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# Silicon/Pyrex Planar Microbattery - A Silicon Process-Compatible Micro-Power Source

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# Silicon/Pyrex Planar Microbattery

## A Silicon Process-Compatible Micro-Power Source

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## ABSTRACT

The design, fabrication, and performance of a planar microbattery made from a silicon wafer with a bonded lid are presented. The battery is designed with two compartments, separated by four columns of micro-posts. These posts are 3 or 5 micrometers in diameter. The posts permit transport of liquid electrolyte, but stop particles of battery material from each compartment from mixing. The anode and cathode battery compartments, the posts, fill holes, and conductive vias are all made using high-aspect-ratio reactive ion (Bosch) etching.) After the silicon wafer is completed, it is anodically bonded or adhesive bonded to a Pyrex® wafer lid. The battery materials are made from micro-disperse particles that are 3-5 micrometers in diameter. The lithium-ion chemistry is microcarbon mesobeads and lithium cobalt oxide. The battery capacity is 1.83 micro-amp-hrs/cm$^2$ at a discharge rate of 25 microamps.

## INTRODUCTION

Silicon devices such as sensors, micro-electro-mechanical (MEMS) devices, and integrated circuits often have requirements for low voltage and low current, resulting in low power. Integrated systems should have power sources that are size consistent with the other micro-sized components. Especially interesting are integrated power sources that are built on the same piece of silicon or on a silicon substrate bonded to the device that needs power. The powered device may also benefit from an integrated back-up power source that provides emergency power when the primary power source is interrupted. If standard silicon processes are used to fabricate the power source, then cost and fabrication times should be reduced as compared to conventional battery making equipment. Many integration schemes prefer to have both electrical contacts on the same side of the device, unlike most miniature batteries that have contacts on alternate sides. Another desirable virtue of a silicon microbattery is the ability to lithographically scale the battery area in the plane of the silicon to provide the suitable current needs or to series connect lithographically to select the voltage required.

## MICROBATTERY DESIGN

The microbattery design consists of two lithographically etched compartments, which are eventually filled with micro-disperse battery materials. These compartments are separated by an array of lithographically etched posts that take the place of conventional porous polymer separators. These posts allow free exchange of battery electrolyte, but because the particle size of the micro-disperse powders is bigger than the separation between posts, no particle movement can occur between compartments. The compartments can be sized appropriately for any battery chemistry to provide the correct stoichiometry for each system. The post size and separation between posts can also be adjusted to fit the size of the micro-disperse particles available for the battery.

The current concept uses a slurry of battery material suspended in a solvent. The battery materials may have other polymeric agents added to help create higher concentration of active battery materials or enhance the flow characteristics of the slurry. After the materials have been added to the compartments, a vacuum bake step is performed to remove the solvents. An alternate loading method is to pre-form the battery materials using a mold and drop them into the compartments. In the bottom of each compartment are 2 fill-holes. These holes are designed to permit a small loading tip to be introduced to admit the battery slurry materials. The second hole is to allow escape of air, if the lid is already bonded on. Electrical contact is made either by electroplated contacts in the oxidized silicon connected to metal contacts in the lid or by sputter-deposition of contact metal in the compartments that comes over the outboard side allowing for metal connection outside the area of the lid. The lid may have recessed electrical contacts that contact both the battery material and the electroplated vias or be completely blank Pyrex® wafer. The Pyrex® lid material is preferred because the coefficient of thermal expansion is closely matched to silicon and because it can be anodically bonded to form a hermetic seal. (see Figure 1)

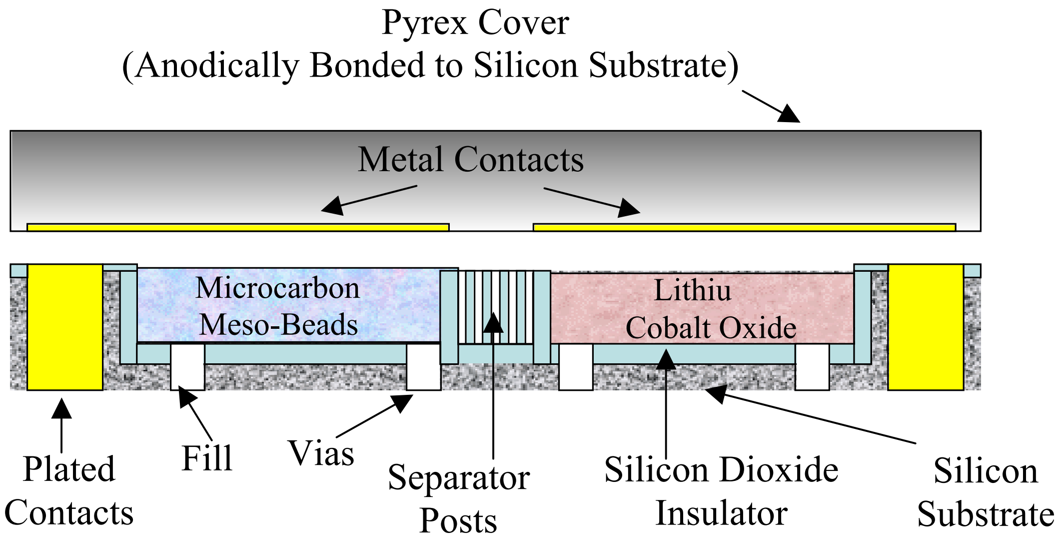


**Figure 1. Schematic of Planar Microbattery**

## MICROBATTERY FABRICATION

Fabrication of the microbattery is completely dependent on deep reactive ion etching (DRIE). DRIE is a plasma etching process that provides high-aspect ratio structures with anisotropic (vertical) profiles and smooth sidewalls in silicon. The process implemented at Sandia National Labs is an alternating deposition and etching procedure licensed from the Bosch Corporation. The Bosch process consists of a polymer deposition step using $C_4F_8$ and an etch step using $SF_6$. These processes last 2-3 seconds each, so that hundreds of these cycles are required to produce a deep etch. A stand photoresist mask is applied. During the process, the polymer deposition covers all the features, but during the subsequent etching step, the etchant ions are arriving with kinetic energy normal to the surface. The result is that the sidewalls are not etched free of the polymer and it remains in place to prevent lateral etching. The polymer also protects the photoresist mask, but the horizontal open surfaces are rapidly etched. A schematic of this process is shown in Figure 2.

One consequence of this type of etching is that as lateral dimensions decrease, the movement of etch gas and etch products into and out of narrow openings causes the etch rate to be dependent on the aspect ratio of the features being etched. An example of aspect ratio dependent etching is shown in Figure 3.

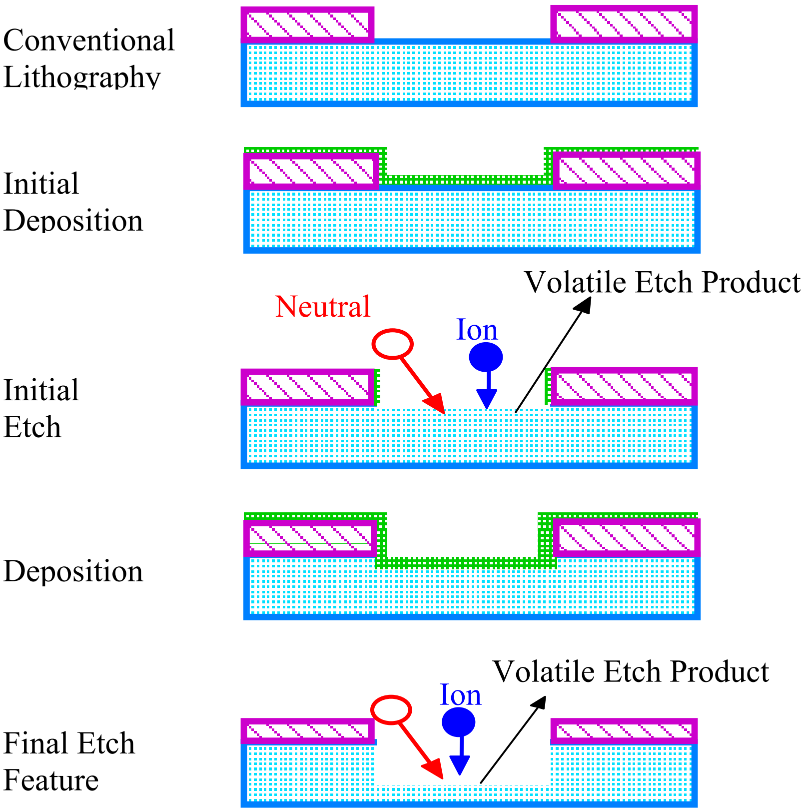


**Figure 2. Deep Reactive Ion Etching**

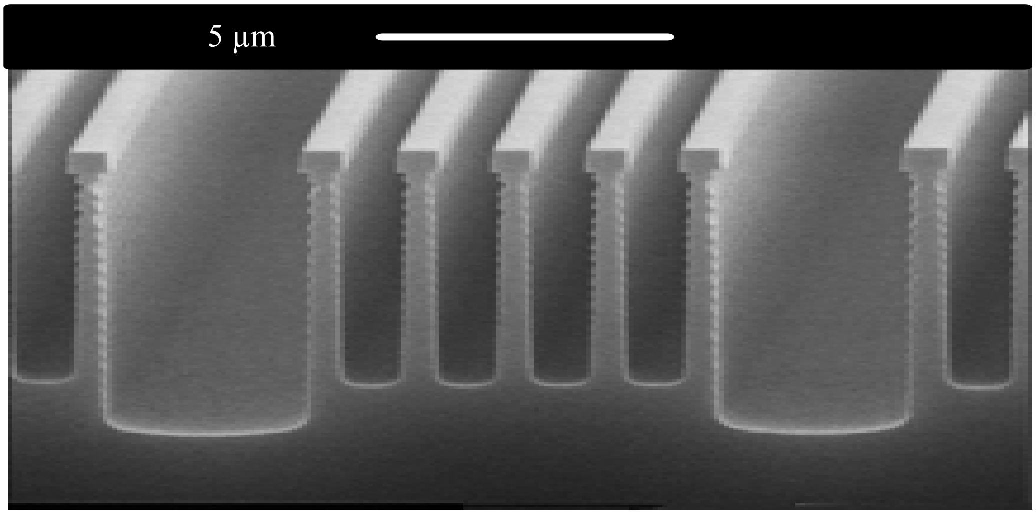
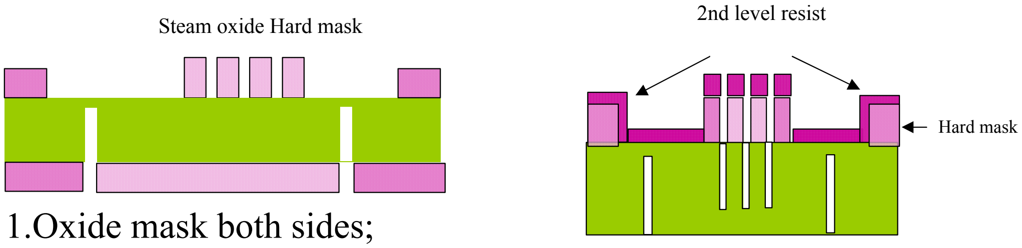


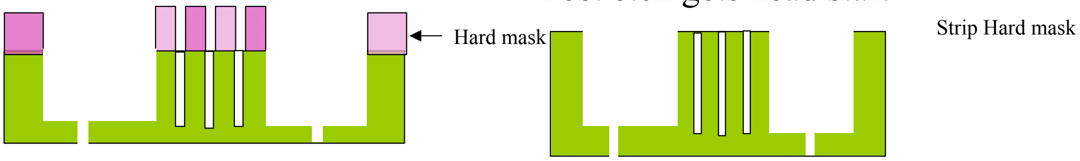
**Figure 3. An Example of Aspect Ratio Dependent Etching**

Since the aspect ratio of the posts is large and the aspect ratio of the compartments, fill holes and vias is small, they will have markedly differing etch rates. A process was developed that provided extra etch time for the posts and the appropriate etch times for the compartments, vias, and fill holes. This process is described in Figure 4.



1.Oxide mask both sides;
Back vias partially etched

2. Second level resist patterned
Post etch gets head start



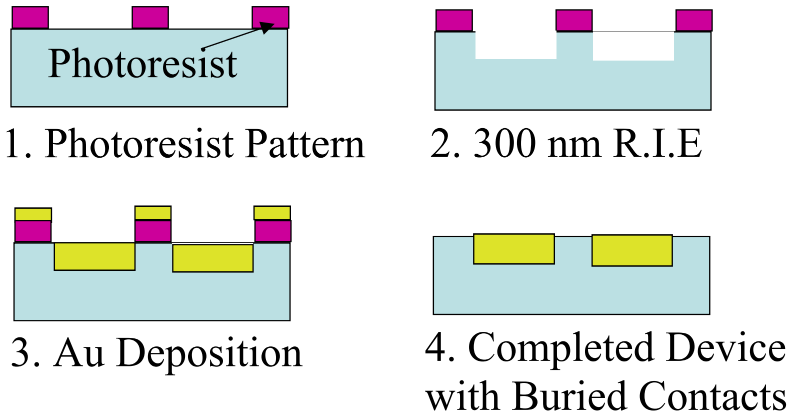
3.Resist Stripped;
Hard mask completes etch

4. Completed device

**Figure 4. Microbattery Silicon Fabrication Sequence**

In this process, steam oxide is grown on both sides of the wafer. The oxide is patterned on both sides. The back vias are partially etched so that resist can be easily applied to the front side of the wafer. The second level resist is patterned, covering all features but the posts. The posts are given a head start in the Bosch etch because the etch rate is slow compared to the larger features. The posts are etched about 50 micrometers at this stage. The wafer is removed from the etcher and the resist is stripped. The wafer is returned to the Bosch etched, where the etch is completed, opening the compartments, fill holes, and vias ( not shown) to a depth of 100 micrometers. The oxide mask is stripped and the etch sequence is complete. The wafer is cleaned and oxidized to 100 nm thickness to prevent chemical attack and electrical shorting. If a patterned lid is employed, the metal contacts must be recessed to allow good bonding to the silicon wafer. The Pyrex® is etched in a fluorocarbon plasma etch to 300 nm depth. Metal contacts (gold) are then fabricated using a liftoff process so that the metal is flush to the surface. See Figure 5.

A completed silicon compartment set is shown in Figures 6 and 7.



1. Photoresist Pattern

2. 300 nm R.I.E

3. Au Deposition

4. Completed Device with Buried Contacts

**Figure 5. Pyrex® Lid Fabrication**

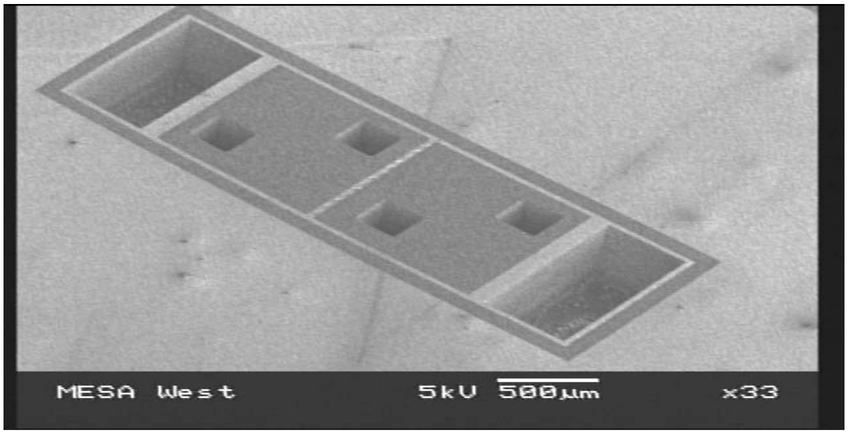


**Figure 6. Completed Silicon Microbattery**

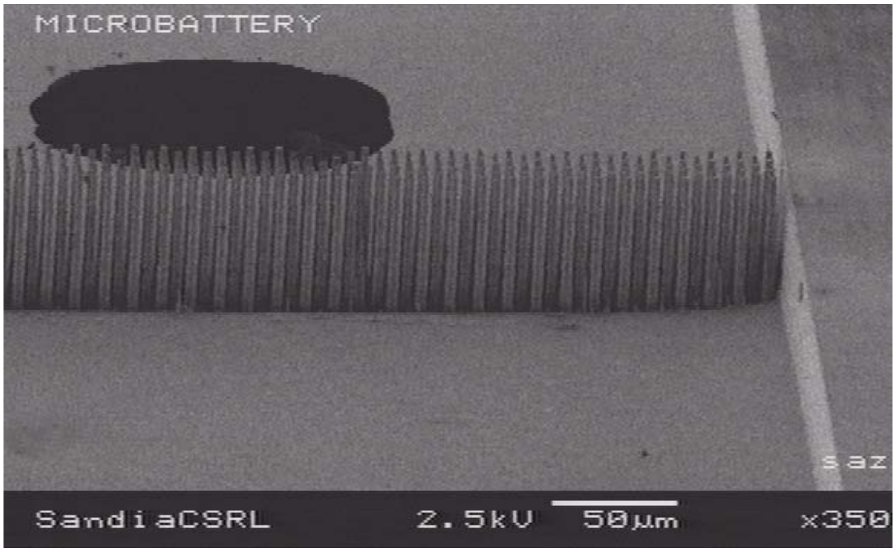


**Figure 7. Close-up of Microbattery Showing Posts and Fill Holes**

The device layout was made for 100mm wafers. Four different sizes of batteries were designed. The dimensions of a square compartment best describe these sizes. The four sizes are: 10mm; 5mm; 1mm and 0.5mm. Each size had 2 variations: 3 micrometer posts on 6 micrometer centers and and 3 micrometer posts on 8 micrometer centers. Each wafer created 129 battery compartments. An equal number of lids were made on 100mm Pyrex.

## BATTERY ASSEMBLY

The battery was designed to be assembled using anodic bonding in wafer form. In the anodic bonding process, the devices are heated to 300C in intimate contact. A high voltage (1000v) is used to attract the sodium ions to the negatively charged electrode. This causes a depletion layer to form at the silicon-Pyrex® interface. A thin layer of silicon dioxide is grown at the interface, causing the Pyrex® and silicon to bond. This bond is hermetic. Silicon devices with up to 100nm of oxide can still be bonded to Pyrex® with this method. Figure 8 shows a close up of the silicon posts anodically bonded to the Pyrex lid.

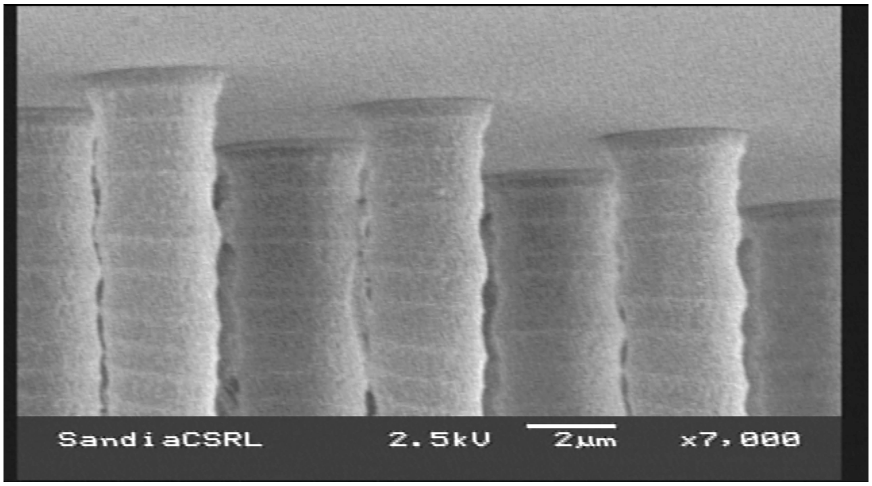


**Figure 8. Posts Anodically Bonded to the Pyrex® Lid**

After successfully bonding the device lid to the battery compartments, battery filling was attempted. As described in the next section, battery filling with the lid already attached was not successful. A re-design was performed to allow lid bonding (after compartment filling) using a UV-curing adhesive, Norland 81. In order to prevent the adhesive from mixing with the battery materials, a glue barrier was added to the design to be etched into the silicon at the same time and depth as the compartments. This "glue moat" would capture the excess glue that wicked into the interface before it reached the battery compartments. In this assembly approach, the devices were diced from the wafer and filled with battery material. The lid was placed over the cavities. A drop of Norland 81 adhesive was touched to the side of the silicon/ Pyrex® interface. The drop would wick into the interface between the 2 components, fully wetting the bond areas, but stopping at the glue moat. Figure 9 shows the moat around the compartments. If the devices are not bonded in wafer form, a plain Pyrex® lid can be used, if metal contacts are sputter deposited in the compartments and brought outside the compartment onto the adjacent silicon dioxide surface

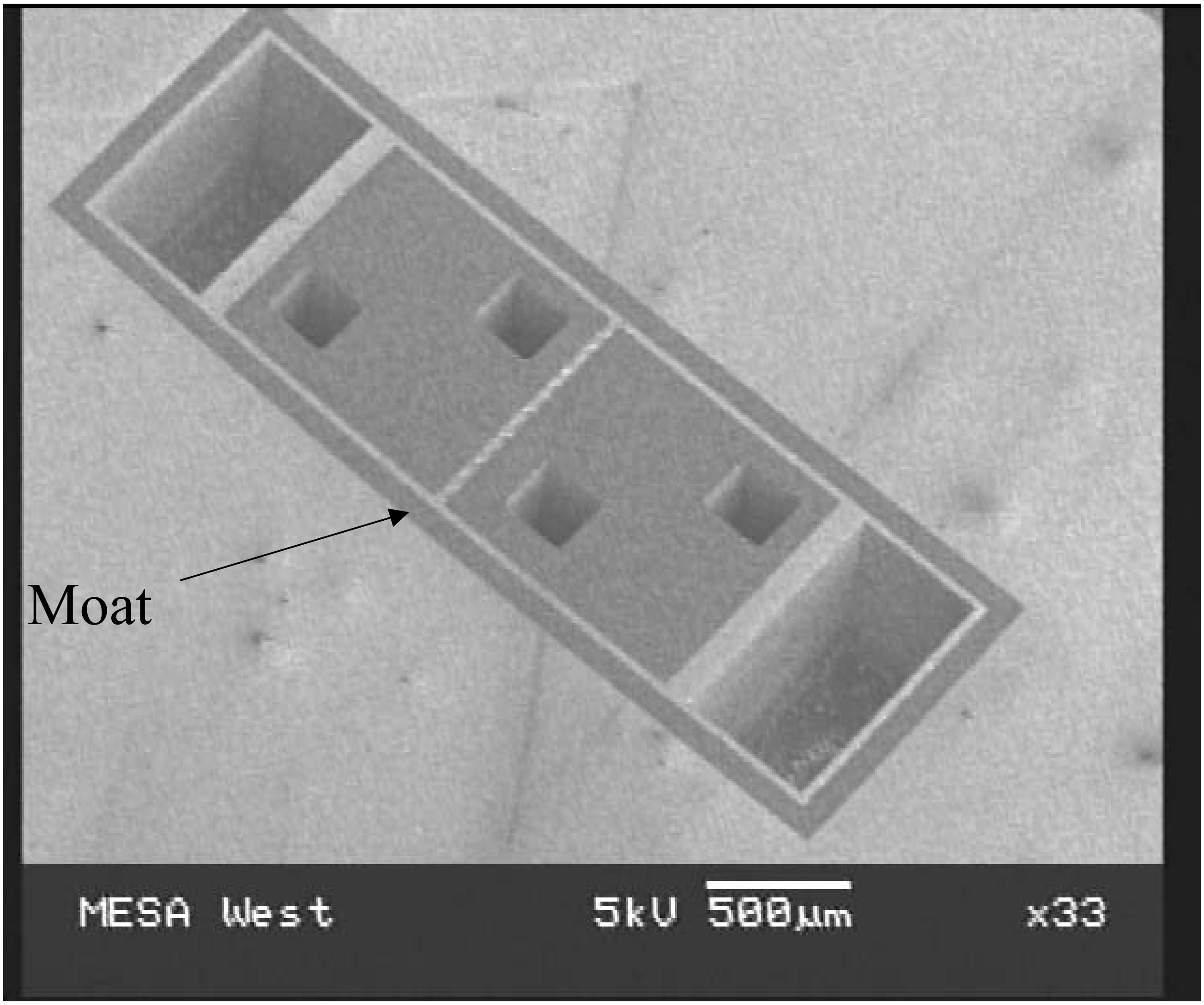


**Figure 9. 1-mm Compartment with Glue Moat**

## BATTERY FILLING

The original concept for battery filling of sealed devices was to make a suspension of battery materials in a solvent and dispense it in a cavity through the fill holes in the back. The solvent would be baked off and electrolyte added. The fill holes would then be closed with epoxy. This approach was tried repeatedly with no success. The cavity was first wetted with the same solvent used to make the suspension. Then the battery material was forced into the cavity. The cavity has a second hole to allow air to escape. After cross-sectioning the failed batteries to determine the cause of failure, the main failure mechanism was that the pressure of the suspension coming into the compartment broke the posts. The result was that the compartments were shorted together. A less prevalent failure mechanism was that the compartments were empty or only partially filled. There is no good explanation for partial filling, except trapped air causing a bubble which prevented suspension flow. As mentioned previously, we redesigned the compartments with a moat around the outside to allow adhesive attachment, without contaminating the battery materials. The initial experiments were performed on the larger cavities using an eyedropper. The smaller cavities were later filled using a Robocaster, a thick film deposition system. In this system a 150 micrometer needles were used to extrude the suspension at a rate of 0.001mm/s. The suspension had a consistency of paste and needed accurate alignment over the cavity to insure that no extra material overflowed into the adjacent cavity. The solvent used to make the suspension was N-methyl-2-pyrrolidone. This solvent was baked out at 100C in vacuum for one hour. The lithium-ion chemistry used was: positive electrode 89.2% lithium carbonate 7.1% binder; balance SAB carbon; for the negative electrode 94.3% microcarbon mesobeads; 4.7% binder and the balance SAB carbon. The electrolyte is LP40, which is 1M lithium hexafluorophosphide in a 50:50 mixture of ethylene carbonate and diethylene carbonate.

## RESULTS

A planar battery was produced with a clear lid, using gold on the adjacent sides as shown in Figure 10.

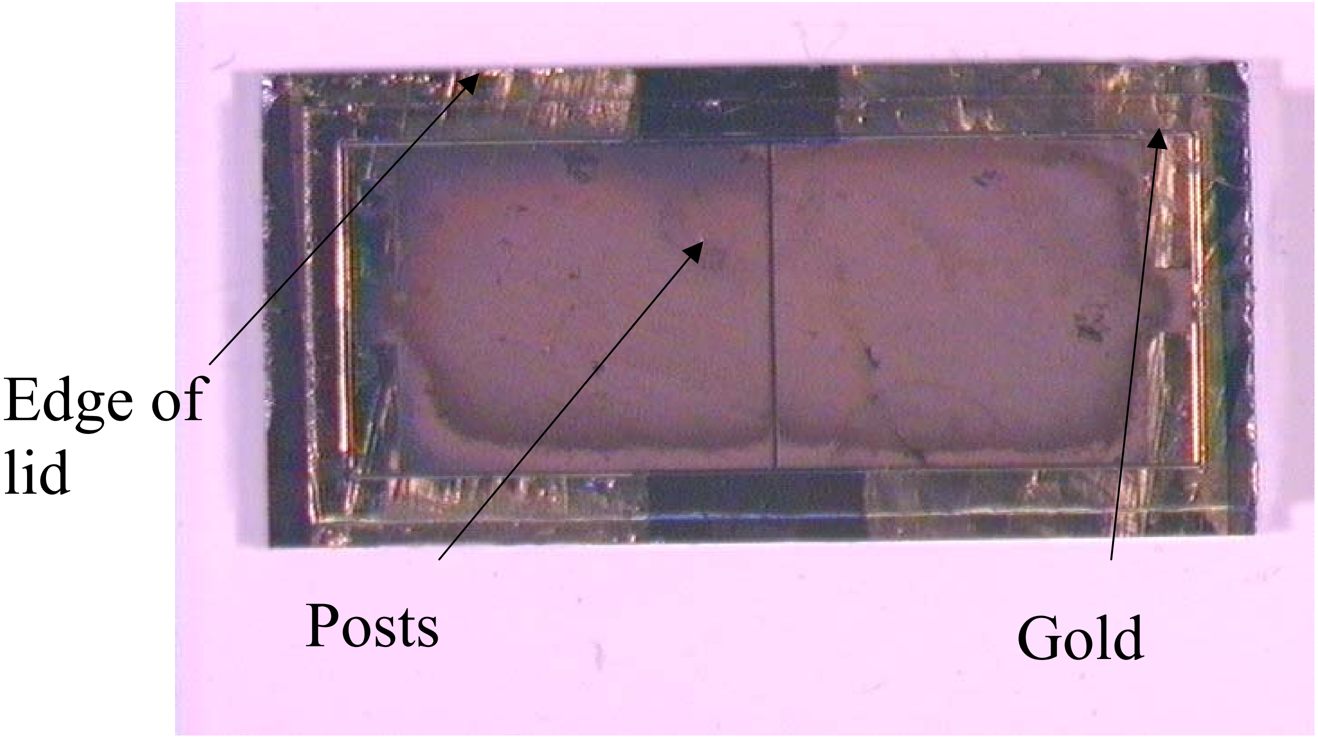


**Figure 10. Sealed Planar Microbattery with Clear Lid and Side Contacts**

A discharge curve at a constant current of 25 microamps is shown in Figure 11 for the above cell. The electrode area is 0.0075 $cm^2$ with a capacity of 1.83 microamp-hrs/$cm^2$. The large IR drop shown from 4 volts to 3.8 volts is due to the geometry of the cell. Current can only be transferred at the contiguous sides of the compartments, unlike conventional batteries that are co-facial.

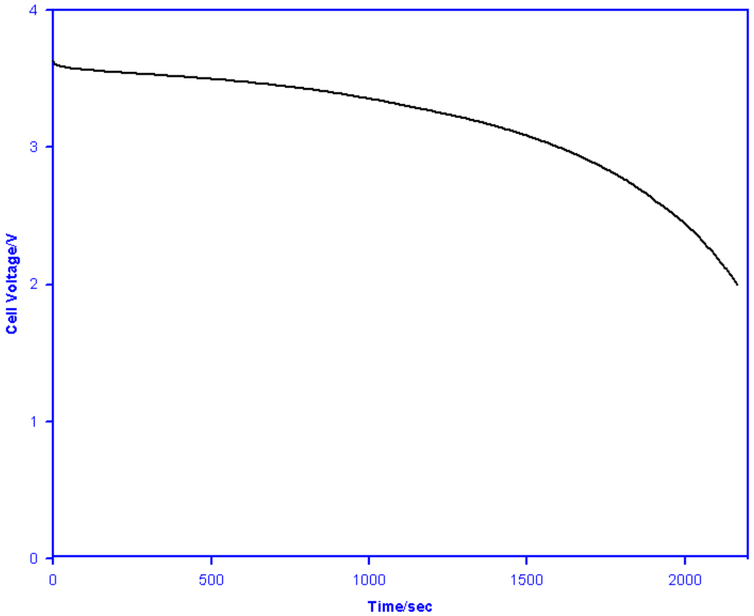


**Figure 11. A Cell Discharge Curve for a Planar Microbattery**

Future work includes lithographic series connection, new battery materials, adjustment of compartment sizes to provide stoichemetric balance, and different current collector materials, other than gold.

## CONCLUSION

We have designed and fabricated a silicon process compatible planar microbattery. Four different size battery compartments have been chosen. The battery materials are separated by high-aspect ratio etched posts, which allow free electrolyte transfer. The lid can be attached by anodic bonding or by adhesive. A moat is designed around compartments to prevent adhesive from entering the compartments. The battery is filled by a dispensing system that uses a suspension of lithium-ion chemistry materials. Presently, the lid is not attached during filling. The capacity of the battery is 1.83 microamp-hrs/$cm^2$. The cell voltage is 3.7 volts, due to the IR drop caused by having only one of the four sides of each compartment able to transfer electrons.

## REFERENCE

Grant M. Ehrlich, *Handbook of Batteries, 3rd ed*., D. Linden and T.B. Reddy, editors, McGraw Hill Books, Chapter 35, “Lithium-Ion Batteries,” (2002).

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