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Comparison of Dielectric Properties of Additively Manufactured vs. Solvent Cast Polyimide Dielectrics

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Abstract* – The permittivity, dielectric loss, and DC dielectric breakdown strength of additively manufactured, solvent-cast, and commercial polyimide films are reported. As expected, commercial films performed better than both AM and solvent-cast lab-made films. Solvent-cast films generally performed better than AM films, although performance depended on the optimization of the material for the specific deposition technique. The most significant degradation of performance in all the lab-made films was in the dispersion of both the κ/Df measurements and the dielectric breakdown strength (Weibull β). Commercial films had a breakdown strength of 4891 kV/cm and β = 13.0 whereas the highest performing lab-made films had a breakdown strength of 4072 kV/cm and β = 3.8. This increase in dispersion in all the lab-made samples is attributed to higher variability in the preparation, a higher defect level related to fabrication in the lab environment and, for some AM samples, to morphology/topology features resulting from the deposition technique.

I. INTRODUCTION

Additive manufacturing (AM) is being used in an increasing number of high tech applications. However, one area where additive has not made significant inroads is the field of dielectric materials for capacitive energy storage. The materials challenges are significant due to the sensitivity of dielectric performance to morphology, including bulk density, topology, and defect density. However, if successful, the application of additive manufacturing methods in capacitor fabrication could lead to significant advancements in the flexibility of polymer capacitor fabrication and design.

Previous work on the dielectric properties of additively manufactured polymer dielectrics has demonstrated that, for a range of polymers manufactured by additive techniques, dielectric breakdown strength is significantly diminished in additive materials relative to traditionally fabricated commercial materials and/or the manufacturer specifications for commercial materials. [1], [2]

In this work we will compare the performance of two types of AM polyimide films both with commercial polyimide and with lab-made films produced by small scale solvent-casting. Performance of lab-made films is often inferior to that of commercial films of the same material simply due to the lower level of process control and higher variation in small-batch R&D level sample production. The comparison of AM performance to both commercial samples and samples made by alternative small-scale fabrication techniques (solvent-casting) allows some differentiation of performance deficits as being due to lab-scale processing versus the deposition or fabrication technique. Although ultimately AM materials will have to match commercial performance, identification of key issues in AM performance *unrelated* to lab-scale production issues can be better facilitated by performance comparison to films produced by other R&D level fabrication techniques.

II. EXPERIMENTAL AND ANALYSIS

A. *Materials*

Two polyimides were tested in this work. The first material is a polyamic acid, poly(pyromellitic dianhydride-*co*-4,4′-oxydianiline) amic acid solution (Sigma-Aldrich 575828) 15wt% in NMP/aromatic hydrocarbons referenced as “SA polyimide” or “SA PI” throughout the paper. The second material is a proprietary formulation of a polyimide precursor in ethanol (UT Dots PI1-AJ). This material is referenced as “UTD polyimide” or “UTD PI”. The final material is a commercial polyimide, Kapton HN 50G film. This material was purchased from American Durafilm and used as received.

B. *Sample Preparation*

All samples were prepared on Au coated (50nm Au) Si wafers with an Cr/SiO_2 adhesion layer. Si wafers were plasma cleaned immediately prior to polymer deposition. For solvent cast samples an aliquot of polymer solution was deposited at the top of the wafer and a doctor blade was passed over the wafer to spread the solution into an even layer. Additive manufacturing samples were prepared using an in-house designed and built Direct Write System (DWS) configured with motion control in the X, Y, Z, and W axis. [3] Two print deposition methods were used, syringe and spray deposition. For syringe deposition a 10mL disposable syringe was filled with polymer solution and fitted with a 250 μm tip. The polymer solution was degassed at 60 ˚C in a vacuum oven prior to deposition. The syringe was then mounted on the Z-axis of the DWS and positioned 250 μm above the surface. The substrate (Au/Si wafer) was heated to 90 or 100˚C and the material dispensed as dictated by the program/toolpath. The toolpath was written in g-code and run with FlashCut 4 software. On completion of the deposition the material is thermally treated for solvent evaporation and/or polyamic acid to polyimide conversion. For spray deposition the polymer precursor is dispensed using an ultrasonic spray nozzle system from Sono-Tek (Sono-tek 54569) using air as the sheath gas. The Sono-Tek was set to an operating voltage of 7.5V for all depositions. The polymer solution was loaded into a syringe and degassed as described above. For spray deposition the SA PI solution had to be further diluted with NMP (1:8 v/v). The spray nozzle was positioned approximately 1 inch above the substrate. The platen was heated to 90 or 100˚C and the material dispensed as dictated by the program/toolpath.

For the SA polyimide, deposition via AM or solvent casting is followed by conversion/solvent evaporation above 215 ˚C for >12 hours. The UTD polyimide was cast or deposited and then cured at 300 ˚C for >12 hours. For some samples a 2-3 hour lower temperature phase (90-130 ˚C) was added prior to the final cure to mitigate film cracking or bubbling due to rapid solvent evaporation. No significant differences in dielectric performance were observed in the samples studied based on cure profiles, but this was not the focus of this study so the variation in conditions and sample sizes are too limited to make any definitive conclusions.

After curing samples are metallized on the top surface with an array of 6.3mm diameter Au electrodes (50 nm Au). Commercial polyimide films are metallized with the electrode array (top) and a blanket Au metallization (50 nm) on the back to mimic the electrode geometry of the samples deposited on the Au/Si wafers. Each film sample accommodated between 20-30 test electrodes per sample. Group data is a compilation of results from between 2-5 individual films.

C. Thickness Measurements

Film thicknesses were measured with different methods depending on the thickness/opacity and surface roughness. The methods used are: optical profilometry using a Wyco NT9800, used for thick, rough, or visibly opaque samples; for thinner smooth samples spectral reflectance profilometery using a Filmetrics F20 or F50-UV; and contact profilometry using a Dektak XT with Vision64 operating system was also used for some samples. Thickness was measured at four positions outside the electrode area (optical methods). Measurements by contact profilometry were made directly in the electrode area, after electrical testing was completed, by mechanically removing a small strip of film through the middle of the electrode area and measuring the film height on either side of the stripped area.

D. Permittivity and Dielectric Loss

Dielectric permittivity and dielectric loss were measured on metallized samples prior to dielectric strength testing. The permittivity and loss are measured using a calibrated Agilent LCR meter (Model E 4980A). Ground and source contacts are made via contact probes. The probes are Signatone S-725 micropositioners with BNC connections equipped with Signatone SE TB Tungsten 20 mil diameter probe tips. The end of the probe tips are bent around a small diameter to provide a smooth, curved surface for contact to the film and ground plane. Permittivity and loss are measured at 20 Hz, 250 Hz, 1 kHz, 10 kHz, 100 kHz, and 1MHz. Open and short corrections are performed on the circuit prior to testing using the automated LCR meter functions and corrections are automatically applied at each test frequency. A LabVIEW program records five measurements of capacitance and dielectric loss (Df) at each frequency, averages the measurements and outputs the results for each individual test electrode. The averaged values are used without further correction. Permittivity values are calculated from the capacitance and the electrode area and sample thickness. Test electrodes with a Df >1 were either not measured or excluded from data analysis as shorts. Exclusions are tabulated in Table I. In addition several data points where the capacitance was extremely high due to poor electrode contact during measurement are excluded from the analysis. Samples are stored and tested under ambient humidity.

E. Dielectric Breakdown Strength

Dielectric breakdown strength (DC) testing is performed on films metallized as described above. A copper plate, freshly polished on both sides, is placed in a flat evaporating dish and immersed in a pool of Fluorinert FC-40 (Sigma-Aldrich, F9755). The ground electrode probe (Signatone SE TB Tungsten 20 mil, rounded as described above) is contacted to the ground (copper plate for commercial samples, bottom Au layer for films on Au/Si wafers) by a spring force contact. For samples on Au/Si wafers breakdown events were found to damage the metallization at the ground probe contact, degrading the quality of the ground over the course of testing. To mitigate this an additional ground electrode consisting of ~5x5mm 3-5 mil copper foil soldered to the Au layer with In99 or InPbAg solder was applied and used as the ground contact during breakdown testing. The polymer sample with gold electrodes is immersed in the Fluorinert with insulated metal weights used to help keep the film immersed and immobile. The source electrode probe is then placed on top of the test electrode. The test electrodes are always tested in numerical order from 1 to 30. Dielectric breakdown strength testing is performed by a ramp-to-fail method. An Agilent E 4980A LCR meter controlled by a LabVIEW program serves as the voltage source for a Trek 30/20 amplifier ramping the voltage in steps of 50V/100msec for an overall ramp rate of 500V/s. Voltage and current readings are recorded every 100 msec and breakdown is detected by a spike in current >1 mA. Twenty to thirty test electrodes are tested for each sample and breakdown strength is determined by fitting the data to a Weibull distribution. Samples are dried at 50 ˚C overnight prior to testing and stored in a desiccator until placed in the Fluorinert bath for testing.

III. RESULTS AND DISCUSSION

A. Permittivity and Dielectric Loss

Fig. 1 and Table I show the permittivity and dielectric loss at 1 kHz for each of the sample groups. The commercial sample has a slightly lower permittivity than reported for Kapton HN (3.4 at 1kHz) [4] likely due to differences in test setup, particularly testing at ambient conditions (RH 12% on test date) rather than 50% RH as specified in ASTM D-150. The dispersion in both permittivity and loss is much higher in the lab made samples than in the commercial samples, as expected.

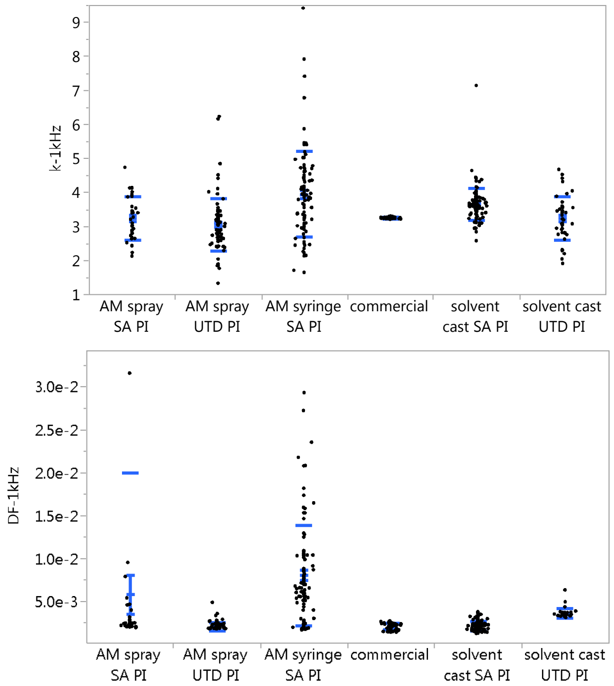

Fig. 1. Permittivity and dielectric loss at 1kHz (mean and standard deviation in blue and in Table I). One high Df value is off-scale in the 'AM spray SA PI' group but is included in the calculation of mean and standard deviation.

TABLE I: PERMITTIVITY AND DIELECTRIC LOSS
MEAN (ST. DEV)

Group	**N***	**N_{ex}***	**avg. thickness (µm)**	**κ**	**Df**
AM spray SA PI	38	6	9.7 (2.5)	3.25 (0.63)	0.0058 (0.0141)
AM spray UTD PI	83	2	6.6 (1.8)	3.05 (0.77)	0.0021 (0.0005)
AM syringe SA PI	97	2	37.3 (14.7)	3.94 (1.26)	0.0080 (0.0058)
commercial	90	0	13.3 (0.2)	3.25 (0.02)	0.0021 (0.0004)
solvent cast SA PI	104	0	16.1 (6.2)	3.64 (0.47)	0.0020 (0.0005)
solvent cast UTD PI	42	11	2.6 (0.9)	3.25 (0.64)	0.0036 (0.0005)

* N is the total number of electrodes measured. N_{ex} is the number of electrodes either not measured or excluded after measurement (as described in methods section). N + N_{ex} is the total number of test electrodes fabricated for each group.

Some of the increased variation is likely due to greater thickness variability in the lab-made samples. Particularly for the AM samples, there was often significant thickness variation over the diameter of the electrode, which is not captured by the single thickness measurement. As the permittivity is calculated from the capacitance using the thickness measurement this introduces some additional stochastic variation into the permittivity values. However, the major contributor to the increase in dispersion in the AM and solvent cast samples is likely the inherent variability and higher defect density in lab-scale versus commercial production methods. The dispersion is particularly high in the 'AM syringe SA PI' samples. These samples were on average much thicker (see Table I) than other lab-made samples and the high dispersion in the permittivity and loss values may indicate entrapment of solvent or small molecules within the films that are not removed effectively with the cure profiles used for these samples. The thicker samples may also experience more induced strain during conversion/cure at the Au/Si interface, leading to degradation of the electrode/dielectric contact, which could also increase the dispersion in the measurements. Analysis of permittivity and loss over the measured frequency range (20 Hz to 1 MHz) shows similar results for the sample groups at all frequencies.

B. *Dielectric Breakdown Strength*

The dispersion in dielectric breakdown strength, as measured by the Weibull β parameter, is also much higher for the lab-made samples than for the commercial films (see Fig. 2 and Table II). The dielectric breakdown strength (Weibull α) is lower for lab-made samples, as expected. Although still inferior to the commercial films the solvent cast SA PI group performs the best for lab-made films, both in terms of dielectric breakdown strength and dispersion. For the breakdown strength measurements, as for permittivity and loss, the high variability in thickness within the lab-made sample groups is likely a contributor to the increase in dispersion. It is well-known that the dielectric breakdown strength of a material tends to decrease with increasing thickness, due to the increased probability of encountering a defect in the larger volume under test in a thicker sample. Having greater variability in thicknesses within a sample group will therefore increase dispersion.

TABLE 2: DIELECTRIC BREAKDOWN STRENGTH

Group	**N**	**Weibull α (kV/cm)**	**Weibull β**
AM spray SA PI	47	1110	0.8
solvent cast UTD PI	54	2060	1.0
AM spray UTD PI	69	2402	1.5
AM syringe SA PI	101	3835	2.1
solvent cast SA PI	103	4072	3.8
commercial	89	4891	13.0

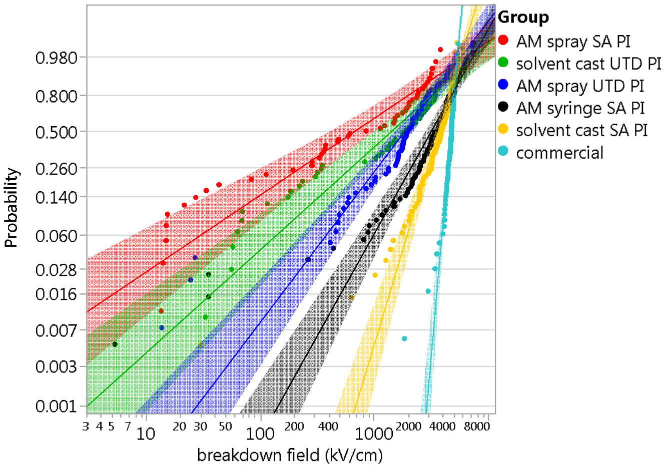

Fig. 2. Weibull distributions and 95% confidence intervals of DC breakdown fields by sample group.

To illustrate, for a subset of the 'AM syringe SA PI' group, limited to electrodes on film areas with thicknesses in the 20-32 µm size range (N=23) the Weibull β parameter increases to 3.3 from 2.1. In contrast, for a randomly selected subset of the same sample size (N=23) the Weibull β parameter remains ~2. Nonetheless the breakdown strength and dispersion are significantly worse for all lab-made samples relative to commercial, with the major contributor likely contamination and film quality of the lab-made films.

C. Comparison of Methods

Within the lab-made sample groups the 'solvent cast SA PI' had the best performance in terms of dielectric breakdown strength, followed by the 'AM syringe SA PI'. 'AM spray SA PI' and 'solvent cast UTD PI' had the worst performance. The poor performance of these two groups reflects more on the optimization of the formulations for the deposition method than their intrinsic properties. The high percentage of test electrode exclusions (Table I) in addition to the poor performance of the test electrodes that were tested indicate that the deposition methods/materials for both groups did not produce good quality dielectric films. The UTD PI formulation is optimized for spray application and is a low weight percent, low viscosity formulation. The films made by solvent casting UTD PI were very thin (< 3 µm on average) and this increases the susceptibility to failure by particulate contamination, pin holes, or other through-film defects, which are likely to occur in a lab environment. In the 'AM spray SA PI' group, even when the starting material was diluted with additional NMP, the SA PI formulation, which has not been optimized for spray deposition, deposited very unevenly by the AM spray process, resulting in many shorts. Optimization of the formulations for the target deposition method and further process optimization should correct these issues suggesting that significantly improved breakdown strength could be reached for both groups. The 'AM spray UTD PI' breakdown strength was intermediate. With an average thickness of 6-7 µm this group could be more sensitive to particulate contamination than the two higher performing groups which had higher average thicknesses (Table I). However, the 'AM spray UTD PI' films also exhibited significant surface roughness including beading on the surface (Fig. 3) which could negatively impact the dielectric breakdown strength through field enhancement.

Although the 'AM syringe SA PI' group had the best performance of the AM groups in terms of breakdown strength, it had the worst performance in terms of dielectric permittivity and loss, with very high dispersion. In addition, with the current methodology, this technique is not applicable for deposition of multilayers or on non-planar substrates, as the polymer solution remains liquid after application to the substrate. Since this is a very similar deposition method to solvent casting it is not clear why the dispersion in permittivity and loss are so much higher in the 'AM syringe' versus 'solvent cast' SA PI groups, but the method offers no advantages relative to solvent casting as currently realized.

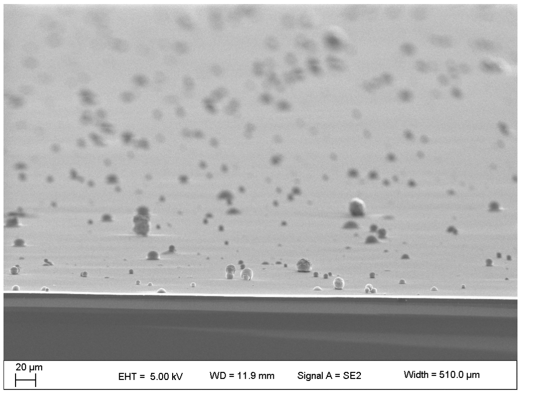

Fig. 3. Cross-sectional view of AM spray UTD PI sample, showing surface roughness and beading of polymer on the film surface.

The 'AM spray' technique is more applicable to multilayer deposition and deposition on non-planar substrates but does not yet equal the performance of solvent-cast films. The dispersion in both permittivity and dielectric loss is slightly higher in the 'AM spray' groups than in the equivalent 'solvent cast' groups for both SA and UTD PI and the breakdown strengths are lower. Both these outcomes are likely due, at least in part, to the high surface roughness and topology in the AM spray films. With process optimization it may be possible to minimize these features and significantly improve the dielectric performance of materials deposited by AM spray methods.

IV. CONCLUSIONS

This work compares the dielectric performance of traditionally manufactured commercial polyimide films to lab-made AM and solvent-cast polyimide films. As expected, commercial films perform the best, while solvent-cast films generally outperform AM films. Morphological/topological features were identified for the spray AM technique which may contribute to the lower performance of some of the AM samples. Optimization of polymer solutions to the deposition techniques is important to improving performance.

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