

UNDERSTANDING SOURCES OF DEFECTS IN POLYIMIDE FILMS USING AEROSOL BASED PRINTING

J. M. Lavin, D. M Keicher, S. R. Whetten, P. B Moore, and S. S. Mani.

Sandia National Laboratories, 1515 Eubank SE, Albuquerque, NM 87123

Abstract

A study of the sources of defects in films of commercially available polyamic acid fabricated using aerosol based printing was carried out. Printing was conducted using a Sono-Tek spray nozzle on multi-modular Direct Write Additive Manufacturing System. The driving force behind this work stemmed from the need to form smooth, defect free films to be used in electronic components. While numerous process conditions give rise to defects such as the obvious substrate cleanliness, efforts here focused on the more subtle conditions such as deposition temperature, deposition speed, nozzle height from the substrate and cure temperature. The results of this study led to the identification of the most critical source of defects and to a set of optimal process conditions in the printing of polyimide films using aerosol based printing.

Introduction

Polyimides are widely used given their desirable material properties including lightweight, flexible and resistant to heat and chemicals. Polyimide films are of particular interest in the semiconductor industry as a high-temperature adhesive or as a photoresist. Polyimide films have excellent thermal and electrical properties making them especially important in various applications [1-4]. While commercially available polyimide films including Kapton, Apical and Vtec PI are readily available, having the ability to print discrete films of a polyimide directly onto a substrate via an additive manufacturing approach enables the study of countless unexplored opportunities while at the same time resulting in decreased cost.

Herein, the direct write spray dispense additive manufacturing (AM) approach of aerosol based printing of polyimides is investigated. The AM approach offers the advantage of zero assembly requirements, minimal waste and minimal to zero design constraints and thus greater innovation. In this work, an aerosol based AM approach using a Sono-Tek spray nozzle is used to form films of polyimide on gold coated silicon wafers. [5] Here, polyamic acid (a precursor to polyimide) is sprayed by direct write AM and later cured at elevated temperature to make AM polyimide films. The Sono-Tek spray nozzle operates at a specific resonant frequency resulting in the atomization of the polyamic acid solution creating an aerosol or fine mist of the material. The size of the droplet is dictated by the resonant frequency (it does not rely on pressure). The polyamic acid is deposited on a substrate in aerosol form. These nozzles offer the benefit of decreased waste, controllable spray, uniform micron thick coatings and the ability to coat any substrate material be it planar or 3-dimensional.

The impetus for this work in understanding the source of defects in polyimide films stems from the need to produce smooth, defect-free films as the dielectric material for electronic

components. Previous work on the fundamental dielectric properties of AM polymer dielectrics has demonstrated that for a range of polymers dielectric breakdown strength is significantly diminished in AM films relative to traditionally fabricated commercial materials and/or the manufacturer specifications for commercial materials. [6-7] This poor performance of the AM films is directly attributed to undesired morphology/topology, surface roughness, and defects in the films. [8] These film defects in the dielectric material contribute to heterogeneity of the dielectric and usually create a permittivity contrast leading to field enhancement and add resistive regions to the film. In this work, surface roughness is referred to as a defect due to this negative effect on device performance. The spray dispense AM of polyamic acid onto planar substrates is conducted in an effort to identify the source of defects when printing and determine how best to eliminate these defects. Profilometry and imaging offer insight into the extent of the defects and under what conditions defects can be minimized.

Experimental

A. Materials

A commercially available precursor of a polyimide, polyamic acid, was tested in this work. Poly(pyromellitic dianhydride-co-4,4'-oxydianiline) amic acid solution (Sigma-Aldrich 575828) 15 wt% in NMP/aromatic hydrocarbons was used in all instances.

B. Sample Preparation

All samples were prepared on Au coated (50nm Au) Si wafers with a Cr/SiO₂ adhesion layer. 6-inch Si wafers were diced in quarters in a FAB facility and used as received. 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. [9] To form an aerosol with the Sigma Aldrich (SA) polyimide, solutions of polyamic acid were further diluted in *N*-Methyl-2-pyrrolidone (NMP) (1:8 v/v). Aerosol spray deposition of the polymer precursors is carried out using an ultrasonic spray nozzle system from Sono-Tek (Sono-Tek 54569) using air as the sheath gas. The Sono-Tek power supply was set to an operating voltage of 7.5V for all depositions. The polymeric solution was loaded into a syringe and degassed at 60 °C in a vacuum oven prior to deposition. The toolpath was written in g-code and run with FlashCut 4 software. The substrate (Au/Si wafer) was placed on a heated platen (temperature of platen was one variable studied as source of defects) and the material dispensed as dictated by program/toolpath. On completion of the deposition the material is thermally treated for both solvent evaporation and polymerization of polyamic acid to polyimide. The resulting polyimide films are referred to as SA polyimide and SA PI throughout the paper.

C. Thickness Measurements

Film thicknesses were measured using two methods of profilometry.

- i. Optical profilometry was carried out using a Wyco NT9800, measuring the height profile at five locations on the sample (four corners and center). This provided measurements of the average film thickness across the substrate. In addition 3D views and surface statistics including root-mean-squared (RMS or Rq), peak to valley difference (Rt), maximum peak height (Rp), and minimum valley depth (Rv) were measured.

- ii. Contact profilometry using a Dektak XT with Vision64 operating system was also used for some samples. Measurements by contact profilometry were made starting on a clean unexposed area of the Au/Si wafer transitioning onto the polymeric material.

Results and Discussion

A. Deposition Temperature

To investigate the effect of substrate temperature on film defects a study was carried out where the platen was heated to 80, 100, 110, and 120 °C. The table speed was set at 20 mm/second and spray nozzle 25.4 mm (1-inch) above the substrate. Figure 1 shows how the thickness varies with deposition temperature.

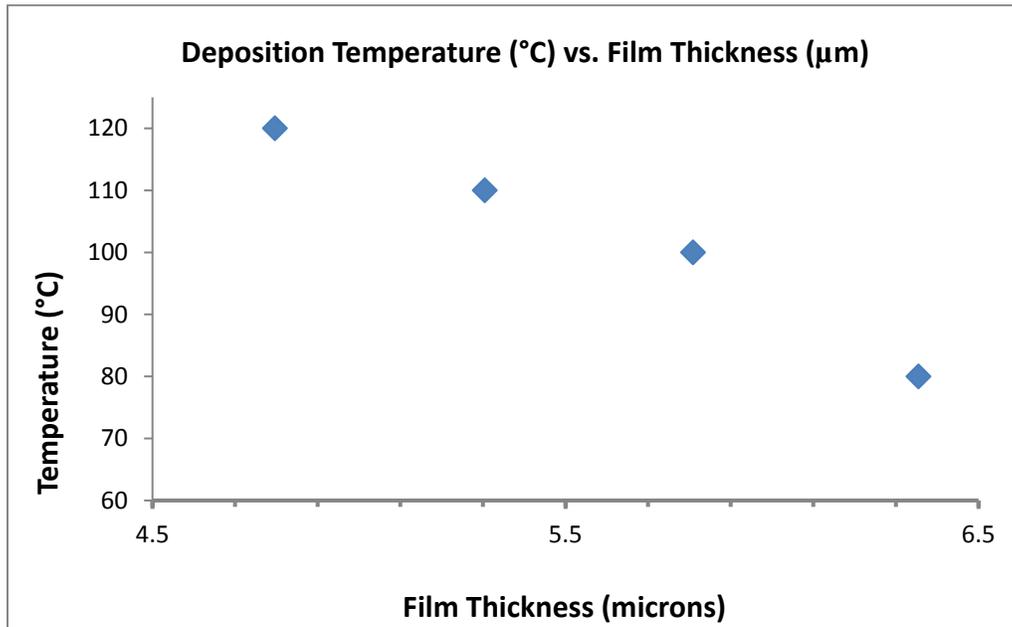


FIGURE 1: Plot of deposition temperature (°C) as a function of film thickness (µm) measured using optical profilometry

Increasing deposition temperature results in a decrease in measured film thickness because of faster solvent evaporation kinetics at higher temperature, as expected. Figure 2 shows micrographs of the films at varying deposition temperature. Qualitatively, these images clearly show that more uniform and smooth films are formed at lower temperatures. Table I shows a ~15% increase in roughness (Rq) in films deposited from 80 to 120 °C, which is consistent with the qualitative observations made in the optical images.

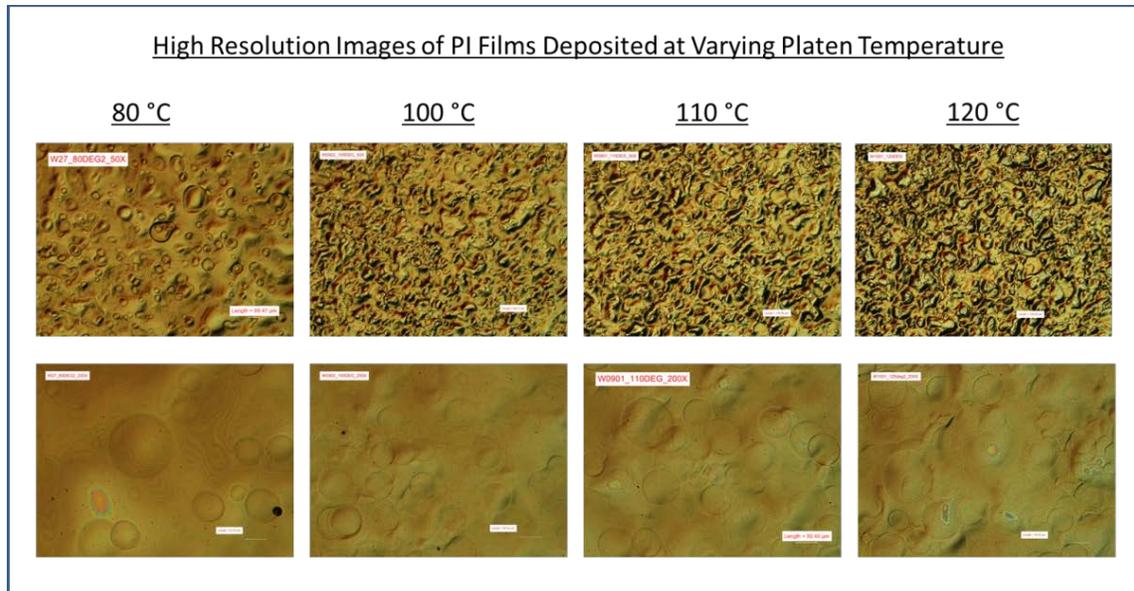


FIGURE 2: Optical micrographs of films deposited with platen heated to 80, 100, 110, and 120 °C. Upper micrograph at 50X and lower micrograph at 200X.

Deposition Temperature (°C)	Film Thickness (µm)	Film Roughness (Rq, µm)
80	6.3548	2.0788
100	5.8088	2.2869
110	5.3046	2.3564
120	4.7963	2.3831

TABLE 1: Effect of increasing temperature on film thickness and film roughness (Rq)

Based on these results associated with deposition temperature it was shown that a lower deposition temperature of 80 °C yielded lower surface roughness when compared to the higher deposition temperatures and the film thickness at the lower temperature of 80 °C was greater by 1.5 µm when compared to the higher deposition temperature of 120 °C. Further studies will be carried out at temperatures of 60 and 70 °C to determine the effects of even lower temperatures on film thickness and roughness.

B. Table/Deposition Speed

To explore the effect of table speed on film quality and number of defects, depositions were carried out on wafers where the platen temperature was set to 95 °C and the nozzle was set 25.4 mm (1-inch) above the substrate. A temperature of 95 °C was chosen for this and all subsequent studies described herein as these experiments were carried out prior to the analysis of the data from the temperature study. The g-code toolpath was adjusted to run the table speed at 15mm/sec, 20mm/sec, 27mm/sec, 35mm/sec and 45mm/sec. Figure 3 shows the effects of increasing table speed on film thickness and film roughness (Rq).

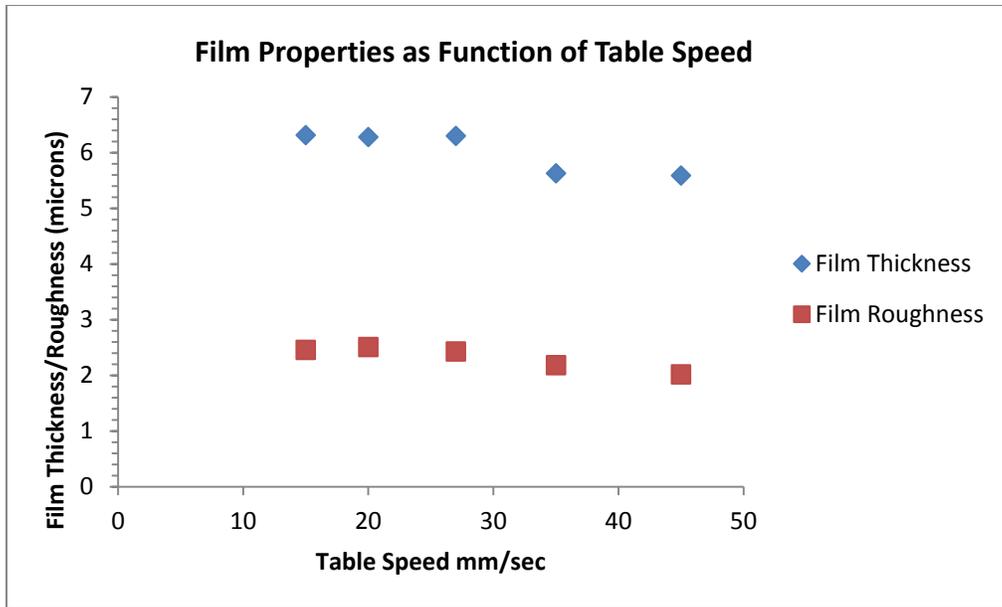


FIGURE 3: Plot of film thickness (μm) and film roughness (R_q , μm) as a function of table speed (mm/sec) measure using optical profilometry.

From this plot it can be seen that both the film thickness and film roughness generally decrease with increasing table speed, but the change is subtle. A table speed of 45mm/sec was identified as being the optimal table speed in minimizing film defects.

C. Nozzle Distance from Substrate

It was expected that nozzle height would give rise to significant defects on the surface of the substrate. Having the nozzle too close to the substrate could potentially lead to blotches, back-spray or an area void of material. If the nozzle is set too far from a substrate uneven coverage is likely.

To study the effects of nozzle height on film roughness and the overall presence of defects depositions were carried out with the nozzle set at 12.7 mm ($\frac{1}{2}$ -inch) and 25.4 mm (1-inch) above the substrate. The platen temperature was set at 95 °C and a table speed of 15mm/sec, 20mm/sec, 27mm/sec, 35mm/sec and 45mm/sec. Figure 4 shows a plot of film roughness (R_q , microns) versus table speed (mm//sec) with a nozzle height of $\frac{1}{2}$ -inch and 1-inch.

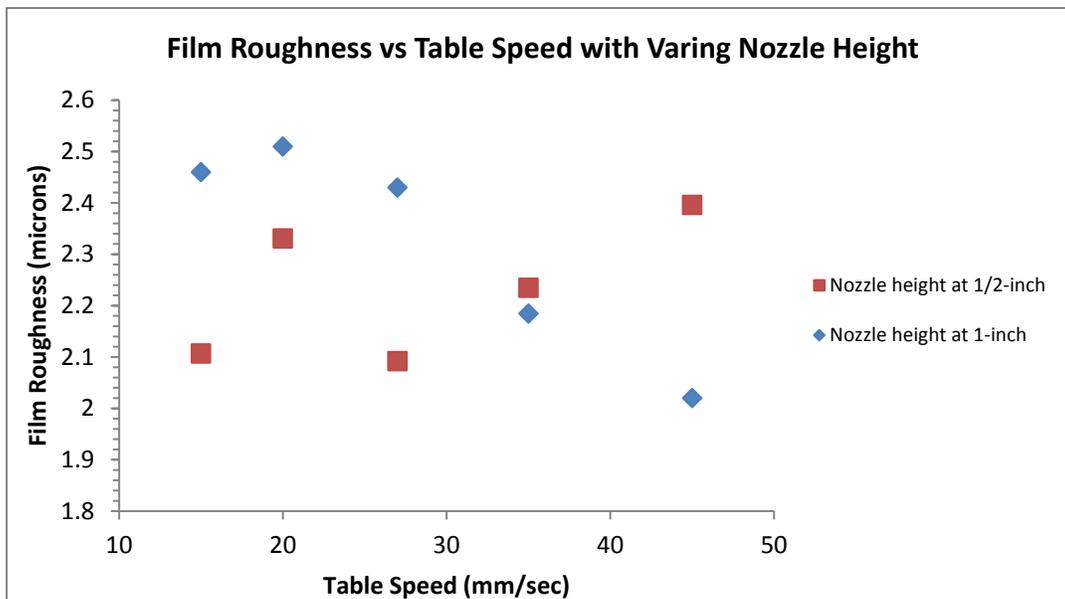


FIGURE 4: Plot of film roughness (μm) as a function of table speed (mm/sec) with varying nozzle height. Height was set at $\frac{1}{2}$ -inch and 1-inch above the substrate surface.

From the data in Figure 4 there are two mechanisms that affect film deposition from nozzles at different heights. With a nozzle closer to the substrate surface it can be seen that film roughness increases with increasing table speed. For a spray nozzle further away from the surface the measured roughness (R_q) decreases with increasing table speed. A nozzle height 1-inch above the substrate surface shows increasing table speed leads to decreased film roughness. When making a direct comparison of nozzle height for a given table speed a nozzle height $\frac{1}{2}$ -inch above the substrate yields lower surface roughness compared to that at 1-inch above the substrate for all speeds barring that at 45mm/sec. In addition the surface roughness at 20mm/sec for a nozzle height at $\frac{1}{2}$ -inch is higher than adjacent values and does not follow the overall trend, thus further studies should be carried out on the effect of nozzle height on surface roughness before any conclusions are reached. Differences in surface roughness may be attributed to aerosol aerodynamics, film density, back-spray however further studies need to be conducted to ascertain the exact cause. Non-uniformities due to overspray or back spray during deposition appear to be reduced at closer distances. At faster table speeds, it appears the drying kinetics are sufficiently fast that non-uniformities associated with overspray or back spray increase the measured roughness of the films. Results of nozzle distances further from the substrate and slower speeds suggest the drying kinetics are slower and particle agglomeration leads to higher surface roughness. With faster table speeds the deposition and drying kinetics are sufficiently fast enough to limit particle agglomeration and thus heterogeneity.

Figure 5 shows representative 3-D images for a smooth and rough film. The smooth 3-D film was obtained from the sample with nozzle set 1-inch above the substrate and a table speed of 45mm/sec. The rough 3-D film was obtained from the sample with nozzle set $\frac{1}{2}$ -inch above the substrate and a table speed of 45mm/sec.

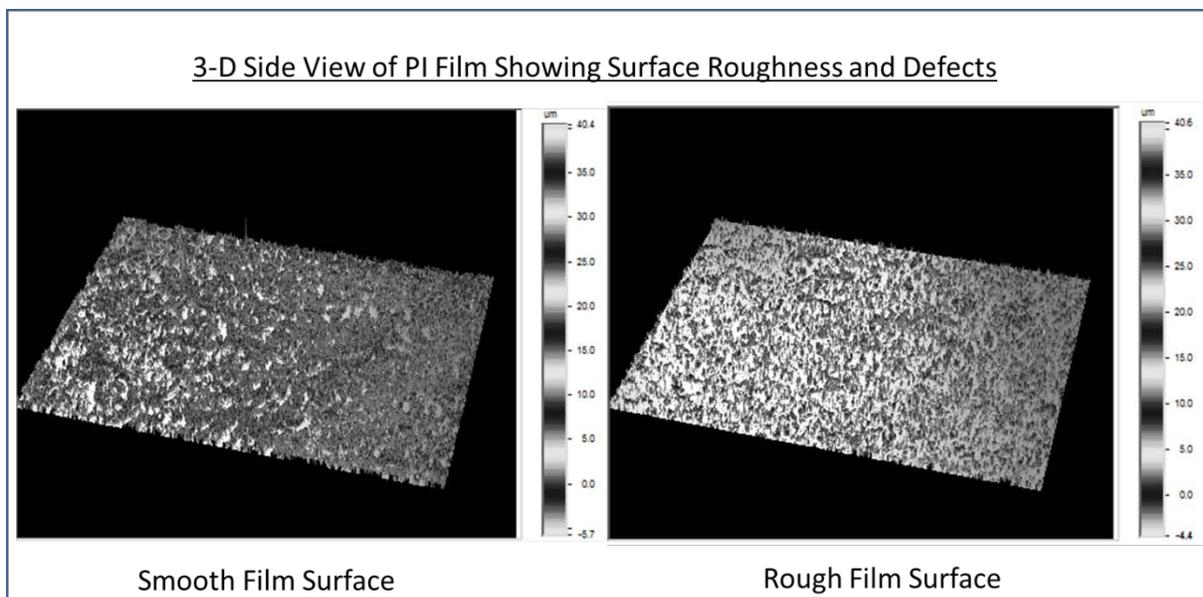


FIGURE 5: 3-D side view images of PI film deposited on gold coated silicon wafers showing surface roughness. Higher contrast features are indicative of greater surface roughness.

D. Cure Temperature

After the spray deposition, polyamic acid films are cured at elevated temperature to both evaporate and drive off solvent and to convert the polyamic acid to polyimide by a dehydration reaction. Drying and polymerization conditions can have a significant impact on the macroscale defects of the resulting films. Figure 6 shows pictures of films bearing a range of macroscale surface defects that occurred using sub-optimal curing conditions.

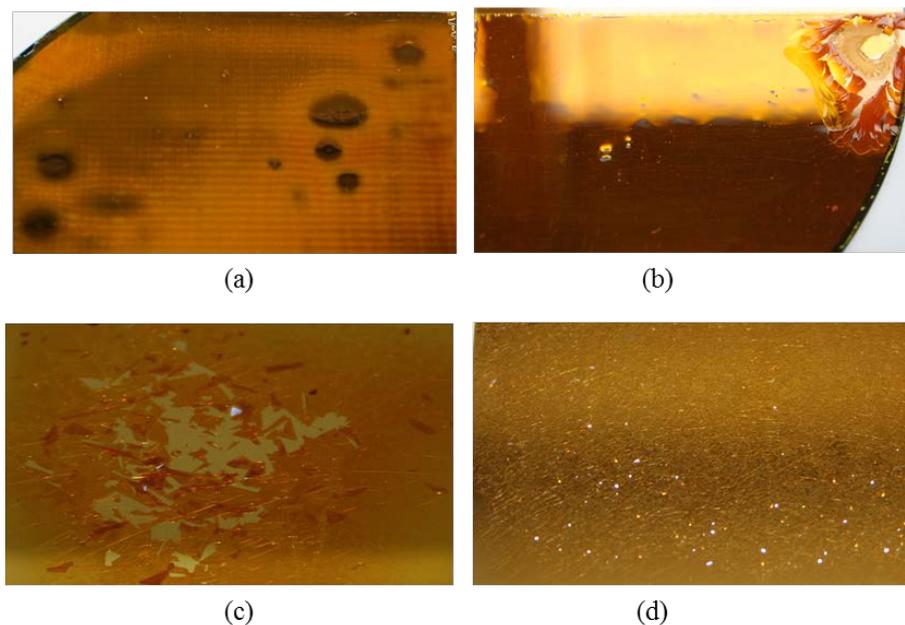


FIGURE 6: (a) Bubbles present of the film surface due to solvent evaporating too rapidly. (b & c) Cracking and peeling of film from substrate due to too high a cure temperature. (d) Crazing of film due to the thermal shocking too rapid a cooling event of the film.

As mentioned above the cure temperature yielded the most pronounced effect when dealing with macroscopic film defects. The bubbles that occurred in picture Fig. 6 (a) were the result of solvent evaporating too quickly, causing the vapors to become entrained in the film yielding bubbles. This was found to occur at a temperature above 150 °C. Similarly pictures (b & c) show the effects of solvent evaporating too quickly, the difference here being the temperature, 300 °C compared to 150 °C. The result of this higher more rapid cure temperature was the development of higher stresses in the film resulting in cracking, peeling and delamination. The image shown in picture (d) is that of a shattered film. This effect is caused by the thermal shocking of the film by cooling it too rapidly. To prevent the occurrence of these film defects associated with cure temperature, a systematic design of experiments was performed to define the optimal drying/curing parameters. It was found that a gradual temperature ramp followed by a gradual cooling ramp resulted in smooth films free of macroscopic defects associated with cure temperature. Figure 7 shows an image of film with optimized cure temperature.

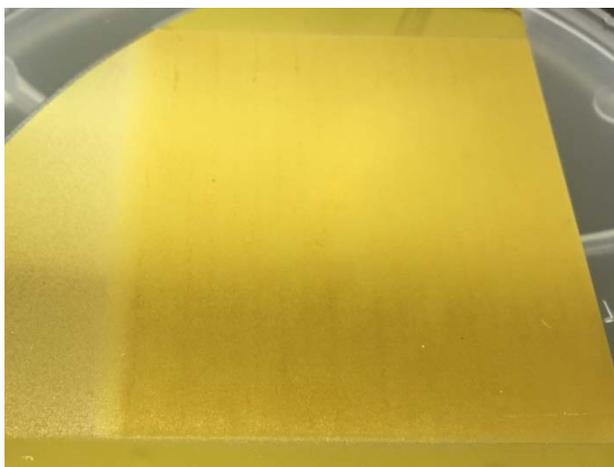


FIGURE 7: PI film free of defects associated with cure temperature. The film was cured by a temperature soak at 125 C for 3 hours, followed by a gradual temperature ramp of 5 °C/min to 225 °C for 12 hours, followed by gradually cooling to ambient temperature.

This film free of defects associated with cure temperature was obtained by a step cure profile, starting with an initial lower temperature phase of 125 °C for 3 hours and then increasing the temperature at 5 °C/min to 225 °C for 12 hours. Following the 12 hour higher temperature cure the oven was turned off and the substrate was allowed to gradually cool to ambient temperature. The oven temperature decreased at a rate of 5 °C/min.

Conclusion

The work presented here focused on deposition parameters and processing conditions of films of polyamic acid deposited by direct write spray dispense additive manufacturing and the role each played in generating defects. The driving force behind the understanding of sources of defects in polyimide films stemmed from the interest in producing high performance dielectric materials for capacitive energy storage. Since any surface roughness, uneven topology/morphology or defect is detrimental to the performance of a dielectric material

identifying their source and how best to mitigate these shortcomings was desired. Deposition parameters of platen temperature, platen speed and nozzle height above the substrate and the processing conditions of cure temperature and profile were studied. It was found that the most impactful parameter in creating macroscopic surface defects was cure temperature. Minimizing the defects formed during the cure process was achieved by a ramping approach on heating followed by gradual cool to ambient temperature. Optimal deposition parameters for minimizing surface roughness were identified as a platen temperature of 80 °C, a table speed of 45mm/sec and nozzle-height 1-inch above the substrate. Optimal cure conditions were found to be a cure temperature of 125 °C for 3 hours followed by a gradual temperature ramp of 5 °C/min to 225 °C for 12 hours followed by gradually cooling to ambient temperature.

References

1. M. K. Ghosh “Polyimides: Fundamentals and Applications”. Marcel Dekker, New York, 1996.
2. C. Feger, M. M. Khojasteh, M. Htoo “Advances in polyimide science and technology”. CRC Press, London, 1993.
3. K. L. Mittal “Polyimides: Synthesis, Characterization, and Applications”. Plenum Press, New York, 1984.
4. M. I. Bessonov, V. A. Zubkov “Polyamic acids and polyimides: Synthesis, transformations, and structure”. CRC Press, London (1993).
5. www.sono-tek.com
6. F.E. Peterkin, J.L. Stevens, J.F. Sharrow, and R.K. Pitman, “High voltage breakdown strength of rapid prototype materials” IEEE 14th Pulsed Power Conference, Vol. 2, pp. 1025-1028, 2003.
7. W.J. Monzel, B.W. Hoff, S.S. Maestas, D.M. French, and S.C. Hayden, “Dielectric Breakdown of Additively Manufactured Polymeric Materials” IEEE Trans. Dielectr. Electr. Insul., Vol. 22, No. 6; pp. 3543-3549; Dec. 2015.
8. L.N. Appelhans, D. M. Keicher, J.M. Lavin “Comparison of Dielectric Properties of Additively Manufactured vs. Solvent Cast Polyimide Dielectrics” CEIDP Proceedings, 2016 in press
9. P. Sarbol, A. Cook, P.G. Clem, D. Keicher, D. Hirschfeld, A.C. Hall, N.S. Bell “Additive Manufacturing of Hybrid Circuits” Ann. Rev. Mater. Res. Vol.46, 2016 in press.

Acknowledgements

Thank you to the following people for assistance and input in this work: Zach Beller, Adam Cook, Mike Russell, Nathan Acree and Marce Essien.

Sandia National Laboratories is a multi-program 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.