ELECTROMAGNETICALLY ACTUATED GAS DIVERTING VALVE USING LTCC TAPE

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ABSTRACT

This research attempted to fabricate a gas-diverting valve using LTCC technology for the emerging field of meso-scale devices. A photolithographic process for patterning Low Temperature Co-Fired Ceramic (LTCC) tapes utilizing DuPont Green Tape™ tape coupled with DuPont Riston® 9015, a dry photoresist, is described in detail. Based on the device design, calculations determining the theoretical resistance and magnetic flux were made. These numbers will determine the voltage necessary to run the device once built. Although the device was not constructed since the resolution of the dry photoresist system was being pushed led to difficulty in etching the tape, lamination and development techniques of the Riston® were perfected, and insights into the composition of the tape prior to and after etching were made. Suggestions for improvements in the process are given, as well as thoughts on what should be the next step in this research.

1. INTRODUCTION

This research attempted to fabricate a gas-diverting valve using LTCC technology for the emerging field of meso-scale devices. A multiplicity of hybrid devices can be developed using this flexible technology; because it is a hermetic and compatible material and it is ideal for fluidic systems. Due to its suitability for the fabrication of three-dimensional structures and the ability to fire with thick films, the LTCC technology is emerging as a strong alternative to silicon for the meso-scale fabrication of sensing and actuating systems. This kind of miniaturized hybrid device is important in the fields of chemical analysis, for exampl, in a flow injection analysis manifold, environmental data acquisition and bio-analysis (PCR reactors) [1,2]. Other important fields where this hybrid technology may be of importance are electronic device package heat management and fluid (drug) delivery systems [3]. Device design and construction are discussed, and pictures of selected parts of the device are shown.

1.1 LTCC

LTCC is an acronym for Low Temperature Co-Fired Ceramics. This tape is so named because of several material properties including firing cycle, firing capabilities, and composition. It is considered to be a low-temperature material because it is fired at a temperature below 1000°C. Since the tape and all passive elements that may be embedded in it can be fired at the same time, it is said to be co-fireable. It is a ceramic because the major component of the tape is oxides.

LTCC tapes can be used in a wide array of applications. They are easy to laminate on top of each other, creating the possibility of fabricating complex 3D structures. Once fired, the tapes are thermally stable compared to silicon devices which generally work best at or near room temperature, 22°C. LTCC devices have been shown to work in temperatures exceeding 150°C [4]. Another advantage of the LTCC system is that the devices are self-packaged; thus there is no need to mount the completed device onto a substrate. A final advantage of LTCC tape over silicon is price - a 2” wafer of silicon costs approximately $12, whereas the same area of LTCC costs merely $.07 cents.

In this project, DuPont’s LTCC 951 Green Tape™ was used. The composition of this tape is 45% glasses, such as PbO and SiO_2; 40% Alumina, Al_2O_3; and 15% organic binders [5]. The organics are added to improve the rheology and flexibility of the tape when in the “green” (pre-fired) state, when the tape is soft and easily deformed. Conventional methods of processing the tape involve mechanical punching or drilling in a serial fashion while in this state.

Once all designs have been patterned into the LTCC tape, and all lamination has been done, the tape can then be fired. The firing cycle is summarized in Figure 1 and is described below.

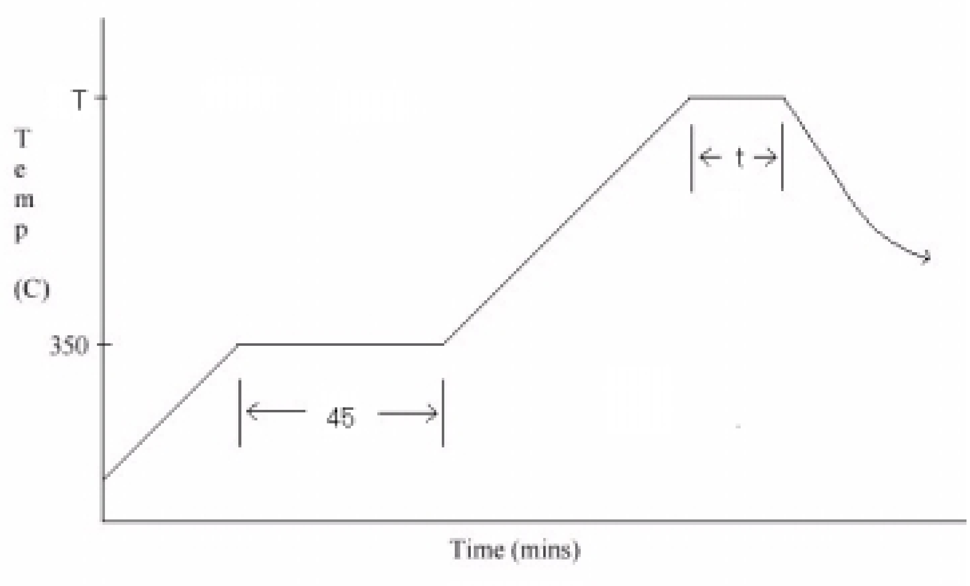


Figure 1: LTCC Firing Cycle.

The tape is first brought from room temperature, approximately 22°C, to 350°C on a 10°C/minute ramp. It stays at 350°C for 45 minutes, during which time all of the organic material in the tape burns off. Had the tape been brought directly to the sintering temperature, these organics would have formed carbonates, which degrade most of its properties; thus it is important that they be completely burned off. The tape is then brought to either 800°C or 850°C (T in Figure 1) for either 2 or 30 minutes (t in Figure 1), depending on whether the desired result is a fully- or semi-sintered sample. Both semi- and fully-sintered samples were utilized at various stages in this project. The glass transition temperature of the glasses in the tape is around 750°C; at 800°C this glass has begun to flow and surround the grains of ceramic, joining them together. If the tape is left at 800°C for 2 minutes, the flow of the glass will have just started and the grains of ceramic will be loosely attached. However, if the tape is left at 850°C for 30 minutes, the glass will have completely surrounded the grains, bonding the nearby grains strongly. A more in-depth discussion of the semi-firing process is provided in a later section. After the tape is kept at the sintering temperature for the desired amount of time, the furnace is turned off and the tape is allowed to cool.

During the full firing process, the tape shrinks 12.7 ± 0.2% in the X-Y direction and 15 ± 0.5% in the Z direction as a result of the loss of organic material in the tape and the flow of the glass bringing the grains closer together [6]. This shrinkage needs to be compensated for when designing structures that depend on different layers lining up correctly; otherwise, electrical continuity may not be achieved.

1.2 DuPont Riston®

Conventional methods of processing LTCC utilize serial methods, whereby only a single sample is being worked on at a given time. Although machines can be made to do this very quickly, it is inherently slower than batch processing, where multiple samples can be worked on at a given time.

Photolithography is one such process, in which patterns are transferred using light. Modern photolithography makes use of one of two methods, a positive or negative resist. The term resist is derived from the material's ability to protect the area under the pattern from processing. In both cases, light from a mercury arc lamp source shines ultraviolet source on the resist through a photo mask. Positive and negative resists are distinguished by the subsequent reaction. In a positive resist, the area exposed to the light undergoes a reaction to form an alkali-soluble product [7]. The unexposed area is not soluble in the alkali solution that is used as the developer. In a negative resist, the area exposed to the light becomes strengthened either by cross-linking or polymerization. Thus it is less likely to be washed away when subjected to a developing solution.

DuPont Riston® is a dry, laminable, negative photoresist that comes in sheets and is sandwiched between two materials. On one side is a layer of Mylar^{TM} which protects the resist when it is being handled and promotes good contact between the mask and the tape when its exposed to the UV light. The other side of the Riston® is coated with a thermally activated glue, protected by a layer of polyolefin [8]. The Riston® used in this project was Riston® 9015, which is most sensitive to light whose wavelength is between 350 and 380 nm [9].

1.3 Gas Diverter

The goal of this project was to create a gas flow diverter in the μL/s range. To do this, a top-level schematic of the device was needed. By taking into account the desired overall resistance and throughput, the sizes of each necessary portion were determined. This schematic is shown in Figure 2.

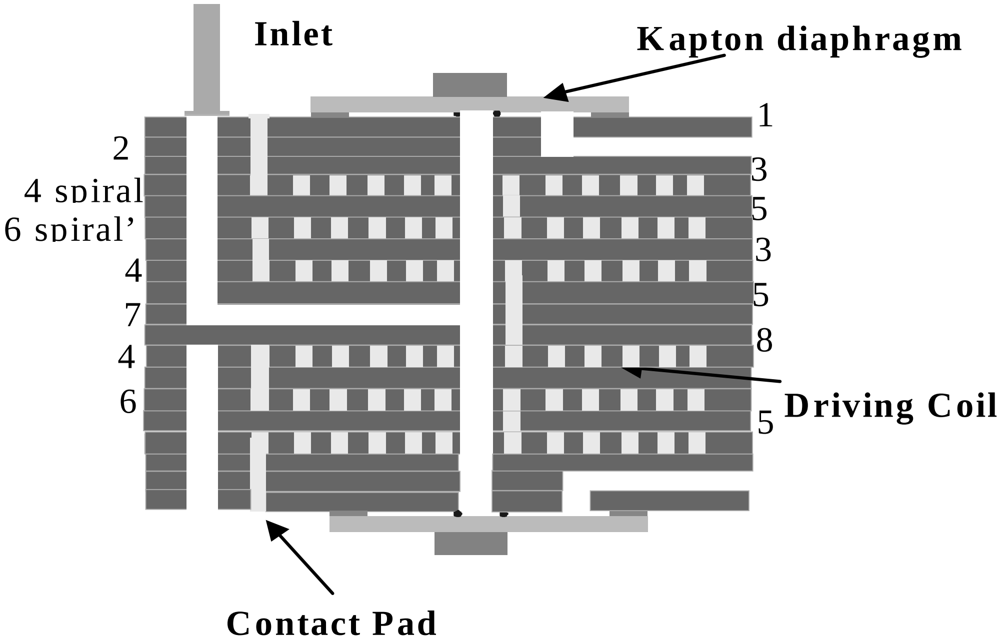


Figure 2: Schematic of the flow diverter. Note the driving coil metallization in layers labeled 4 and 6, and the permanent magnets attached to the Kapton membranes. The inlet and outlets are evident.

The photomasks were designed following this schematic using AutoCAD and are shown in Figure 3.

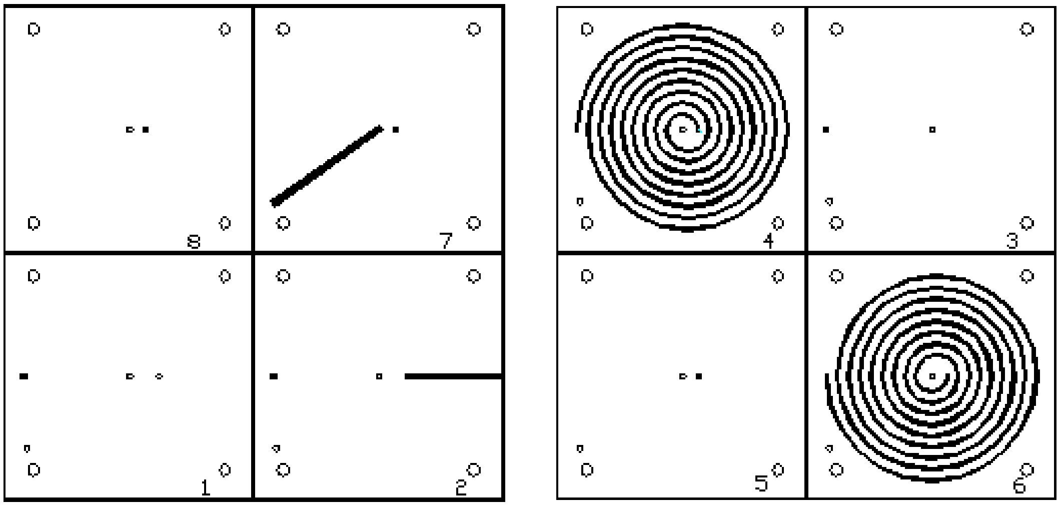
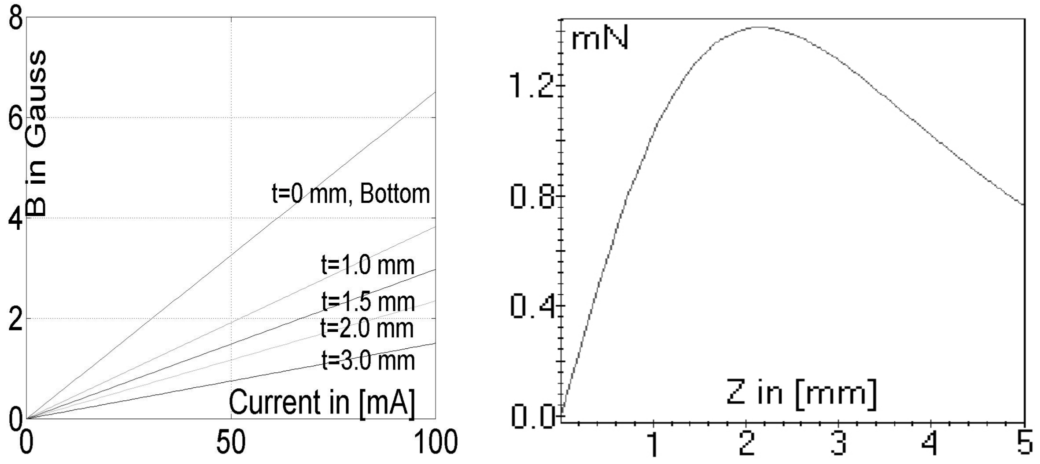


Figure 3. AutoCAD drawing of the two mask designs used in the creation of the device. The four circles at the corners of each layer are used as alignment marks. In the center and bottom left corner of each layer is the 800 micron diameter pathway (400 micron in this drawing) for fluid flow. Electrical continuity of the coil is ensured by the use of the vias, depicted as solid squares in layers 1, 2, 3, 5, 7 and 8.

The overall design utilizes an electromagnet to actuate the valves on both sides of the device. It was found that the patterns developed in the Riston® were the same size as those in the photo mask, but when the process was carried through and the LTCC tape was etched, the resultant patterns were double the width of those in the mask. This fact was taken into account when designing the masks for this device. The mask dimension for the fluid channel is 400 μm and for the coil conductors it is 200 μm. The permanent magnets are $Nd_2Fe_{14}B$ micro-magnets that are 1.5 mm thick with a diameter of 2 mm. The valve membranes are KJ200 Kapton films and the valve seats are a polysiloxane clear paste with a burned-out cavity matching the diameter of the fluid conduit. When current is passed through the planar spiral coils, it creates a magnetic flux that is used to move the permanent magnets mounted to the diaphragm away from or into the device, thereby opening or closing off the pathway for fluid flow. Basic electromagnetics [10] combined with MATLAB was utilized to calculate the magnetic field generated by the conductor coils at different axial positions, corresponding to different displacements of the permanent magnet and the force on the permanent magnet as a function of the same variable [11]. Magnetically generated forces can be made large for micron-size air gaps [12]. Figures 4a and 4b show the results of electromagnetic calculations for the pertinent range of the variables.



(a) (b)

Figure 4a shows the magnetic field versus coil current for different axial positions of the permanent magnet. Figure 4b shows the force on the permanent magnet as a function of the axial position for a constant excitation current. Note that in both cases, for small axial displacements, the relations are linear.

The theoretical resistance of the coil was calculated using the well-known formula:

$$R = \frac{\rho L}{A} \quad (1)$$

where ρ is the resistivity of the material being used, L is the length of the conducting coil, and A is the cross-sectional area of the coil. To determine the length of the spirals used in creating the coil, the following formula was used:

$$L = \frac{\pi N(D + d)}{2} \quad (2)$$

where N is the number of turns in the spiral, D is the total diameter, and d is the inner diameter [13]. To approximate the resistance of the full coil, the resistance of a single spiral layer was calculated, and then multiplied by 6, since this is the number of spirals that will be in the completed device. It was found that the resistance is 18.13 Ω/layer; thus the full device would have a resistance of 108.78 Ω. For currents between 10 and 30 mA, a voltage of 1.09 to 3.26 V would be needed.

1.4 Partial Sintering

The first step in the fabrication of the gas flow diverter is to create some semi-fired LTCC blanks. Pieces of LTCC in the green state are cut to 2.15” x 2.15” since these dimensions will lead to a blank of 2” x 2” due to the shrinkage induced in the semi-firing process. These dimensions are desired because they are the nominal size of the photomasks that were used.

This step provides the means for both a fast, controlled etch rate of the LTCC, and for laminating the layers together once the patterns have been transferred to the LTCC. The importance of these features will be described in a later section.

2. EXPERIMENTAL

2.1 Partial Sintering

As described earlier, its important to this process that the tape be semi-fired first. The LTCC samples are placed on top of an alumina substrate. At first, the samples were placed on a 99% Al_2O_3 substrate that is 7mm thick. To correct bubbling in the center of the tape, silicon wafers were placed on top to provide some pressure and force the samples flat. This worked well, but the samples seemed to be less dense than they had in previous trials. Two theories were formed to explain this. The first is that the alumina plate is too thick, and since it has finite thermal conductivity, all areas of the plate do not heat uniformly. Thus the tape is receiving differing amounts of heat, and this causes the bubbling in the tape. The other theory is that the purity of the alumina plate is too high, and that combined with other atmospheric things (i.e. dirt and hair) that have fallen onto the plate, when heated, combine and release some hydrogen. Some of this hydrogen diffuses into the LTCC, giving it less density, and the hydrogen that cannot diffuse pushes the tape up in certain spots, causing the bubbling. It is not known which of these two theories, if either, is correct. Unfortunately, this was not seen as much of a problem until the end of the summer, when difficulties in etching the LTCC arose. Recently, some 96% Al2O3 plates that are 1mm thick were purchased, and neither of these problems occurs when these plates are used. A schematic of the LTCC in the green state is shown in Figure 5.

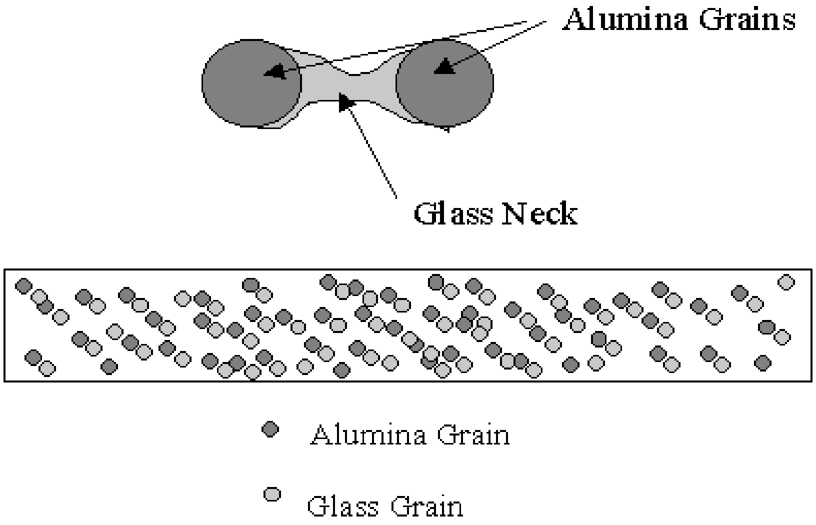
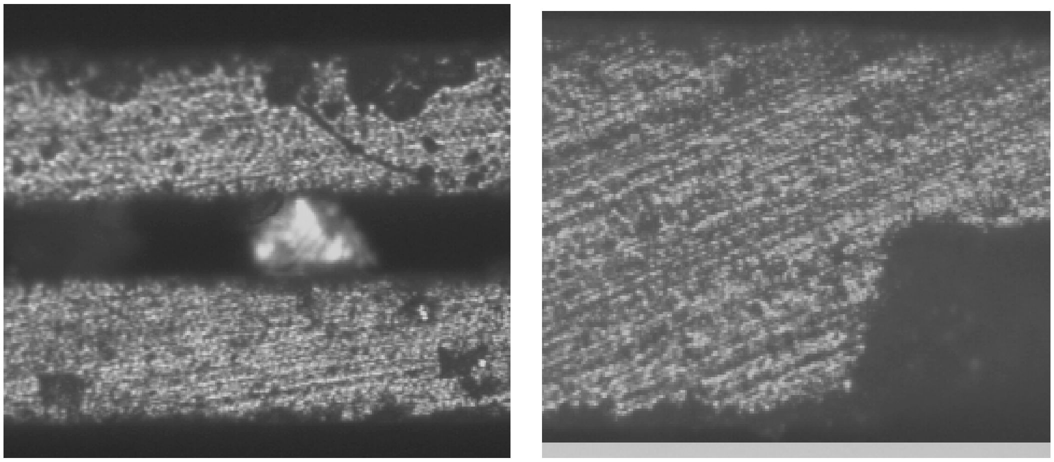


Figure 5: Schematic of LTCC in the green state. The binding of the alumina grains by the flowing glass is shown at the top.

When the sample is heated above the glass transition temperature of the glasses in the tape, the glass begins to flow. Since the tape is only held at this temperature for a few minutes, the glass is not able to fully flow and surround the alumina grains, but they do bind them loosely and a glass neck forms. The tape is etched with a glass etchant, and the thin areas of glass decompose first. Semi-fired tape is therefore more desirable at this point in the process than fully fired tape, since the etchant would have more glass to etch through to obtain the same result if the tape were fully fired.

The other important property of semi-fired tape is that it provides a means for laminating the samples together when they are completely patterned. At first it was believed that something would needed to be added between the layers of semi-fired tape in order to promote adhesion. Since glass is what binds the tape together internally, it was believed that glass grains would be the perfect solution for binding two layers together.



(a) (b)

Figure 6: Semi-Fired pieces that have subsequently been fully fired. The sample in 6a has glass grains in between the two layers, the sample in 6b has nothing between the layers (the bottom layer ends near the center of the picture). Note the large separation between layers in 6a, as well as the sizable glass grain just right of center. Note that the sample in 6b is continuous, and that there is no longer a distinction between layers. (Photos courtesy of P. Espinoza [14]).

This assumption proved to be false as illustrated in Figure 6. When glass grains were placed between the layers of semi-fired tape, they did not bind the tape together as expected, but rather kept them separated, even when a small amount of pressure was provided during the full-firing process. However, when nothing was done to the tape but providing a small amount of pressure from above, the two layers merged seamlessly into one.

2.2 Riston® 9015

2.2.1 Process

Once the tape has been partially sintered, it is ready to be processed. First, the dry photoresist is laminated onto the LTCC. To do this, the polyolefin covering needs to be removed. One piece of Riston® is placed on top of a layer of printer paper and a layer of clean room paper. The LTCC sample is then centered on the photoresist, and the same configuration of paper and photoresist is placed on top of the sample. The sample is then run through a laminating machine, which consists simply of a heating element and two rollers that the sample passes through. A laminating temperature of 100°C ± 5°C works best.

The photoresist must be laminated onto both sides of the LTCC sample because it will later be submerged in a bath of buffered hydrofluoric acid (BHF). Buffered hydrofluoric acid consists of a mixture of hydrofluoric acid and ammonium fluoride in a ratio of 1 to 4. The laminated samples are then exposed to UV light at a power density of 75 mJ/cm^2 as measured at 365 nm from a mercury arc lamp source through the photomasks. Since the Riston® acts as a negative photoresist, those areas that are exposed to the light are cross-linked and remain when the sample is developed; all other areas wash away. For this reason it is necessary to expose the entire back of the sample to light as well.

The samples are then allowed to rest for at least 30 minutes; developing the samples immediately after they are exposed in some cases produced jagged edges and in general led to poor development. After resting, the samples are placed inside a developing machine, which consists of a vacuum chuck situated in the center of a rotating stage. Above the sample, a spray nozzle shoots a jet of the developing sodium carbonate solution at room temperature, approximately 67-72°F (19.5-22.3°C), at a spray pressure of 40 psi for 35 seconds. The samples are then dried with cool air for 5 minutes. In preparation for the etching step, the samples are then re-exposed to a high dose of UV light, >1.0 J/cm^2, in order to further cross-link the molecules and ensure that the BHF does not etch areas that are not selected by the photo mask. The samples require 90 minutes of etching in the BHF.

Once the LTCC has been etched, the dry photoresist must be stripped. Since the organics in the LTCC were burned off in the partial sintering process, it is safe to use an organic stripper to remove the Riston®, and for this acetone is used. Following this, the samples are ready to be bound together and the vias filled with conductor. They are laminated using the methodology described before, and then filled with a Ag-Pd paste, DuPont 6134. They are then fully fired once more.

2.2.2 Results

The dry photoresist worked perfectly. Lamination, exposure and development yielded a crisp, clean pattern transfer from the mask to the photoresist. An example of a developed sample is shown next to the mask design in Figure 7.

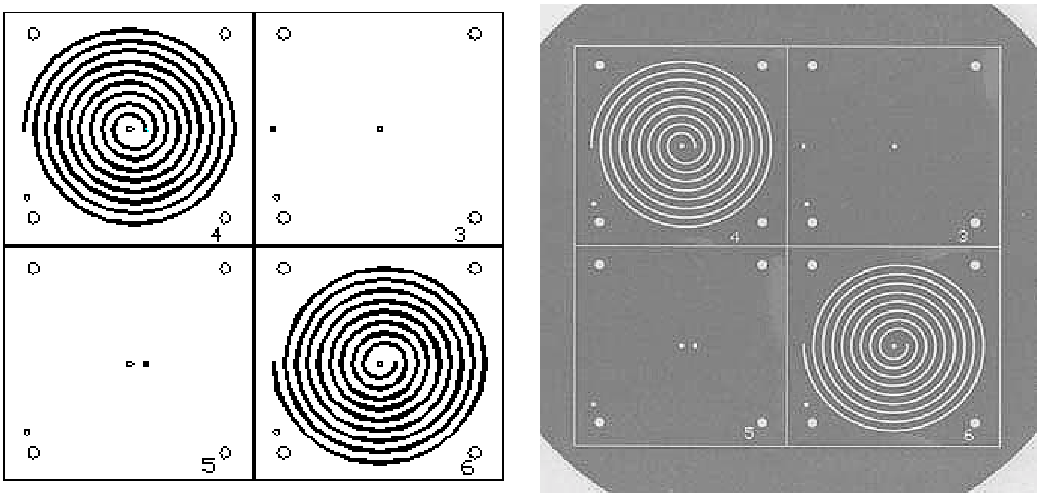


Figure 7: Mask design on the left, and a sample where Riston® 9015 has been laminated to partially sintered LTCC and developed, on the right. Note that all dark areas in the mask are washed away when the sample is developed.

Though development worked well, difficulty arose in etching LTCC completely. When the partially sintered LTCC samples are placed in BHF for 90 minutes, they are not etched all the way through. A theory for this is shown in the schematic of Figure 8.

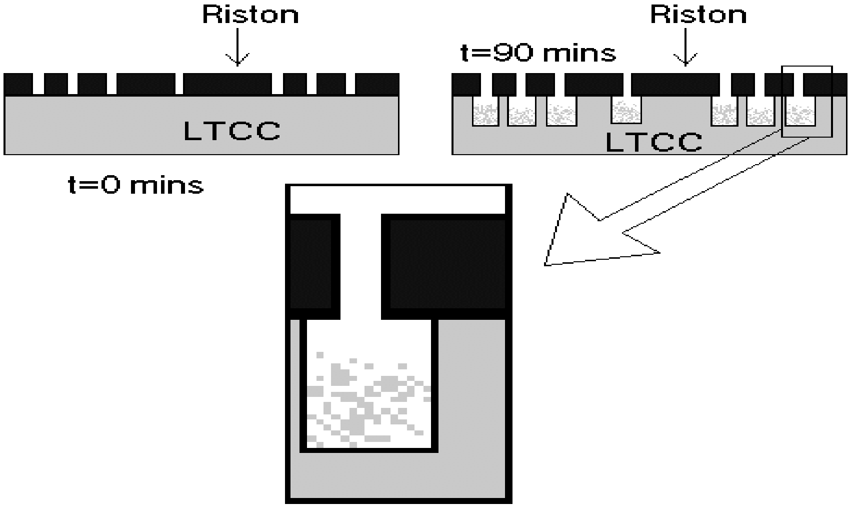


Figure 8: A theory of why the samples do not etch all the way through if simply left in the BHF solution. The opening in the Riston® is so small that there is no fluid flow in the area, and the matter that is broken away from the LTCC does not escape.

The BHF solution does not selectively etch the LTCC; all directions are etched equally. The matter that is broken away from the LTCC tape sits at the bottom of a well that has been etched out. Thus, the BHF has a longer path to reach the desired areas, if it ever reaches there at all. Etch depth versus the square root of time is shown in Figure 9. Note that the best-fit curve is a linear regression, which indicates that the etch rate is diffusion controlled. This fits the model described above, since the BHF has to diffuse through the extra matter to arrive at the bottom of the etched well.

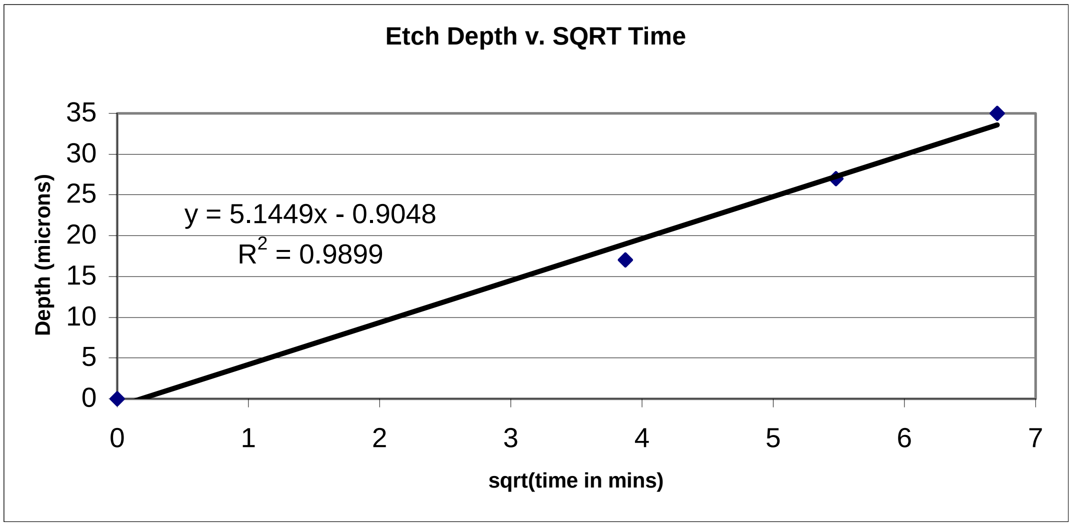
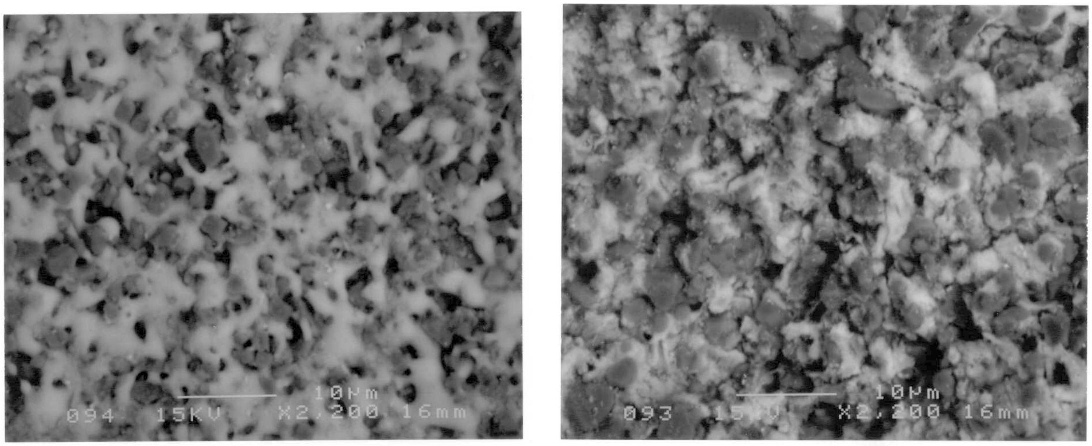


Figure 9: BHF etch depth of the partially sintered LTCC versus the square root of time. The linear slope indicates a diffusion-controlled reaction.

Rotating the samples at a rate of 12 rotations a minute was thought to be a way to promote flow of the BHF across the samples and removal of this matter, but it proved not to work. Increasing the angular frequency was not attempted since the samples are very fragile when etched all the way through, and a fast rotation would tend to break the samples as they are dragged through the solution. Thus another method of removing this unwanted matter was necessary.

To investigate what was happening, one sample was brought to a scanning electron microscope (SEM). The sample was imaged using the backscattering electron detection, because this method is sensitive to atomic number. Since the glass has some Pb in it, which has a high atomic number (82), it shows up white in the image. The assumption that the white parts of the image are glass was confirmed when it was noticed that the dark parts have clear faces on them, which is a sign of that they are crystalline. The backscattering images are shown in Figure 10.

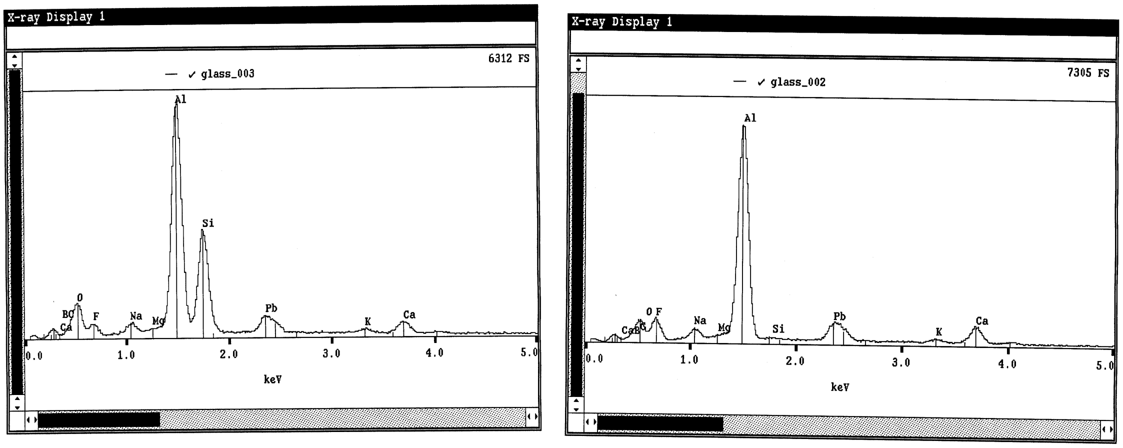


(a) (b)

Figure 10: The image in 10a shows a backscattering electron image of the un-etched section of the partially sintered LTCC taken with a SEM. The image in 10b shows the etched section of the tape taken by the same method. Note there is much more white, glass, in the un-etched section, but that all the glass has not been etched away, as evidenced by the small clusters of white in Figure 9b.

The image of Figure 10a shows that there is quite a bit of glass in the un-etched sections of the tape. In Figure 10b, much of that glass has been etched away, but there are still sections of white in the picture. These bits of glass hold the small particles of alumina together and do not allow them to be washed away, creating a clump of matter at the bottom of the etched well.

The elements present in each section of the sample were analyzed using energy dispersive x-ray analysis (EDX). The results are shown in Figure 11.



(a) (b)

Figure 11: EDX results for both the un-etched (11a) and etched (11b) sections of the partially sintered LTCC tape. Note the large spike for Si in the center of Figure 11a, and the absence of such a spike in Figure 11b.

In the un-etched section of the tape, there is a relatively large amount of silicon, whereas in the etched section there is nearly none. This corresponds to a significant drop in the amount of SiO_2 present in the tape. This is precisely the glass that the BHF was meant to target and it can thus be determined that the acid is doing what was expected of it. The problem, then, is to figure out how to remove the extra matter that is blocking the BHF from reaching the bottom of the etched well.

Phosphoric acid, H_3PO_4, was then used to remove the extra matter. Samples were placed in BHF at 60°C for 15, 30, 45, or 60 minutes and then transferred to phosphoric acid at the same temperature and left for 30 minutes. The phosphoric acid did a great job of cleaning out the added material from the etched sections of the tape. Ideally, a mixture of BHF to etch the tape, and phosphoric acid to clean the etched sections, would be used. Unfortunately, the Riston® photoresist did not hold up in phosphoric acid. It changed colors, became much thinner, and flaked away in many sections. In order to use a combination then, the phosphoric acid would have to be diluted, and it is not known at this time whether the Riston® will hold up under these circumstances.

3. CONCLUSIONS

While the device was never actually completed, it is well on its way. The most difficult part is to pattern the LTCC, since the resolution of this technology is being pushed in this experiment. Patterning the tape was not accomplished this summer, but insights into the mechanisms of etching were found, and will hopefully lead to a successful result in the near future. Attempts need to be made to combine BHF with phosphoric acid in such a proportion that the tape can be etched and cleaned at the same time, while the Riston® is not harmed. Other acids might prove more useful than phosphoric in reaching this goal.

Another method for solving this etch problem may be to increase the temperature at which the BHF etches the tape. Comparing these to previous results [14], it is noted that the etch rate this time around is much slower than before. In tests where the BHF was kept at 90°C, the tape etched at 2.419 μm/min, whereas the rate was 0.767 μm/min in these tests where the BHF was kept at 60°C. If the tape is etched faster, the problem of extra matter congregating at the bottom of the etched well may be erased. Whether this solves that problem or not, etch times will be reduced, speeding up this process considerably. Since the point of using photolithography is to be able to batch process many samples quickly, this is a desirable result.

After patterning the LTCC becomes routine, a good method for aligning the various layers will be needed. Thus far the layers have been aligned by hand, and while this provides working samples, it should not be the preferred method. In the near future it will be shown that this method of using a laminable dry resist in combination with partially sintered LTCC form a suitable technology for the fabrication of three dimensional meso-scale devices.

4. ACKNOWLEDGMENTS

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