# Low-temperature polyimide processing for next-gen backend applications

*By Zia Karim [Yield Engineering Systems, Inc. (YES)]*

The thermal, mechanical and dielectric properties of polyimide materials are critical to meeting the demands of fan-out or wafer-level processing for 3D stacking applications. The team at YES worked together with colleagues at Hitachi Dupont (Melvin Zussman and Ron Legario) as well as colleagues at Fuji to study those properties for various low-temperature polyimides as a function of different process parameters under atmospheric and vacuum process conditions. This article will briefly explain the experimental process used and will present results for HD-7110 (a low-temperature polyimide from Hitachi Dupont), in comparison with HD-4100, Fuji's LTC-9320 (E07 version), and Asahi's BL-301. Some data on Hitachi Dupont's polybenzoxazole (PBO) HD-8820 will also be shared. The characterizations of these low-temperature polyimides under different process conditions will be followed by conclusions and a discussion of the benefits for future packaging solutions.

## Reducing thermal budget while maintaining performance

**Figure 1** lists the low-temperature polyimides known to the YES team from partners and chemical suppliers. The decreasing trend in cure temperatures is evident. Many engineers are familiar with HD-4100 (cured at 375ºC) and and HD-8820 (a PBO that is cured at 320ºC). However, more polyimides are now emerging that are cured between 200–230ºC, to satisfy the ever-lower thermal budgets of 3D stacking and heterogeneous integration applications. Hitachi Dupont offers its HD-7110 with a recommended cure temperature of 205ºC, Asahi offers its BL-301, Fuji offers its LTC-9320, and Toray offers a film that cures between 200 and 230ºC. These polyimides are used for redistribution (RDL) interconnect dielectrics. Even lower temperature dielectrics are being proposed; one from Fuji can be cured between 160 and 180ºC.

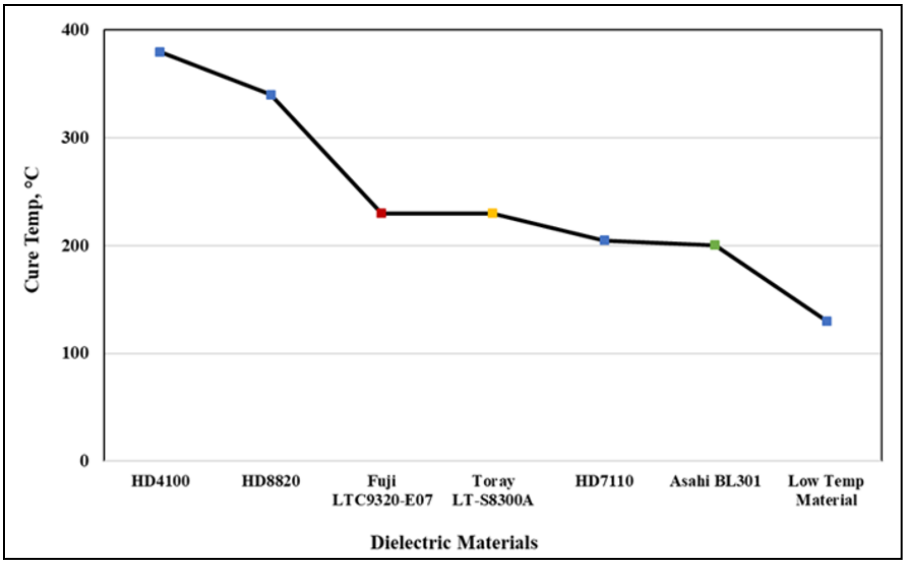



**Figure 1:** Lower temperature polyimide (PI) trend requires vacuum cure.

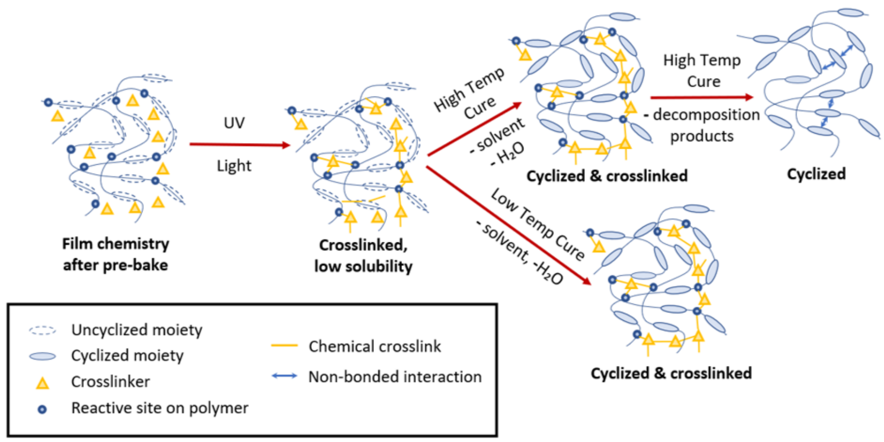



**Figure 2:** Cure chemistry of photosensitive low-temp PI.

Curing polyimide at low temperatures is good for stress and the RDL, but only if the properties of the cured films are also good. So the team tested not only the physical characterizations of outgassing, shrinkage, stress and scanning electron microscope (SEM) profile, but also mechanical, thermal and electrical properties of the cured films to determine how well these cured films would work in the multilevel RDL process.

## How it works

As illustrated in **Figure 2**, photosensitive polyimides designed for high-temperature cure undergo two main types of reactions: cyclization of the backbone to form imide groups, and decomposition and volatilization of the cross-linked compounds, leaving behind only the cyclized polyimide. Low-temperature polyimide curing uses a similar mechanism. The difference for low-temperature cure is that the cross-linked compounds are not decomposed but remain in the cured polyimide.

Low-temperature curing materials are targeted between 200 and 250ºC. This temperature range is sufficient to allow the imidization reaction to proceed, but removing the casting solvent becomes more and more challenging the lower the cure temperature goes. As an example, the boiling point of N-Methylpyrrolidone (NMP), the most common solvent, is 202 degrees at atmosphere. However, if the process pressure is 200Torr, the boiling point goes down to 150ºC. So when pressure is lower, it becomes easier to take the solvent and water out of the film, enabling good imidization. The team's studies revealed how this impacted the properties of the cured polyimides.

## Goals and methods

As mentioned above, this article will first compare results for HD-4100 and HD-7110, and will also discuss results for HD-8820, as well as polyimides from Fuji and Asahi. Four of these are negative-tone polyimides and one is positive-tone. The goal was to cure these films at as low a temperature as possible while maintaining desired properties. For RDL and other backend applications, when a low-temperature polyimide is proposed, the polyimide must exhibit no outgassing, good thermal stability (ability to withstand the thermal cycling process), chemical resistance, good mechanical properties – especially high elongation – and good dielectric properties. The cure process of a dielectric material should perform complete imidization, removing casting solvents and creating highly cured film with good, complete cross-linking.

An additional goal was to reduce cure time in order to reduce thermal budget. The atmospheric cure process usually involves three steps: oxygen removal, solvent removal, and cross-linking. It typically requires 6-8 hours, compared to 3.5 to 4.5 hours for low-pressure cure.

YES systems use a low-pressure vacuum cure process, which maintains excellent temperature uniformity, laminar gas flows and active heating and cooling for effectively curing polyimide and PBO materials. Figure 3 illustrates the low-pressure polyimide cure process that was used in the experiments.

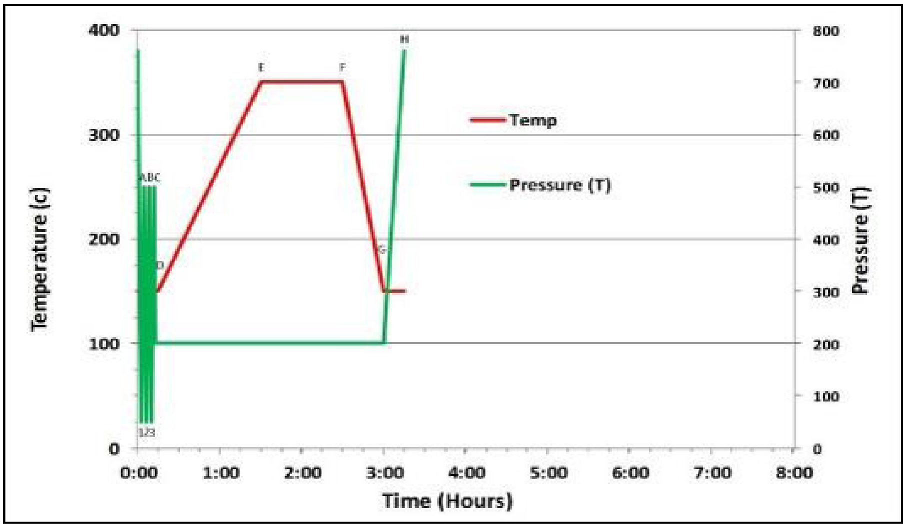



**Figure 3:** YES vacuum cure process.

An initial three-cycle pump-and-purge process took the oxygen to less than 10ppm. The vacuum process consisted of only one step: ramping up to the recommended cure temperature and coming down. In this study, we examined the effects of various cure pressures on the physical, mechanical, thermal, and electrical properties of the cured film.

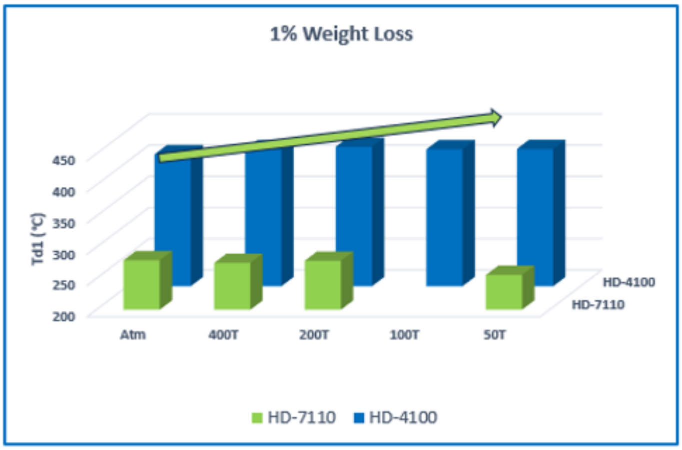
Both HD-4100 and HD-7110 were coated, baked and developed using automated track systems. In some cases, for determining mechanical and thermal properties when the film needed to be released from the wafer after cure, a coating of polyimide 2611 was used as the substrate. The control samples were cured at atmosphere using a commercially-available atmospheric cure oven. For all the studies, cure pressures were varied between 50 and 760Torr.

## Results

The next sections describe our results for various polyimide materials.

**HD-4100 and HD-7110.** The Fourier transform infrared spectroscopy (FTIR) spectra of cured polyimides under vacuum and atmospheric conditions were analyzed to compare the extent of imidization. These FTIR analyses exhibited almost identical profiles, confirming that even though the vacuum cure process requires much less cure time, complete imidization was, nonetheless, obtained for both films.

The FTIR characterizations showed better imidization in the low-pressure curing process for low-temperature polyimide, in comparison to the atmospheric cure process. Seeing better imidization with FTIR, it can be assumed that this process will result in better molecular packing, and will also show an improvement in thermal, mechanical and electrical properties. Gas chromatography mass spectrometry (GCMS) was used to identify volatiles from HD-4100 cured at 200Torr and at atmospheric pressure. The outgassed volatiles were much higher for the atmospheric cured film compared to the vacuum-cured film. Most of the peaks are related to solvent NMP or water, in the case of atmospheric-cured films. No outgassing was observed for vacuum-cured films up to about 300ºC for most of the cured films. Similar GCMS analysis was carried out for HD-7110 cured at the recommended cure temperature of 205ºC, at three different pressures: 200Torr, 400Torr and 760Torr (atmospheric). The volatiles of NMP, the major solvent in HD-7110, were much lower in the vacuum-cured films. For total NMP volatiles, the parts-per-billion (ppb) values were calculated and plotted against the various pressures. They indicated a decrease in NMP content of 35% with a decrease in cure pressure from 760Torr to 200Torr. If we extrapolate this trend to 100Torr, the NMP content decreases by about 50%. The efficient removal of solvent and other volatiles is critical to achieve better cross-linking, to help improve thermal stability, and also to improve dielectric strength. These properties



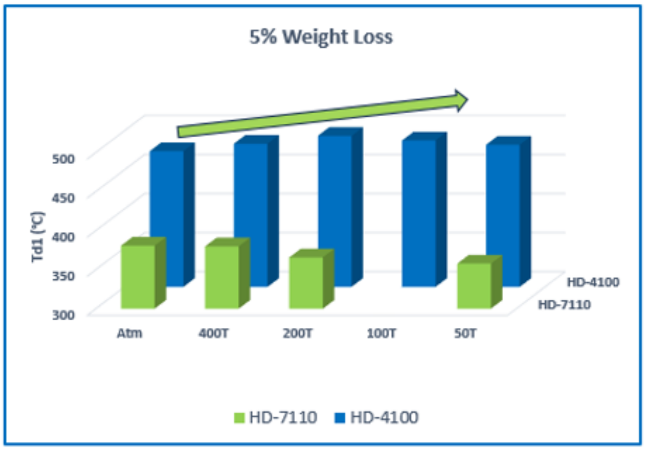




**Figure 4:** Thermal properties of HD-4100 and HD-7110 (Td 1% and 5%).

are, therefore, expected to be better for vacuum-cured films.

Next, the mechanical, electrical, and thermal properties of these films were examined. The tensile strength and the modulus of a film are important indicators of the ability of a film to absorb and withstand the mechanical stresses that occur at the interface between the film and metals. This is especially important for multilayer films that experience inter-layer stress. From the studies of tensile strength at different cure pressures, no variation of the mechanical properties was found as a function of the cure pressures, for either HD-7110 or 4100. So even though HD-7110 is a low-temperature polyimide that may still contain the cross-linker, there was not much change in its tensile strength when it was cured under vacuum. However, we observed that while elongation is 60% for HD-4100, it was only 36% for HD-7110. Similarly, HD-7110's other mechanical properties like modulus, strength, and residual stress were worse compared to the cured HD-4100 film. These results suggest that HD-7110 may have less ability to withstand interconnect stress exerted during material processing.

**Figure 4** shows thermal properties of HD-4100 and HD-7110. These were measured by changes in weight, as determined by thermogravimetric analysis (TGA). The changes in weight are due to the loss of materials in the film that are volatile at higher temperature. The source of these volatiles is not only water, but also other chemical components at elevated temperature, including cross-linkers. This was especially critical for the low-temperature polyimide, HD-7110. For HD-4100, when the Td 1% and the Td 5% were measured (Td 1% is 1% weight loss at temperature and Td 5% is 5% weight loss at temperature), as the cure pressure decreased, there was an increase in Td 1% of 31%. This means the film shows much better thermal stability under vacuum cure. Also, the glass transition temperature of HD-4100 was 15 to 20 degrees higher with vacuum compared to the atmospheric cure process. However, no such effect was found for the low-temperature polyimide HD-7110 with the pressure changes, either for 1% weight loss, or 5% weight loss. This means that there is minimal dependence on cure pressures for HD-7110, showing lower thermal stability compared to the more popular HD-4100, probably due to the decomposition of the cross-linker at elevated temperature.

Next, electrical properties were examined. Dielectric properties (dielectric strength, dielectric constant, and dissipation factor) were the main parameters measured. These properties are solely dependent on the degree of imidization, impurity content, and the packing density of the polyimide. Lower dielectric constant (DK) supports higher transmission speed, and lower dissipation factor (DF) improves signal integrity.

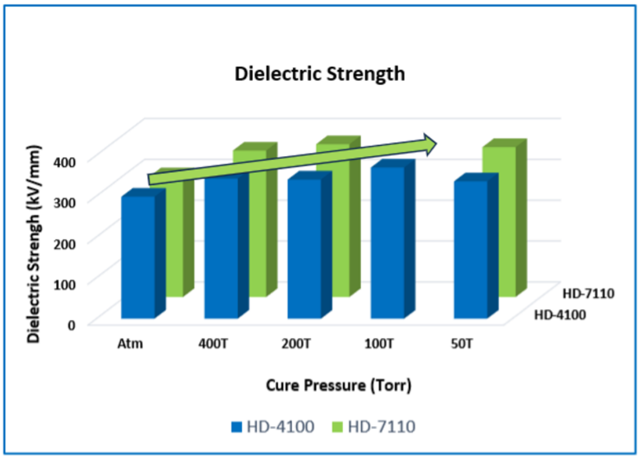



**Figure 5:** Dielectric strength of HD-4100 and HD-7100 at varying pressures.

We measured values of DK for HD-4100 and HD-7110. DK was around 3.3, which is consistent with expected values. Dissipation factor for the low-temperature polyimide was higher. While HD-4100 was around 0.009, DF was 0.016 for the low-temperature polyimide. This higher DF was probably due to the existence of the cross-linker, which is assumed to remain during the curing process in the case of low-temperature polyimide. However, very good results were observed for the dielectric strength, showing the biggest improvement at low pressure compared to atmospheric cure. As shown in **Figure 5**, 20-25% higher dielectric strength was consistently achieved with vacuum for both low-temperature polyimide (HD-7110) and high-temperature polyimide (HD-4100) compared to atmospheric

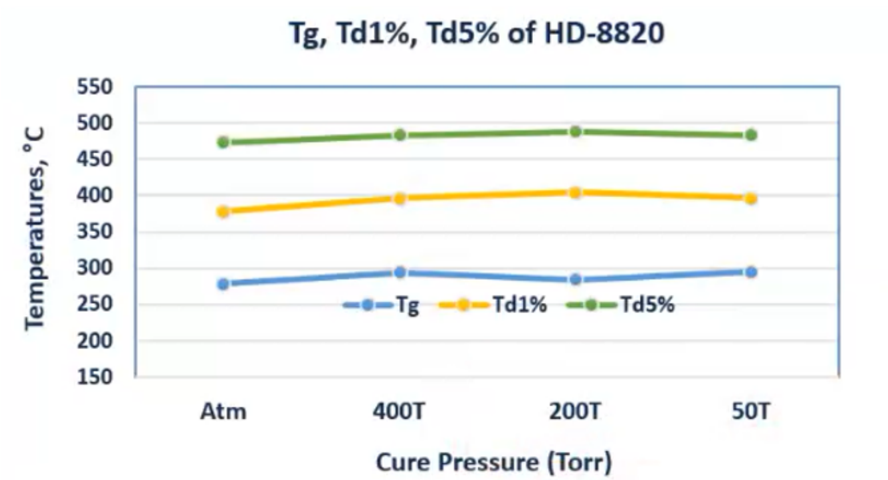



**Figure 6:** Glass transition temperature (Tg), Td 1%, and Td 5% weight loss for HD-8820.

| FILM PROPERTY TESTED | RESULTS |
|---|---|
| Cure condition | YES 230°C |
| 2% weight loss | 321°C |
| 5% weight loss | 335°C |
| Tg | 206°C |
| CTE | 55.7ppm |
| Elongation | 76.9% |
| Tensile strength | 183.1 MPa |
| Young's modulus | 2.6 |
| Imidization index | 100% |

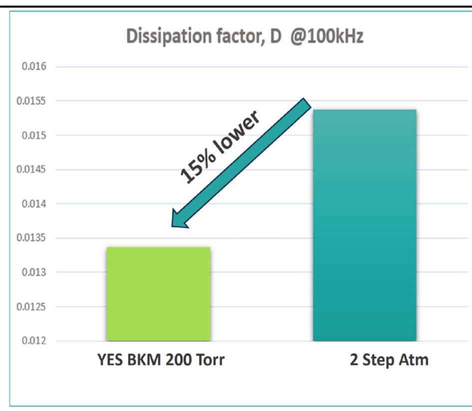



**Figure 7:** Film properties of Fuji LTC-9320 E07.

| Process | Dwell Temp (°C) | Dwell Time (min) | Total Time (hr) | Td 5% | Tg | CTE | Elongation | Strength | Young's Modulus |
|---|---|---|---|---|---|---|---|---|---|
| Asahi Rec. Recipe | 250 | 120 | 6.5 | 370 | 235 | 55 | 55 | 125 | 3.3 |
| YES BKM | 250 | 60 | 4 | 370 | 235 | 55 | 60 | 125 | 3.3 |
| YES BKM | 200 | 60 | 4 | 340 | 215 | 60 | 50 | 130 | 3.4 |

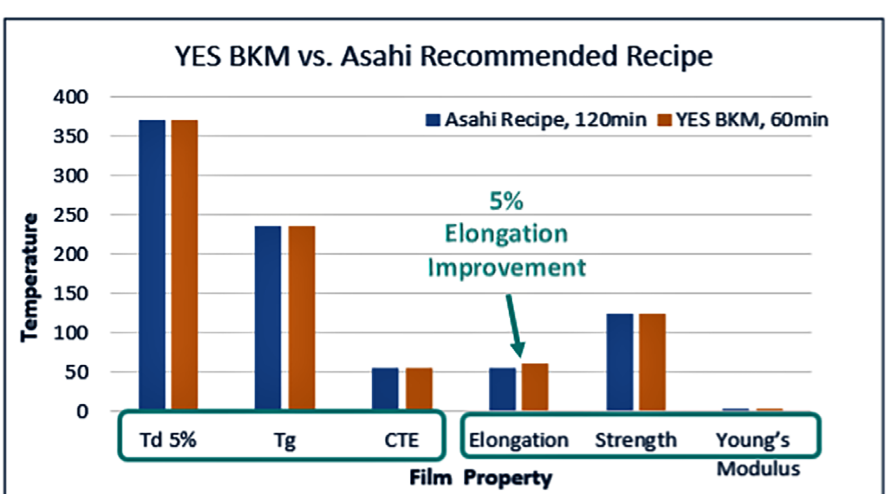



**Figure 8:** Film properties of Asahi BL-301.

cure. This is certainly related to better packing density as well as better dielectric properties of vacuum-cured polyimide films.

**PBO HD-8820.** Though most of our customers are now moving from PBO to polyimide and low-temperature polyimide, some data is included here on PBO HD-8820. The team's study of PBO HD-8820 for physical, thermal, mechanical and electrical properties showed little variation of these properties with cure pressure. **Figure 6** plots glass transition temperature (Tg), Td 1%, and Td 5% weight loss for HD-8820. Most of these values showed minimal variation among atmospheric, 400Torr, 200Torr and 50Torr cure pressures; the same was true of the dissipation factor. One notable observation was that for HD-8820 the dissipation factor was .006, which is even lower than that of HD-4100, so HD-8820 will likely provide a much better signal-to-noise ratio. Most of the properties measured – elongation, modulus, tensile strength, and stress – were very good and were consistent with the literature values. For the most part, HD-8820 PBO showed stable performance overall, and at higher pressure (greater than 400Torr), the results showed better stability of the films.

**Fuji LTC-9320 E07.** A low-temperature polyimide from Fuji (LTC-9320, which has a cure temperature of 230 degrees) was also studied. The recommended atmospheric cure is a two-step process, which was conducted at 230ºC and which took 6.5h. The one-step YES best-known method (BKM) process was then used, which took about 4.5h. Dwell time was further reduced, by 50%, which resulted in a cure time of 3.5h.

As with the Hitachi Dupont films, the team achieved similar characteristics (or better characteristics, for dielectric strength). But we were also able to reduce the cure time by about 35% and thereby improve throughput. Additionally, the objective here was to see if cure time could be reduced while obtaining similar or better film properties. For this film, even when cure time was cut from 8 hours to around 3.5 hours, its physical properties, like shrinkage and stress, remained the same. The intrinsic properties of the film did not change, which probably indicates that the film was already fully cured. This was consistent in the FTIR analysis of LTC-9320 at the above conditions – identical FTIR spectra indicated the same imidization. Even with reduced cure time, fully-cured cross-linked films were obtained, showing that shrinkage, stress and imidization remained the same.

**Figure 7** shows thermal and mechanical properties for the fully-cured LTC-9320 E07 films. The cure temperature was 230ºC, and most of the film properties were very consistent with those from the atmospheric process. However, the team was able to reduce the cure time from 6.5 or 7h to about 3.5h. One interesting thing: the dissipation factor was approximately 15% lower when the films were cured at 200Torr compared to the atmospheric process – a very exciting result for this Fuji polyimide, which will provide better signal-to-noise performance for high-frequency film. To conclude, the thermal, mechanical and reliability tests on this film showed that most of the properties were consistent despite a cure time reduction of about 35%, and tests showed a good dissipation factor reduction for a high-frequency application.

**Asahi BL-301.** Finally, we consider results for another low-temperature polyimide: Asahi's BL-301. Once again, the low-pressure process was compared to the atmospheric cure process recommended by Asahi, for which the temperature is 230ºC. In this case, the dwell time was again reduced by 50%, and cure time was reduced by 38% using low-pressure cure compared to the recommended recipe. As shown in **Figure 8**, total time was reduced from 6.5h to 4h; however, most of the results reported here (e.g., Td 5%, glass transition temperature, CTE, elongation, strength and Young's modulus) are similar. The cured film showed an improvement of approximately 5% in elongation, which gives better mechanical properties, with the vacuum cure process. When, in addition to the reduced cure time, the cure temperature was reduced to 200ºC, the resulting film showed characteristics that would likely be acceptable for this process.

## Summary

The 3D packaging roadmap involves enhancing the capabilities of high-density backend processing by increasing the number of RDLs, shrinking line width and spacing, and reducing pad size and pitch. The trend of the polyimides and the PBO used in these interlevel RDLs is increasingly toward low cure temperatures, where the vacuum curing process offers significant benefits.

For both polyimide and PBO film, using vacuum reduced the thermal budget by reducing both the cure time and cure temperature. Vacuum cure also resulted in better film properties. Further integration studies are needed to qualify these films, and we are working with some partners, including imec, to do that. Overall, a reduction in cure time of approximately 35% was achieved using the vacuum cure process. Reduction in thermal budget, which reduces film stress, is required for 3D stacking and heterogeneous integration. Hopefully, this article will help to position these low-temperature polyimides – with less outgassing, better imidization, and better dielectric strength – as suitable for 3D packaging and the stacking of chiplets, as well as for other heterogeneous integration applications.

## Biography

Zia Karim is CTO of Yield Engineering Systems, Inc. (YES), Fremont, California. Before joining YES, Dr. Karim spent 15 years as VP of Business Development and Technology at Eugenus/AIXTRON/Genus. He also held senior management positions at Applied Materials and Novellus. He received his PhD in Electrical Engineering from Dublin City U. in Ireland, and the Certificate of Business Excellence from the Haas School at UC Berkeley. He holds 16 patents; email: zkarim@yieldengineering.com.