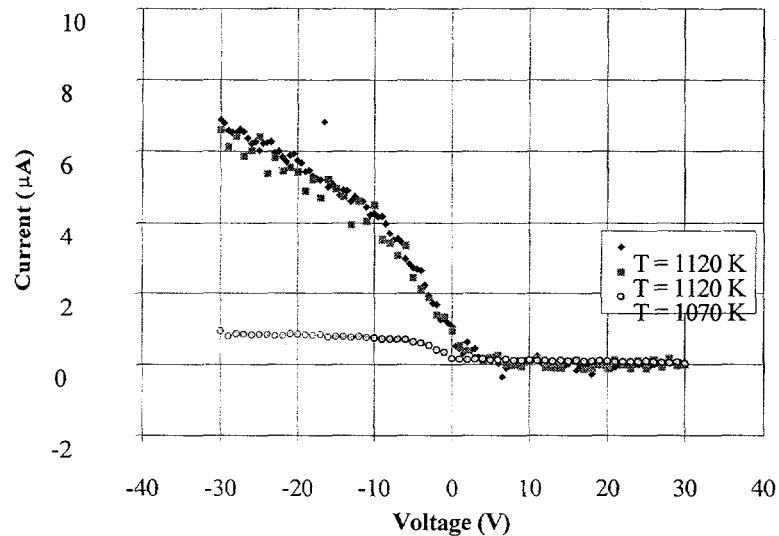


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