SAND2016-12913J

Fabrication of Solid State Multi-Layer Glass Capacitors

Rudeger H.T. Wilke[1], Harlan Brown-Shaklee[1], Adrian Casias[1], Billy Cunningham Jr. [1], Amanda Gomez[1], Michael Vecchio[2], Rohith Vudatha[3]

[1]Sandia National Laboratories, Albuquerque, NM 87185, USA
[2]Materials Research Institute, The Pennsylvania State University, University Park, PA 16802, USA
[3]Cornell University, Ithaca, NY 14853, USA

Abstract - **Alkali-free glasses show immense promise for the development of high energy density capacitors. The high breakdown strengths on single layer sheets of glass suggest the potential for improved energy densities over existing state of the art polymer capacitors. In this article, we demonstrate the ability to package thin glass to make solid state capacitors. Individual layers are bonded using epoxy leading to capacitors that exhibit stable operation over the temperature range -55 °C to +65 °C. This fabrication approach is scalable and allows for proof testing individual layers prior to incorporation of the stack, providing a blue-print for the fabrication of high energy density capacitors.**

I. Introduction

Alkali-free (AF) glass has shown considerable promise as an emerging material for next generation high-energy density capacitors [1, 2]. Realizing the potential of these materials has been slowed by several technological challenges. First, there is a strong thickness dependence to the breakdown strength AF glass [2, 3], necessitating the use of thin (< 30 μm) glass to realize any benefit in dielectric strength relative to sodium-silicate glasses. In addition, while glass as thick as 200 μm is suitable for reel-to-reel processing [4], glasses under 10 μm in thickness will be necessary to achieve bend radii in the mm range. This will be necessary for capacitors since the core of any wound glass capacitor will represent inactive volume that is deleterious to the overall energy density of the device. To date, glass of these thicknesses below 30 μm are not widely commercially available. The most popular route to further thin the glass is with hydrofluoric acid. Such an approach is not readily feasible for manufacturing wound glass capacitors [5], but rather, favors a multi-layered geometry. Second, glass capacitors tend to show relatively poor self-healing properties [6] requiring proof-testing of each individual sheet prior to inclusion within the stack [3]. The challenge then becomes developing a packaging strategy that allows pre-screened individual sheets of thinned glass to be stacked mechanically in series and electrically in parallel.

It has previously been demonstrated that residual alkali-atoms within the glass preclude AF glass from being suitable for high temperature operation [7, 8]. With a target space limited to near room temperature applications many more options exist for packaging. The goal of any strategy is to maximize energy density by minimizing the edge margin that protects against flash over. This could be done in a number of different ways. One possible route is to use a foil/glass approach backfilled with insulating fluid similar to what has been done for decades in foil/paper capacitors (see e.g. [9]). Metallizing the glass directly rather than using a foil electrode as in often done in poly-propylene capacitors provides a more controlled dielectric area and a potential route towards self-healing electrodes [10]. While pure metal electrodes clear only ~50-60% of breakdown events for AF glass [2], research on irreversible phase change materials as the electrode hints at possible routes to improve the self-healing nature of glass capacitors [6]. Conversely, segmented metal electrode designs may pave the way for self-healing using conventional electrodes [11]. With these concepts in mind, our focus is on demonstrating a packaged capacitor based on metallized glass. In this manuscript we demonstrate a solid state capacitor manufactured by laminating sheets of glass with thin epoxy binding layers. A solid state capacitor was chosen due to the greater flexibility in potential applications over oil filled devices, where the development of air-bubbles can lead to premature failure of the capacitor.

II. Experimental Methods

A. *Capacitor Fabrication*

The process flow for the fabrication of the capacitors is shown in Figure 1. The general approach, described in more detail below, is to bond individual metallized sheets of glass into a multi-layer stack and then use a laser to cut out the final dimensions of the capacitor prior to applying the end terminations.

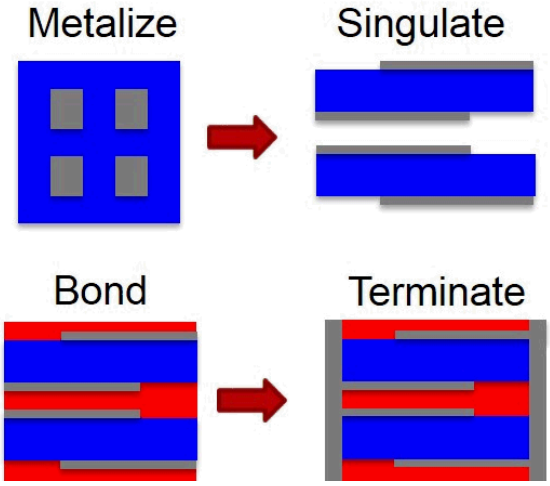


Figure 1 Process flow for fabrication of each of the layers for the multi-layer capacitor (running left to right). Following the initial electroding of the 4”x4” glass, 0.55”x0.65” individual pieces are laser machined for bonding. Stacks are then bonded together within a custom alignment fixture before the capacitor geometry is defined through a second laser cutting step. After cleaning the edges to expose the inner electrodes, terminations are applied to complete the construction.

Commercially purchased Schott AF45 glass was used for the fabrication of the capacitors. The as-received glass was 101 x 101 mm and 30 µm thick. Prior to depositing the electrodes, the glass was cleaned in a low power oxygen plasma using a Harrick Plasma PDC-001 Plasma Cleaner. A shadow mask was used during Cr/Au deposition in a Kurt J. Lesker LAB 18 sputter deposition system to pattern the capacitor in the desired geometry. The layers were 30 nm and 100 nm thick, respectively. The mask defines rectangular electrodes 0.45”x0.5”. Electrodes were deposited on the top and bottom surfaces of the glass sheets with an offset of 0.15”. The mask pattern consists of 25 electrodes and several alignment markers used for orienting the sample in laser cutting (Figure 2). The glass layers are singulated using a LPKF ProtoLaser U3 laser cutter operating at 355 nm. The laser power was set to 4W and operated at a frequency of 75 kHz. The glass is cut to provide an edge margin of 0.1” on each of the four sides – making the final capacitor dimension 0.65”x0.55” with an active area of 0.45”x0.35”. Note that the 0.1” edge margin for the final capacitor indicates the laser cuts through the as deposited electrode at a distance of 0.05” from the edge of the metallization. This was necessary to ensure the buried metal layers ran all the way to the edge of the glass sheets, providing easy access for applying the end terminations.

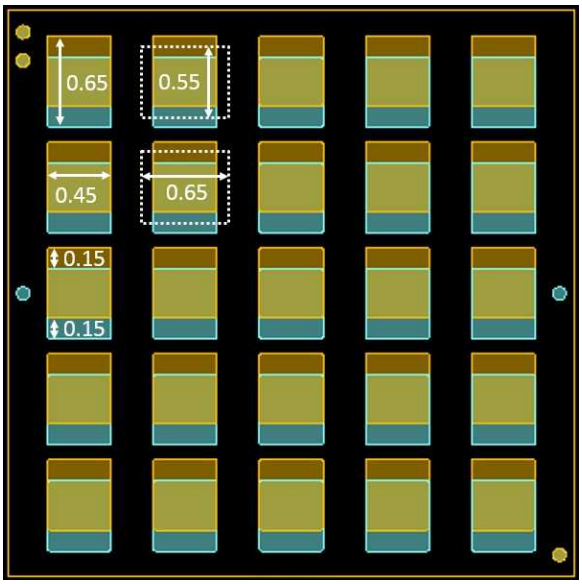


Figure 2 Shadow mask with alignment markings for maintaining registry in the multilayer capacitor. The blue and brown regions represent locations of the metal deposition for the top and bottom layers, respectively. The yellow region is the overlap, which defines the active area of each layer. The dotted white lines show the location of the laser cutting for singulating the layers. All dimensions are in inches.

In order to form a mechanically robust capacitor, the individual glass sheets were stacked and bonded using EPON 828 with Jeffamine T-403 as the curing agent. To ensure the widest possible operating range, a mixing ratio of 1:0.42 was chosen to maximize the T_g of the epoxy [12]. The biggest challenge in scaling up from a single layer design to a multi-layer package resides in maintaining registry between the glass

sheets – particularly given the fact that, depending upon the desired final capacitance, the required number of layers may exceed 100 (For the geometry specified above, each layer has a capacitance of approximately 170 pF). To resolve this problem, we 3-D printed a custom alignment fixture out of PolyJet VeroCyan. The sheets are stacked in an A/B type pattern ensuring each subsequent dielectric layer is connected electrically in parallel as depicted in Figure 1. A small bead of epoxy was applied to the center of the part and allowed to spread during under uniaxial pressure.

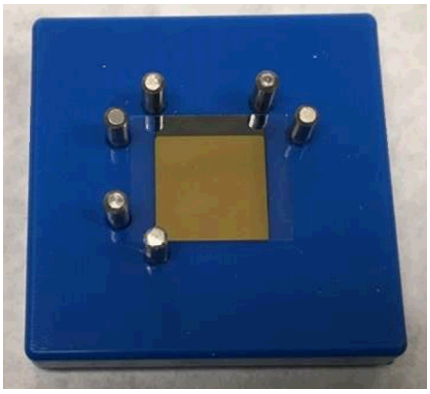


Figure 3 Glass sheets within the custom build alignment fixture. A complimentary cap fits over the pegs to allow for the application of uniaxial pressure.

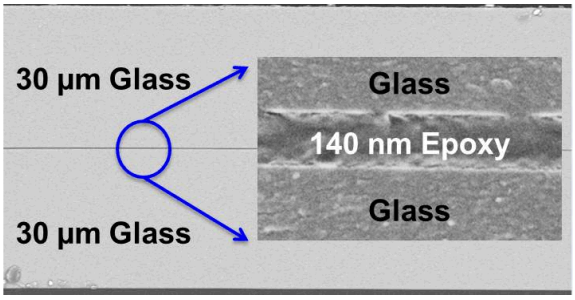


Figure 4 SEM micrograph of a glass/epoxy/glass structure cured under pressure of 4.2 kPa. The thickness across a ~1 inch test piece measured 138±4 nm.

In order to ensure no air-bubbles were present within the bonding layer, the amount of epoxy applied for each layer far exceeded that which was necessary for forming the bond. All of this excess epoxy was squeezed out under the applied pressure. The uniaxial pressure also serves to minimize the thickness of the epoxy layer (Figure 4), which is electrically inactive in this design and reduces the engineered energy density of the final device. In order to ensure the capacitor was not bonded to the fixture, a partial cure at 50 °C was performed for 2 hours. After this partial cure, the capacitor was removed from the fixture and cleaned. The final cure was then performed for 12 hours at 50 °C. The low temperature for both the initial and final cure was necessary to limit the amount of residual stress within the final capacitor that results from thermal expansion mismatch between the epoxy and the glass [13]. Inevitably, excess epoxy on the edges prevents access to the buried inner electrodes immediately after the final cure. This material is readily removed via polishing with a 1200 grit SiC paper (Figure 5). Finally, the end terminations were applied by sputtering a further 100 nm of metal end on.

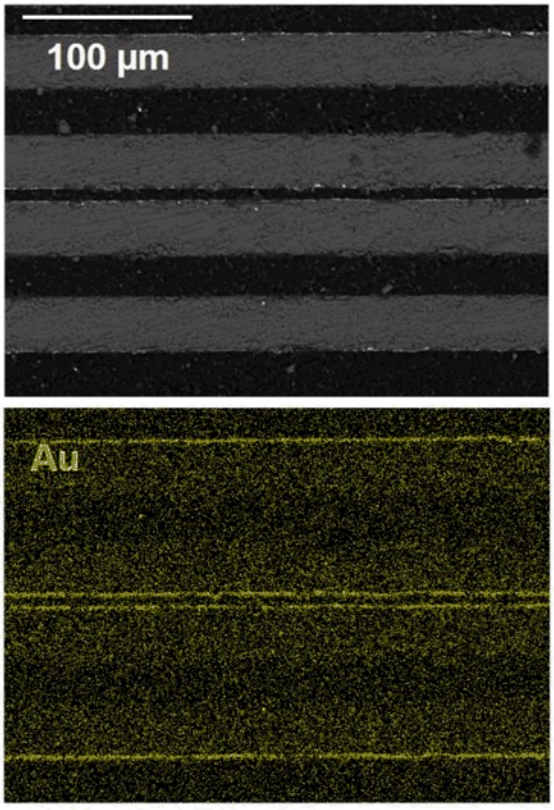


Figure 5 SEM micrograph (top) and EDS map (bottom) of a cleaned edge with exposed Au electrodes. The additional thickness and non-uniformity of the epoxy layers in this sample stems from the curing step being done under lower pressure than the optimized process shown in Figure 4.

III. Results and Discussion

Figure 6 plots the room temperature capacitance and loss for a 10 layer MLGC. Based on the dimensions and thickness of the glass, it is anticipated that each layer should contribute 173 pF. The measured capacitance at 1 kHz was 1.65 nF, indicating the edge terminations are contacting all of the inner electrodes. The slight difference from anticipated value of 1.73 nF reflects minor misalignment errors between the top and bottom electrodes for the individual sheets. The epoxy should not be contributing any measurable capacitance as the 0.1" (0.254 cm) edge margins lead to an estimate in the tens of atto-farads range per sheet arising from the voltage drop through the epoxy between the counter electrodes.

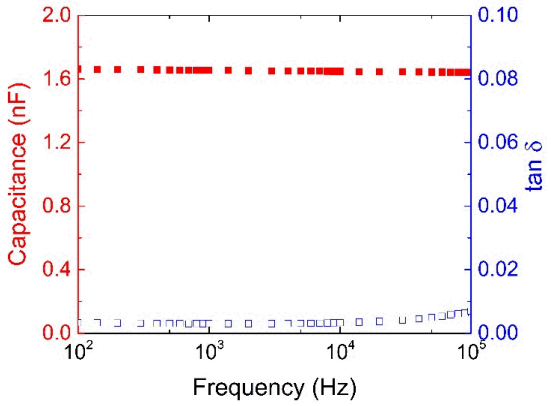


Figure 6 Room temperature capacitance and loss for a 10 layer MLGC.

The temperature dependence of capacitance was measured at 1 kHz over the range -55 °C to +65 °C (Figure 7). There is a slight increase in capacitance with increasing temperature, increasing at a rate of approximately 0.01%/°C. The total variation in the capacitance over this range is 1.65±1.5 nF, indicating the temperature variation is less ±1%. By classification, this exceeds the X4A category. While there is also some temperature dependence to the loss (increasing at a rate of 0.2%/°C), it remains below 0.4% at +65 °C. Measurements of the temperature dependence of the capacitance of a bare single layer of the AF32 glass with ¼" diameter electrodes (not shown) indicate the intrinsic variation in the capacitance over this temperature range is less than ±1%. Additionally, the bare glass shows a loss below 0.4%. The similar temperature dependence of the capacitance and comparable loss values demonstrate that, for small signals, the bonding process does not alter the properties in any significant way. Epon 828 is reported to have loss tangents as low as 0.2% [14], meaning the parallel capacitance associated with the edge margin may actually have lower loss than the glass itself.

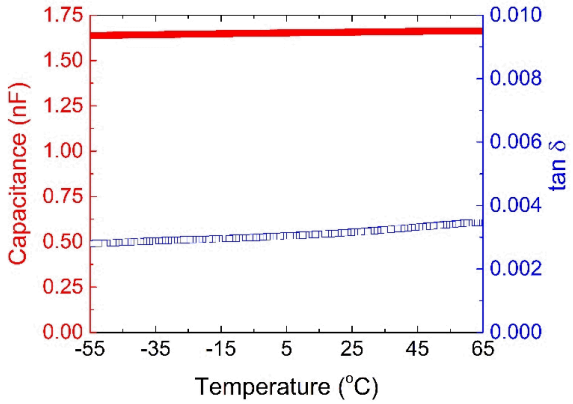


Figure 7 Temperature dependence of capacitance and loss at 1 kHz over the temperature range -55 °C to +65 °C.

To test changes in large signal properties, we measured the leakage current a 1 kV at 65 °C for both the single layer of bare glass and the 10 layer MLGC. The resistance of the MLGC remains above 2.8×10^{13} Ω at 65 °C. If conduction through only the glass is considered, this reflects a resistivity of 9.5×10^{14} Ω · cm. By comparison, the measured resistivity of the bare glass at 65 °C is of 7.0×10^{14} Ω · cm. Likely, the differences in these numbers reflects measurement error as the leakage currents for both tests were in the pA range. Indeed, the leakage current was too low for both types of samples we were unable to measure the resistance over the entire -55 °C to +65 °C. The high resistance in the MLGC does illustrate that the parallel resistance path through the epoxy is of equal or greater resistance than the glass itself.

IV. Conclusion

We have demonstrated a route for fabricating solid state capacitors using alkali-free glass. The approach is scalable and allows for proof testing of individual

sheets prior to incorporation into the multilayer stack. Using epoxy as the bonding material, the operating temperature range of the capacitor is determined by the T_g of the polymer. In the case of Epon 828 with Jeffamine T403, with a T_g near 90 °C, we have demonstrated stable performance over the temperature range -55 °C to +65 °C. The epoxy is electrically inactive in the capacitor and the dielectric and electrical properties of the device are consistent with those of the glass.

ACKNOWLEDGEMENTS

Sandia National Laboratories is a multi-mission laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

REFERENCES

[1] N. J. Smith, Rangarajan, Badri, Lanagan, Michael T., Pantano, Carlo G., "Alkali-free glass as a high energy density dielectric material," *Materials Letters,* vol. 63, pp. 1245-1248, Jun 2009.

[2] H. Lee, N. J. Smith, C. G. Pantano, E. Furman, M. T. Lanagan, "Dielectric Breakdown of Thinned BaO-Al_2O_3-$B2O_3$-SiO_2 Glass," *Journal of the American Ceramic Society,* vol. 93, pp. 2346-2351, Aug 2010.

[3] N. D. Zameroski, K. Spendier, D. Kerwin, M. Spencer, J. M. Parson, C. Hettler, "Investigations Into 25-and 30-mu m-Thick Glass Capacitors at 23 C and 235 C and Area Dependence of Dielectric Strength of Alkali-Free Schott Inc. AF 32 ECO Glass," *IEEE Transactions on Plasma Science,* vol. 44, pp. 973-979, Jun 2016.

[4] S. Garner, S. Glaesemann, X. H. Li, "Ultra-slim flexible glass for roll-to-roll electronic device fabrication," *Applied Physics A-Materials Science & Processing,* vol. 116, pp. 403-407, Aug 2014.

[5] R. H. T. Wilke, A. Baker, A., H. J. Brown-Shaklee, R. L. Johnson-Wilke, C. Hettler, T. Murata, P. O'Malley, S. Perini, M.T. Lanagan, "Fabrication of Wound Capacitors Using Flexible Alkali-Free Glass," *IEEE Transactions on Components Packaging and Manufacturing Technology,* vol. 6, pp. 1555-1560, Oct 2016.

[6] B. Akkopru-Akgun, S. Trolier-McKinstry, M. T. Lanagan, M. T., "MnO2 Thin Film Electrodes for Enhanced Reliability of Thin Glass Capacitors," *Journal of the American Ceramic Society,* vol. 98, pp. 3270-3279, Oct 2015.

[7] T. J. Patey, C. Schlegel, E. Logaskis, "Glass as dielectric for high temperature power capacitors," *MRS Proceedings,* vol. 1679, 2014.

[8] D. H. Choi, C. Randall, E. Furman, and M. Lanagan, "High electric field conduction in low-alkali boroaluminosilicate glass," *Journal of Materials Science-Materials in Electronics,* vol. 26, pp. 9288-9296, Dec 2015.

[9] D. A. McLean, L. Egerton, "Paper Capacitors Containing Cholrinated Impregnants - Stabilization by Anthraquinone," *Industrial and Engineering Chemistry,* vol. 37, pp. 73-79, 1945.

[10] W. J. Sarjeant, J. Zirnheld, and F. W. MacDougall, "Capacitors," *IEEE Transactions on Plasma Science,* vol. 26, pp. 1368-1392, Oct 1998.

[11] V. O. Belko, O. A. Emelyanov, "Self-healing in segmented metallized film capacitors: Experimental and theoretical investigations for engineering design," *Journal of Applied Physics,* vol. 119, Jan 2016.

[12] B. Burton, D. Alexander, H. Klein, A. Gariby-Vasquez, A. Pekarik, and C. Henkee, "Epoxy Formulations Using Jeffamine Polyetheramines," 2005.

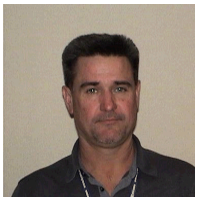
[13] Schott. (2013). Available: http://www.us.schott.com/advanced_optics/english/products/wafers-and-thin-glass/glass-wafer-and-substrates/ultra-thin-glass/index.html

[14] Hexion (2005). Available: http://www.hexion.com/Products/ShowTechnicalDataSheet.aspx?id=3942

Rudeger (Derek) Wilke received his Ph.D. in Condensed Matter Physics from Iowa State University in 2005. He is currently a staff member at Sandia National Laboratories studying electro-ceramic materials and devices.

Harlan Brown-Shaklee received his Ph.D. from Missouri University of Science and Technology in 2011 in Ceramic Engineering. He is currently a Senior Member of Technical Staff at Sandia National Laboratories. His research focuses primarily on electroceramic fabrication and testing methods.

Adrian Casias got his master's in mechanical engineering from Oklahoma State University. He is currently a staff member at Sandia National Laboratories in the Microsystem Packaging and Polymer Processing Department.



Billy Cunningham Jr. studied engineering at UNM/CNM. A former member of the US Navy, he spent 15 years in charge of the final clean process at Sumco. He currently works at Sandia National Laboratories as a microelectronic and semiconductor technologist in the Microsystem Packaging and Polymer Processing Department.

Amanda Gomez received her BS in Chemical Engineering from New Mexico Institute of Mining and Technology in 2014. Before coming to Sandia National Laboratories, Amanda was a cement engineer at Halliburton Energy Services. At HES, she designed cement for the different temperatures, pressures, and depths used to case wells. Currently, she works with Low-Temperature Co-Fired Ceramics (LTCC).

Michael Vecchio received his bachelor's degree in physics from Dickinson College. He is currently a graduate student in the Material's Science and Engineering Department at The Pennsylvania State University.

Rohith Vudatha is currently and undergraduate student in the Department of Materials Science and Engineering at Cornell University in Ithaca, NY. He is currently finishing a capstone research project on tunable dielectric materials with the Schlom group.