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APPLICATION OF MICROFABRICATION TECHNOLOGY
TO THERMIONIC ENERGY CONVERSION

Progress Report 6

Covering the Period 1 November 1980 to 31 January 1981

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ABSTRACT

During the report period, effort was directed toward the fabrication of a micron-spaced thermionic converter diode by the technique presented in Progress Report 5. This technique demonstrated that interelectrode spacings down to $1.5\text{ }\mu\text{m}$ could be obtained. Several methods of duplicating the emitter and collector surfaces were also investigated.

In the report period, two new techniques were proposed. Both stem from an earlier idea of using evaporation, photolithography, and etching techniques. These two fabrication methods yield a one-piece diode structure with a thick-film copper collector, eliminating the need to physically duplicate the electrode surfaces and realign the electrodes.

Effort has also been directed toward a more detailed theoretical analysis of micron-spaced thermionic converter performance. Taking into account heat losses through the interelectrode support structure, it is likely that the maximum energy conversion efficiency may be greatest at a spacing somewhat larger than 1 micron (μm), but less than $10\text{ }\mu\text{m}$.

I INTRODUCTION

This is the sixth progress report in a theoretical and experimental program to evaluate those areas where three-dimensional microfabrication techniques could be important to improving methods of thermionic energy conversion. SRI International (SRI) is conducting the program for the Division of Fossil Fuel Utilization, Department of Energy (DOE), under Contract DE-AC02-79ET15423.

The scope of work encompasses a three-year level-of-effort program to evaluate the significance of application of ultramicrofabrication techniques to thermionic energy conversion. To this end, the following specific steps will be attempted:

- Step 1--Prepare structure electrode.
- Step 2--Build and evaluate a submicron close-spaced diode.
- Step 3--Study field ion injection for space-charge neutralization.
- Step 4--Conduct microfabrication service for programs in the thermionic energy conversion field.

The current year's effort is directed mainly toward Step 2. This report covers the period 1 November 1980 through 31 January 1981.

II PROGRESS DURING THE REPORTING PERIOD

The effort in the period covered by this report has been directed primarily to the experimental study of microstructure thermionic diode fabrication methods. The purpose of this study has been to test the feasibility of the fabrication procedure outlined in Progress Report 5.

The fabrication technique consists of building a two-piece diode structure of separate disc electrodes (molybdenum or tungsten and copper), between which an insulating pillar array is evaporated. This method eliminates the difficulty of etching a pillar array from a solid aluminium oxide film through a thin-film copper collector, as originally proposed (Progress Report 4). The planned diode configuration consists of a "top-hat" shaped emitter with three equilaterally placed sapphire/ruby spheres in the rim. These spheres help support the copper collector, which is hydraulically pressed on the emitter structure, and also help realign the collector after it has been removed to evaporate the pillar configuration. Pressing the copper on the molybdenum configuration conforms the copper surface to the molybdenum surface.

Because it is the copper collector electrode that yields when the discs are pressed, it was 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 done 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).

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 for the balls to seat in 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 μm 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 without it.

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 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 and thus more pressure is required there 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 1) 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 μm center to center. Because the mask holes slowly closed during the evaporation, the resulting pillars were in the shape of truncated pyramids 1 μm high, covering about 6.25 percent of the electrode area.

The copper disc was then replaced on the molybdenum disc, using the ruby spheres for realignment. The completed diode structure (Figure 2) was placed in a test fixture with a 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 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

$\epsilon_0 = 8.85 \times 10^{-12}$ farads/meter

A = electrode area (m^2)

C = capacitance (F).

SCALE: 17cm = 100 μm

FIGURE 1 PILLAR ARRAY CONFIGURATION

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

(a) SIDE VIEW

(b) OPEN-FACE VIEW

FIGURE 2 THE COMPLETED DIODE STRUCTURE

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.

To solve the problems of duplicating the electrode surfaces and the possible difficulties of keeping the interelectrode gap clean and free of debris in the two-piece diode, two new methods of fabricating a one-piece diode structure (as originally proposed) have been formulated.

The first consists of the following steps (Figure 3):

- Step 1: A 1- μm aluminum oxide film will be evaporated onto a micropolished surface of a 0.5-inch diameter molybdenum (or tungsten) disc.
- Step 2: A negative resist will be spun onto the oxide surface. The resist will be exposed in the areas corresponding to the pillar configuration and will then be developed by the usual method.
- Step 3: The unexposed area will then be etched away, leaving the 1- μm high pillar configuration covered with a thin layer of resist.

FIGURE 3 FABRICATION PROCEDURE USING FILLER MATERIAL

- Step 4: A filler material will be evaporated onto the substrate to a thickness of 1 μm or slightly less. The remaining resist (which acts as a separation layer) will be dissolved, eliminating the filler material that has collected on top of the pillars.
- Step 5: The copper collector film will be 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 will then be 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 material. 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 4).

- Step 1: A 1- μm aluminum film will be evaporated onto a 0.5-inch diameter micropolished molybdenum (or tungsten) surface.
- Step 2: A positive resist will be spun onto the aluminum surface and exposed through a mask that corresponds to the pillar arrangement. The resist will then be developed, leaving the pillar locations exposed.
- Step 3: These exposed areas of aluminum will then be anodized using standard aluminum anodization techniques. The resist will then be removed, leaving the 1- μm aluminum oxide pillars surrounded by the original aluminum film.
- Step 4: The copper collector will then be evaporated over the existing layer and plated to the required thickness.
- Step 5: An etchant will then be 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- μm diode structure with a sufficiently thick copper collector. This method eliminates the potential problems of using an organic filler material.

FIGURE 4 FABRICATION PROCEDURE USING ANODIZATION

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, because it is only 1 μm wide. A preliminary test will evaluate the extent of this problem.

In addition to the work in fabrication techniques, we began a theoretical study on the performance of a cesium-filled thermionic converter with 1 μm -spaced electrodes.

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 rate conducted 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 in Progress Report 1 and took 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 1650K and 700K, 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, there exists a Knudsen regime in the interelectrode space. 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 sec). 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

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

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 sec, 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 1175K, 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 $2000 \mu\text{m}^2$ per 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-caesium atom mean free path; greater spacings would add detrimental collision losses in the interelectrode.

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

III PROPOSED WORK DURING THE NEXT PERIOD

During the next reporting period, we propose to concentrate most of our efforts on the fabrication technique that uses aluminum anodization. In addition, we propose to attempt to duplicate electrode surfaces by copper-film evaporation for the two-piece diode design. We also propose to pursue further the theoretical study of close-spaced diode performance to find a diode design and a set of operating parameters for which the energy conversion efficiency is maximized.

IV PERCENTAGE OF TIME SPENT ON CONTRACT

During the report period, the principal investigator, Dr. Ivor Brodie, spent approximately 6 percent of his time on this project; microfabrication technologist C.A. Spindt, about 6 percent; and staff member Clay Shepherd approximately 73 percent of his time.