High Electrical Reliability Glass-Polymer Laminates

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ABSTRACT

Low-alkali boroaluminosilicate glasses have attracted increasing attention in high temperature dielectric applications due to their excellent dielectric and mechanical properties, and superior thermal stability. Here, we explore an effective approach to greatly improve the electrical reliability of a low-alkali glass by coating a thin polymer layer on top of the glass. In particular, it is shown that the primary breakdown mechanism of the glass is associated with the intensified electric fields in the depletion layers, and the polymer coating can substantially mitigate the local fields in the depleted regions, thus leading to a markedly improved distribution of electrical failures for the glass-polymer laminate. The laminate can exhibit a large breakdown strength of 10.5 MV/cm and a significantly increased Weibull shape parameter of 49.

Index Terms — **glass, polymers, breakdown, energy storage, Weibull distribution**

1 INTRODUCTION

HYBRID electric vehicles and plug-in hybrid vehicles require advanced technology in the areas of energy storage and power conditioning. The next-generation DC link capacitors should possess larger high field endurance and lower dielectric loss, and meanwhile be able to operate at enhanced temperatures over a prolonged service life [1-3]. Recently, with the revolution in the display industry, thin films of low-alkali boroaluminosilicate glasses with excellent mechanical flexibility are produced. They can offer an outstanding level of mechanical impact and bending strength [4]; besides, due to the minor ion contents, these low-alkali glasses can also exhibit a large electrical breakdown strength up to 10 MV/cm, low dielectric loss, and extraordinary thermal stability (the glass transition temperature of the glasses is above 650°C) [2, 5-7]. All of these make these low-alkali glasses a promising candidate for high temperature dielectrics.

Many efforts have been devoted to exploring the breakdown mechanisms of the low-alkali boroaluminosilicate glass. Vermeer [8] has proposed the thermal breakdown as the main mechanism. Lee [9] and Dash [10, 11] attribute the high field failure to the existence of the depletion layer. Namely, under an applied field, the sodium ions in the low-alkali boroalumino-silicate glass are driven towards the cathode side, leaving the anode region depleted of most of the ions. The substantial conductivity contrast between the depleted region and the bulk glass distorts and intensifies the local electric field in the depletion area, thus incurring the premature breakdown [9].

It is well known that the electrical breakdown is a stochastic process which should be best described by Weibull statistics. Beyond the characteristic breakdown strength (E_{BD}), the distribution of electrical failures — characterized by Weibull shape parameter β_w — also has important implications for the reliability and the lifetime of dielectric devices, as it is usually the measured low field failure that dictates the operating voltages in practical applications [12, 13, 14]. Besides, the β_w shape parameter also determines the breakdown strength of dielectrics with increased size [14]. The development of approaches to improve the distribution of breakdown failures necessitates the understanding of breakdown mechanisms in dielectric materials. For the low-alkali glass system, it has been reported that the thermal breakdown is mainly responsible for the dielectric failures [15]; other researchers have also correlated the intensified local electric fields in the ion-depleted regions with the dielectric breakdown [10, 16, 17]. In this manuscript, we will present an alternative approach to mitigate the inhomogeneous electric field distribution by coating an insulating polymer layer on the anode side of the glass.

2 EXPERIMENTAL

2.1 SAMPLE PREPARATION

The glass (OA10G, NEG, Shiga, Japan) was a ribbon with dimensions of 4 m×2 cm×10 μm as-received, and

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subsequently diced to 2 cm×2 cm×10 μm test samples with a diamond scribe.

Three grams of fluorene polyester (FPE,9,9-bis[(4-hydroxyphenyl) fluorene],1,4-benzenedicarbonyl dichloride 1,3-benzenedicarbonyl dichloride copolymer, (Ferrania Technologies, Italy) resin was dissolved in a solvent mixture of 90 ml N-Methylpyrrolidine (NMP, 97% purity, Sigma-Aldrich) and 10 ml tetrahydrofuran (THF 99.9% purity, Sigma-Aldrich), and the solution was stirred for 4 hrs; the trimmed glass was then coated with FPE by dipping the glass into the solution; finally, the laminate was hung in a gravity oven to dry at 130^{o}C for 18 hrs. One side coated laminate is done by pre-sputtering a 50 nm Au layer (Quorum EMS 150RS, Quorum Technologies Ltd, East Sussex, UK) on one side of the glass before dip coating to serve as the electrode.

Silica nanoparticle solution is made by dissolving 0.5 ml colloidal silica suspension (Colloidal Silica Suspension, Non-Crystallizing, 0.02 micron, SIGMA-ALDRICH) in 9.5 ml ethanol, and ultrasonic for 15 min to mix well. Use a spray bottle to spray on the desired side of the glass and blow dry by compressed air. The particle size is substantially larger than the RMS surface roughness of the glass (<1 nm) [7].

2.2 INSTRUMENTATION

SEM of the laminate cross-section was conducted by Merlin FE-SEM (Carl Zeiss, Oberkochen, Germany). The laminate was frozen in liquid nitrogen and bent to reveal the cross-section.

High-field breakdown measurement was performed on the samples in a bath containing dielectric fluid (Galden HT-200, Solvay Solexis, Houston, TX), with 30 kV-max DC high voltage supply (Model 30/20, Trek, Lockport, NY). The voltage was ramped at a constant linear rate of 500 V/s. Samples subjected to the high field measurements were coated with 50 nm Au by sputtering, with a top electrode of 2 mm diameter and a bottom electrode of 3 mm.

ModuLab (XM MTS, Solartron Analytical, Hampshire, UK) was adopted to measure the permittivity and loss of the glass and laminate.

3 RESULTS AND DISCUSSION

In order to confirm the breakdown mechanism of the low-alkali glass, silica nanoparticles are deposited on the glass surface for it can greatly enhance the local electric field distribution near the surface. 20 nm sized silica nanoparticles are sprayed over one side of the pristine glass (Figure 1a), and the electrical failures of the silica-coated glass are measured. The measurement is conducted with the silica coating facing either the anode electrode or the cathode electrode. The measured breakdown fields are plotted within the framework of Weibull statistics, as shown in Figure 1b. A schematic of the test specimen cross-section is shown in Figure 1c. Thermal poling of the low-alkali glass [17, 18] shows that with the applied electric field, sodium ions are driven towards the cathode, leaving behind a depletion layer with low conductivity thus supports most of the electric field. The thickness of the depletion layer is ~5 μm for thin low-alkali glasses [18], and the internal electric field in the depletion region is ~10 MV/cm for room temperature (extrapolation from high temperature value of 2.2 MV/cm, calculated from second-harmonic generation results) [17].

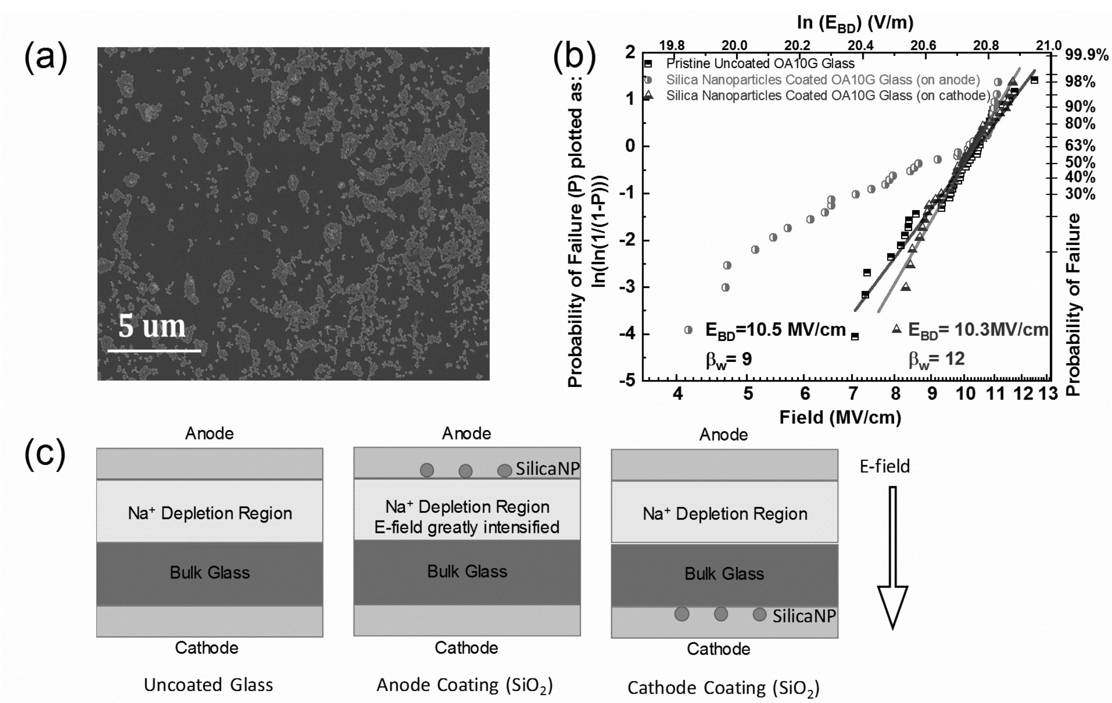

Figure 1. (a) SEM image of the silica coating on the glass surface; (b) dielectric breakdown strength of the pristine glass, the anode silica-coated glass, and the cathode silica-coated glass, plotted by Weibull statistics; (c) schematic depiction of the high field depletion and bulk glass regions.

The breakdown behavior of the silica-coated glass is mainly dependent on the position of the silica concerning the electrodes. When the silica coating is on the cathode side, the Weibull plot of the coated glass is similar to that of the pristine glass. They can be well described by the unimodal Weibull distribution—the characteristic breakdown strength (E_{BD}) is measured to be 10.5 MV/cm and 10.3 MV/cm for the pristine glass and the coated glass, respectively; and the Weibull shape parameter is measured to be 9 and 12. However, when the silica coating is on the anode side, the performance is considerably deteriorated by the silica deposition, especially for the lower field failures. The breakdown strengths at low probabilities of failure are dramatically reduced for the coated glass with silica on the anode side, compared to the pristine glass and the cathode silica-coated glass. Besides, the distribution of the breakdown fields cannot be fitted with a unimodal Weibull equation, indicating the existence of extrinsically controlled breakdown mechanisms.

The dependence of breakdown performance on the electrode polarity suggests that the extrinsic surface defects at the anode play an important role. On the other hand, it has been extensively studied and shown that there exists a depletion layer with substantially increased local electric fields in such glass [10, 16, 17]. The depletion layer is near the anode side, originating from the diffusion of sodium ions towards the cathode region under an applied field. The absence of sodium ions in the depletion regions accounts for the local field intensification in these regions due to a large difference in conductivities between the depletion region and bulk glass. In our previous study [19], simulation results have shown that the deposition of impurities, such as silica, on the surface of glasses, can greatly increase the local electric field beneath those impurities, e.g., up to 6 times (from 20 MV/cm to 130 MV/cm) increase in the electric field can be achieved when the particle size is on the order of 10 nm radius and of sphere shape (Figure 3a).

As shown in Figure 1c, it can thus be envisaged that when the silica is coated on the anode side of the glass, the electric field in the depletion layer is further strengthened by the silica deposition, thus greatly increasing the chance of initiating localized electrical breakdown in this region; however, when the silica is coated on the cathode surface, the presence of a large population of mobile sodium ions can offset the electric field amplification to some extent, which could mitigate the adverse effects of the impurity introduction. In fact, both the pristine glass and the cathode silica-coated glass exhibit a similar breakdown performance, implying the electrical failures in these two glasses are very likely to be dictated by the localized breakdown occurring in the depletion layer, as the cathode coating of silica nanoparticles should not exert considerable impacts on the electric field distribution in this region. It is also worth mentioning that the multiple breakdown mechanisms in the anode silica-coated glass could arise from the non-uniform silica coating on the glass surface. The failures at higher fields and lower fields may correspond to the regions with few and many silica particles, separately.

Since the dielectric breakdown for the anode silica-coated glass is attributed to the electric field intensification in the depletion layer, approaches to reduce the enhanced E-field should improve the breakdown performance of the silica-coated glass. The vicinity (50 nm of the depletion region/polymer layer) of the particle defect (of 10 nm radius

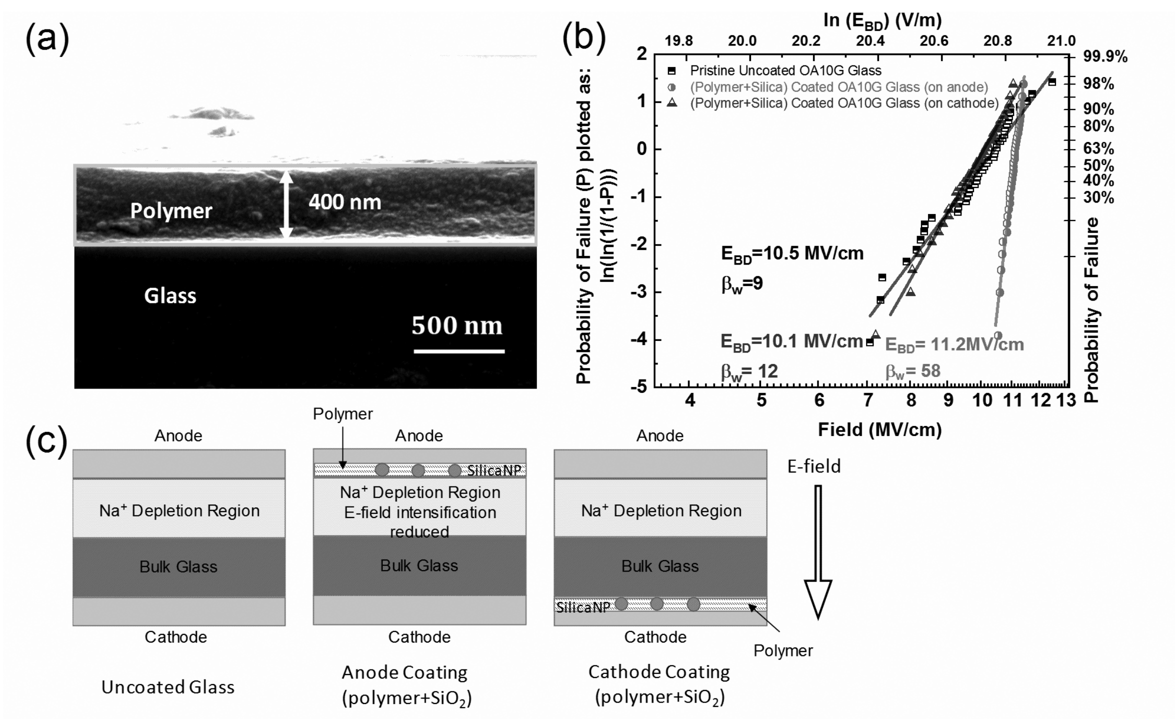

Figure 2. (a) SEM image of the polymer coating on the glass; (b) dielectric breakdown strength of the pristine glass, the anode polymer/silica-coated glass, and the cathode polymer/silica-coated glass, plotted by Weibull statistics; (c) schematic depiction of the electric field distribution in the depletion layer.

and of sphere shape) area has been modeled using Ansys Maxwell®. The excitation voltage is applied on the top electrodes and the bottom electrode are zero potential. Electric field simulation is based on the electrical conductivity of the materials. The applied voltage for the bulk samples is assumed to be 11 kV, which is close to the E_{BD} in the breakdown experiment. The electrical conductivity of the glass in this study is assumed to be 1/10 of the bulk glass [18]: $1e^{-11}$ S/m. The conductivity of silica nanoparticle is set to be $1.3e^{-18}$ S/m. The conductivity of the polymer is calculated based on the electric flux density at the glass/polymer interface: $5.7e^{-12}$ S/m. The simulation results in Figure 3a have shown that the deposition of impurities on the surface of glasses, can greatly increase the local electric field beneath those impurities, showing as red lines, while after a thin layer of polymer coating, the maximum local electric field is around the particle showing as green lines in Figure 3b and has been reduced to about 1/2 of the uncoated The actual values of the local field are probably overestimated in the simulation due to local conduction in the high field regions. As a result, the double-layer-coated glass is prepared with a ~400 nm polymer layer superimposed on the silica coating (Figure 2a). Figure 2b presents the Weibull distribution of breakdown fields for the pristine glass and the coated glass. Again, the coated glass is measured twice with the coating side facing either the anode side or the cathode side.

As expected, the polymer coated glass with silica particles on the cathode side behaves similarly to the pristine glass with E_{BD} of 10-11 MV/cm and β_w ranging from 9 to 12. When the polymer coating is on the anode side, overlaying the silica nanoparticles, the improved dielectric breakdown strength is attributed to the reduction of the electric field in the depleted region (Figure 2c). Moreover, it is interesting to note the breakdown performance of the anode double-layer coated glass even exceeds that of the pristine glass, i.e., E_{BD} and β_w of the double-layer coated glass is 11.2 MV/cm and 58, respectively; while they are measured to be 10.5 MV/cm and 9 for the pristine glass. The polymer coating not only mitigates the adverse impacts imposed by the silica nanoparticles but also reduces the influences of the extrinsic dust particles preexisting on the surface of the pristine uncoated glass.

The pristine glass is also coated with polymer and its breakdown strength is compared with that of the uncoated glass, as shown in Figure 4a. E_{BD} can be slightly improved by the polymer coating, increasing from 10.5 MV/cm for the uncoated glass to 11.1 MV/cm for the coated glass; but what is more impressive is the significantly enhanced β_w: the β_w shape parameter for the pristine glass is 9, and increases to 49 for the polymer-coated glass laminate. The large β_w indicates a dramatic improvement in the lower field failure, which has important implications for the reliability of dielectric materials [20]. For instance, the breakdown field corresponding to 10% probability of failure is degraded to 8.0 MV/cm for the uncoated glass, but it is still maintained at 10.7 MV/cm for the coated glass, which is even greater than the characteristic breakdown strength of the uncoated glass. Moreover, the silica/polymer double-layer coated glass demonstrates a similar high field behavior to the polymer-coated glass, suggesting the polymer coating can tolerate the presence of various impurities (e.g., silica particles and preexisting dust

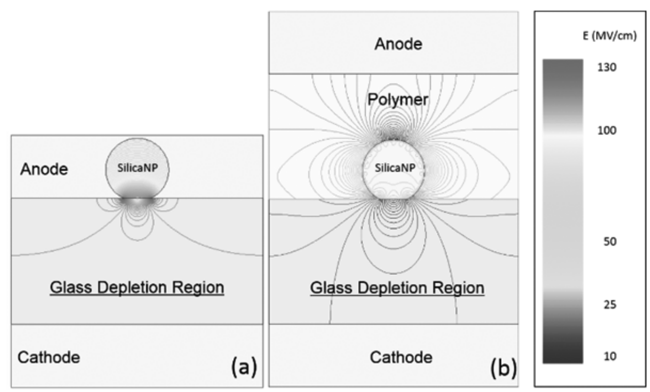

Figure 3. Ansys Maxwell simulation of the electric field distribution of (a) silica-deposited glass and (b) polymer/silica double layer coated glass.

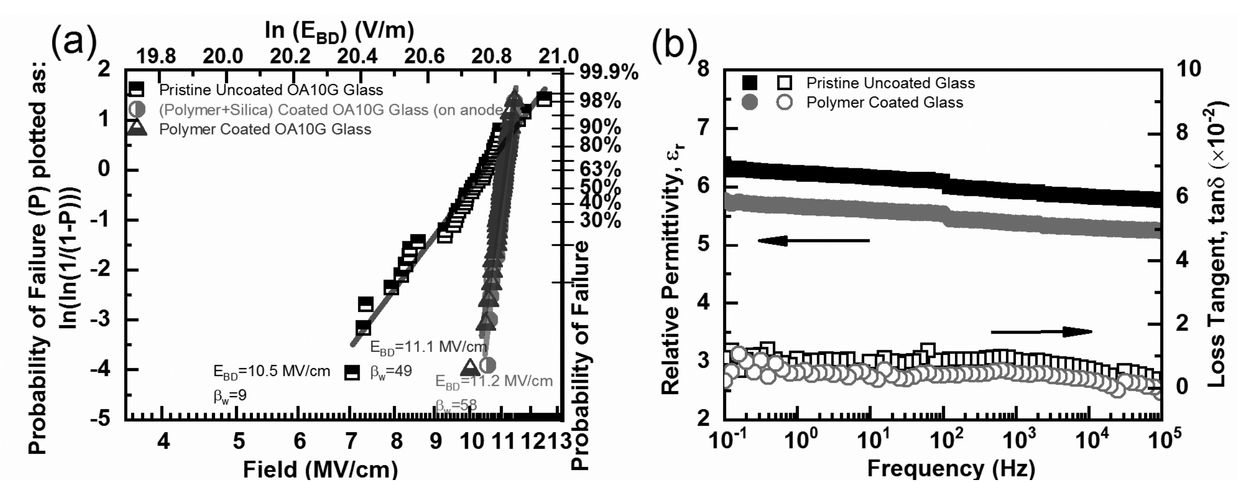

Figure 4. (a) Dielectric breakdown strength of the pristine glass, the polymer/silica-coated glass, and the polymer-coated glass, plotted by Weibull statistics; (b) dielectric constant and dielectric loss for the polymer coated glass and the uncoated pristine glass, measured as a function of frequency.

particles on the glass surface) and reduce their adverse effects to the same level. This observation also implies improved reliability in the application of these dielectric glasses, as different types of impurities or defects introduced during the production and assembly of these materials can be alleviated by a final polymer coating.

Finally, the dielectric properties of the polymer coated glass and uncoated glass is measured and compared, as shown in Figure 4b. The introduction of a polymer layer of a low dielectric constant will slightly reduce the overall dielectric permittivity of the laminate, which follows the general mixing rule (the permittivity of the glass and the polymer is ~5.5 and ~3.1, respectively; the thickness of the glass and the polymer is ~10 microns and ~0.4 microns, respectively). The dielectric loss is not affected by the coating over the entire frequency range. The energy density of pristine glass is calculated to be 31 J/cm^3, and that of the laminate is 29 J/cm^3.

4 CONCLUSIONS

The electrical failures of the low-alkali boroaluminosilicate glass are primarily affected by the greatly intensified electric field in the depletion layer. Application of a polymer coating on the anode side of the glass can reduce the electric field intensity in the depletion region. The high field properties, especially the electrical reliability, are improved, which is manifested by the significantly increased breakdown strengths at low probabilities of failure and by the great tolerance of defects.

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