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Characterization of the Surface Structural, Mechanical, and Thermal Properties of Benzocyclobutene Dielectric Polymers using Scanned Probe Microscopy

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SUMMARY: Scanning probe microscopy (SPM) techniques are used to characterize surfaces related to the processing of benzocyclobutene (BCB) dielectric thin films. Thermally cured resins and photodefineable resins are sold under the trade name CYLCOTENE™[1] for electronic applications. TappingMode AFM (TMAFM) imaging is used to follow changes in adhesion promoter morphology upon baking to help explain adhesion performance. Power spectral density (PSD) analysis of TMAFM images of plasma treated BCB surfaces are unique and can be used to 'fingerprint' processes. Selective oxidation of the BCB surface can be used to fabricate a phase imaging standard for TMAFM. Near surface modulus of the BCB materials is 3.6 ± 0.2 GPa and the hardness is 0.38 ± 0.2 GPa measured by depth-sensing nanoindentation. Creep recovery of indents can be used to qualitatively distinguish between thermal and photocureable materials. A heated tip in a scanning thermal microscope can induce the thermal curing of BCB over micron sized areas. Local thermal analysis with the same probe allows the measurement of the changes in the glass transition, T_g, at the surface with cure temperature.

Introduction

Benzocyclobutene (BCB) polymers[2, 3] represent a family of spin on, curable low k dielectric thin films for use in electronic devices. The materials have found a wide range of applications including bumping/redistribution/wafer level packaging, passivation/stress buffer, multichip modules, printed circuit boards, and active matrix liquid crystal displays. The polymers can be thermally cured and dry etched or can be made photodefineable by incorporation of a photoinitiator. The polymer is formed via a Diels-Alder addition of the vinyl group of one monomer with the cylcobutene group of another. The reaction uses no catalysts and does not give off any volatile by-products. The general cross-linking chemistry is shown below:

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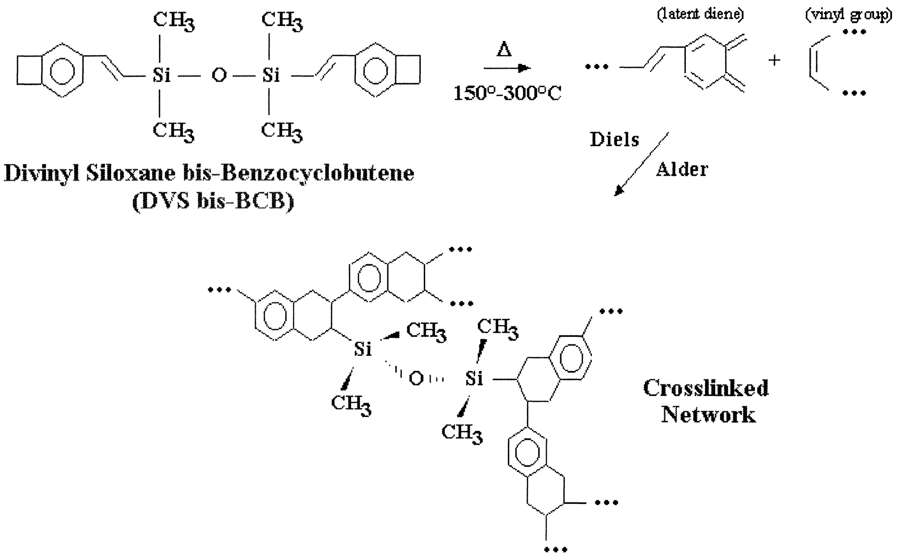


Fig. 1: The thermal cure chemistry of Divinyl Siloxane bis-Benzocylobutene ('BCB') monomer.

This paper will focus on the scanning probe microscopy characterization of two commercial BCB products, a photodefineable resin (CYCLOTENE™ 4026) and two "dry-etchable" resins (CYCLOTENE™ 5021 and 3022)[4]. BCB formulations can be readily processed by spin coating. Final curing may be achieved using a hot plate or oven over a range of 210 - 250°C under nitrogen with < 100 ppm oxygen[4]. The glass transition temperature of BCB following full thermal cure is > 350°C.

Experimental

TappingMode AFM images were obtained on a Dimension 3000 SPM (Digital Instruments – VEECO, Santa Barbara, CA). Standard etched silicon cantilevers and probes were used which were 125 µm long. Two-dimensional isotropic 2D-PSD analysis was performed using the standard software supplied by Digital Instruments (software version 4.3r6). Depth-sensing nanoindentation was carried out using a Triboscope (Hysitron, Inc., Minneapolis, MN). The indenting head replaces the AFM head on a Digital Instruments Multi-Mode SPM. A Berkovich diamond tip was used for the measurements. In this way the diamond tip can be used for both indenting and contact mode AFM imaging. The load frame compliance and tip area function were determined using a fused silica standard[5)], and the standard was measured along with the BCB samples to insure calibration. The current software version is 3.2FL. BCB films used for nanoindentation were between 10 μm and 12 μm thick. Scanning thermal microscopy was obtained on a MicroTA-2990 system (T.A. Instruments, Inc., Newcastle, DE). Commercially available Wollaston probe tips were used. The temperature scale was calibrated using a 2-point method. A linear fit of the probe resistance at the point of room temperature kick-on and the onset of Nylon 6 melting were used to establish the scale. In many cases plotting of graphical data was done using version 3.12 of IGOR Pro (WaveMetrics, Inc., Lake Oswego, OR). BCB wafers were coated and cured in a cleanroom facility at The Dow Chemical Company, Midland, MI, unless otherwise specified.

Tapping Mode AFM (TMAFM) characterization

TMAFM was used to examine the morphology of a vinyl alkoxysilane based adhesion promoter used to improve adhesion between the polymer dielectric and silicon oxide wafer substrates[6)]. The AP3000 promoter formulation consists of 0.3 wt% vinyl triacetoxysilane, pre-hydrolyzed in water, dissolved in a carrier solvent of 1-methoxy-2-propanol. It is applied by spin coating at 3000 rpm. Imaging can be used to monitor the wetting characteristics, thickness, and formation of ordered layers following application and subsequent baking steps. Fig. 2 shows the surface morphology of the promoter layer after deposition at room temperature, and after baking.

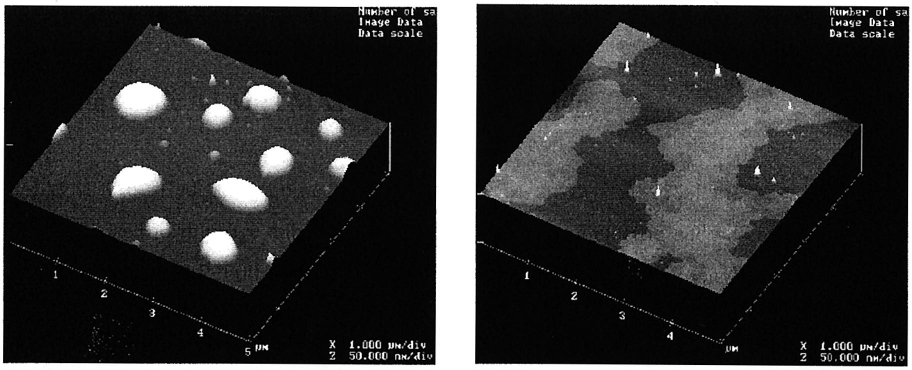


Fig. 2: TMAFM images of AP3000 adhesion promoter after spin coating at room temperature (left) and following a hot plate baking step at 100°C (right).

The TMAFM images show droplets and ridges that are as high as 11 nm on the room temperature deposited film. After baking briefly at 100°C, the droplets thin, spread, and form up to 3 multilayers of promoter molecules with each layer about 0.9 nm thick. Baking at 180°C leads to a thinner, continuous layer of adhesion promoter (not shown). This adhesion promoter system provides excellent adhesion between the polymer and substrate wafer under dry or hot-wet conditions. BCB films applied without the promoter show poor adhesion6). This latter result seemed at odds with the heterogeneity of the promoter films, however scanning photoemission microscopy has revealed a continuous layer of promoter between islands of promoter at room temperature, and after the baking step at 180°C, the vinyl group survives7).

As spun and cured, BCB surfaces are quite smooth and homogeneous, with typical Ra values less than 1 nm over a 1 μm x 1 μm area. Processing of BCB on wafer may involve steps where the polymer is plasma treated to remove, clean, or roughen the polymer for subsequent processing. The plasma composition, time, and power are all variables that affect the surface chemistry and morphology. For one application it was desirable to back-sputter etch (BSE) the BCB surface to remove material. Fig. 3 shows the results of three different BSE processes.

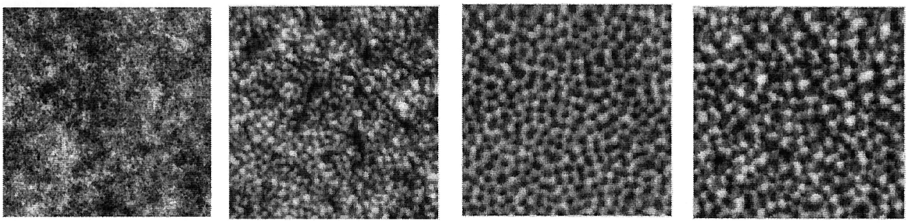


Fig. 3: Comparison of CYCLOTENE™ 5021 surface morphologies after cure and after back-sputter etch (BSE) treatments (1μm x 1μm TMAFM topview images).

The morphologies of the BSE treated surfaces are not visually unique and the resulting roughness measurements by TMAFM are similar. Image analysis using isotropic 2D power spectral density (PSD) reveals unique distributions of spatial frequencies as shown in Fig. 3.

We use isotropic 2D PSD because there is no directional orientation to the roughness due to the BSE process. The PSD can then be used as a fingerprint of the plasma process used to treat the BCB surface. For example, another surface treated using one of the three BSE treatments was followed by a 40Å Ti deposition. Using the PSD analysis we are able to identify the specific process used (process B, in this case).

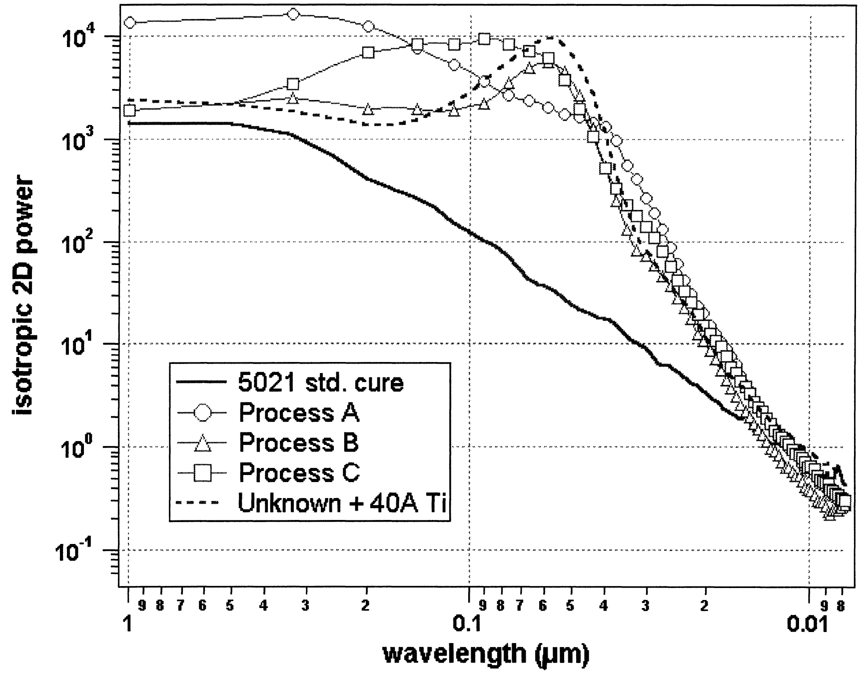


Fig. 4: Isotropic 2D power spectral density analysis may allow fingerprinting of plasma processing. For example, the Unknown process PSD resembles that of Process B.

It is also possible to convert the surface of BCB to a quartz-like material by selective removal of carbon using plasmas containing O_2[8]. It is routine in processing photodefineable BCB (pBCB) to employ a "plasma descum" procedure to remove polymer and/or photoresist residues left in via holes after imaging and developing a pattern. Selective oxidation of the surface of pBCB can be achieved using a defined photoresist and a brief O_2 plasma exposure. To illustrate this case, a mask with circles of various diameters was used to pattern a photoresist layer on top of BCB. The photoresist was exposed and developed leaving circular regions of photoresist on the BCB surface, masking these areas. Subsequently, the partially masked BCB surface was exposed to an oxygen plasma for 5 minutes. The conversion of the selected areas to oxide was confirmed by imaging XPS and imaging static SIMS. Tapping Mode AFM with phase detection was also able to distinguish the oxidized surface from the masked areas as shown in Fig. 5.

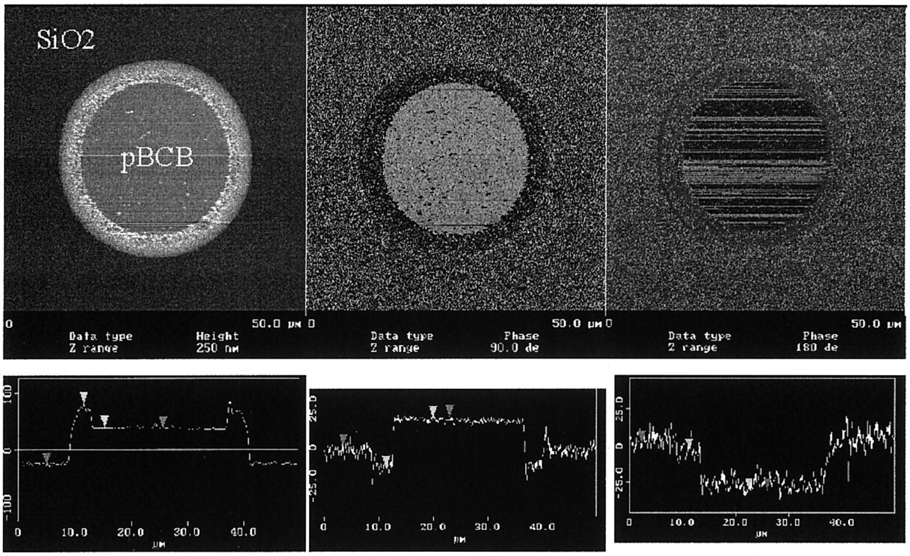


Fig. 5: Tapping mode height (left) and phase imaging (center, right) of pBCB surface which has been selectively masked, patterned, and oxidized leaving circular patterns of pBCB (30 micron circle shown) surrounded by surface SiO_2. The tapping parameters may be changed to bring about reversible changes in phase contrast for pBCB and SiO_2 patterns (see text).

The goal was to produce a topographically flat surface with patterns of different surface chemistry and mechanical properties; in other words, a standard for phase imaging. In reality, there is still topographic relief due to densification of the pBCB during oxidation to SiO_2 with loss of C and H in the near surface region. Nonetheless, the pBCB circles are raised only about 75 nm. Tapping parameters can be adjusted to reversibly cause phase contrast changes between the pBCB and SiO_2. The pBCB has positive contrast at high amplitude, moderate tapping (A_o = 200 nm, r_{sp} = 0.77, Fig. 5, center) and negative contrast lower amplitude, moderate amplitude (A_o = 100 nm, r_{sp} = 0.79, Fig. 5, right).

Nanoindentation Coupled with Imaging

For surface mechanical studies we use a commercial depth-sensing nanoindentation system which operates in conjunction with our AFM for imaging. This system replaces the flexible cantilever with a stiff Berkovich diamond indenter that can be driven into a surface and retracted while the surface displacement is measured independently and continuously to generate a load vs. displacement curve. The same indenter tip can be used for contact mode imaging before and after indenting, under the control of our Multi-Mode SPM. These measurements are quantified using published methods5) where the tip shape and system compliance are calibrated. Measuring the stiffness of the contact at the onset of unloading provides a means to determine modulus and hardness. We have used this instrument to make mechanical property measurements of all BCB thin film materials, e.g., CYCLOTENE™ 4026, as shown in Fig.6.

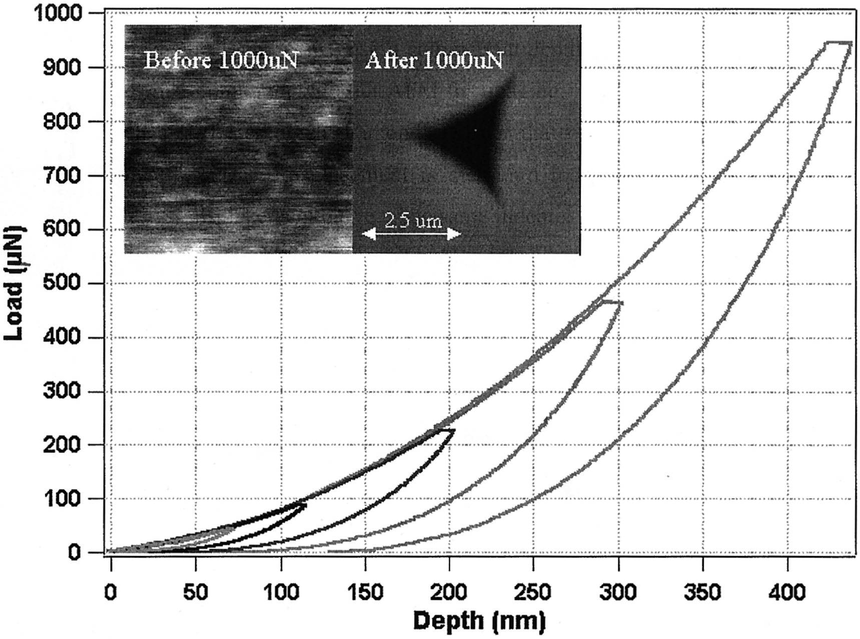


Fig.6: Depth-sensing nanoindentation of CYCLOTENE™ 4026 after normal, full cure. The indentation at each load consisted of a 25 second loading – 10 second hold - 25 second unloading profile. AFM images of the surface before and after indentation are inset and were obtained with the indenter tip.

Replicate measurements were made at each load and the resulting mechanical properties can be plotted as a function of contact depth as shown in Fig. 7. The hardness is observed to be uniform in depth while a slight minimum in modulus occurs at around 80 nm.

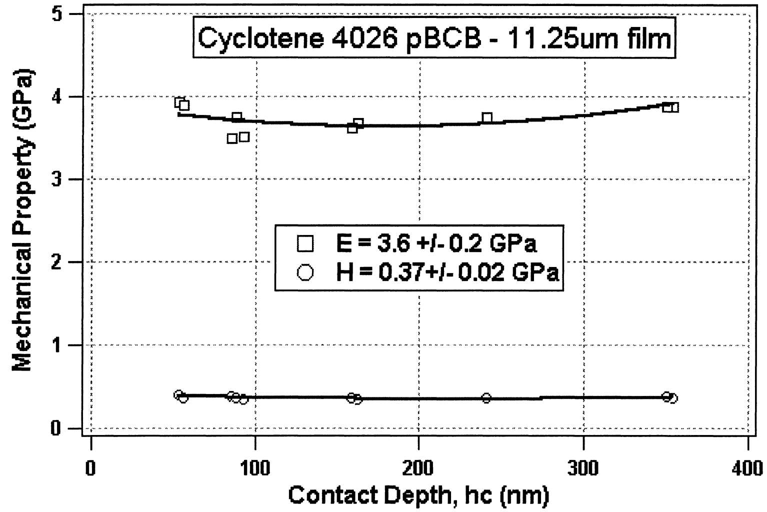


Fig.7: The near surface mechanical properties of CYCLOTENE™ 4026 after normal, full cure are nearly uniform in depth.

The average mechanical properties for all BCB materials are compared in Tables 1 and 2. For each film, 15 measurements were taken over a contact depth range of 50 – 400 nm. The uniformity of the properties with depth allows inclusion of all data to evaluate average, near surface values. At this level of sampling, the mean values have a relative standard deviation of less than 15%.

Table 1. Near Surface Modulus of Fully Cured CYCLOTENE™ Resin Films

Resin Film	Mean E (GPa)	1 Std. Dev. (N=15)	% Std. Dev.	Minimum	Maximum
3022	3.44	0.20	6	3.21	3.87
4026	3.74	0.15	4	3.49	3.93
5021	3.59	0.21	6	3.35	3.95

Table 2. Near Surface Hardness of Fully Cured CYCLOTENE™ Resin Films

Resin Film	**Mean H (GPa)**	**1 Std. Dev. (N=15)**	**% Std. Dev.**	**Minimum**	**Maximum**
3022	0.36	0.05	14	0.32	0.45
4026	0.37	0.02	5	0.37	0.40
5021	0.40	0.06	15	0.35	0.54

Within the error of the measurements we are not able to distinguish between the different BCB products. The average value for all resins is 3.6 ± 0.2 GPa for the modulus and 0.36 ± 0.02 GPa for the hardness. Bulk mechanical measurements of the tensile modulus of BCB thin films have been measured from laser cut strips lifted off wafer[9)]. The bulk measurement for pBCB indicates a lower value for the modulus, 2.9 ± 0.2 GPa, or about 24% difference. Several factors can contribute to this difference. One important factor is viscoelastic creep. Fig. 6 shows that the pBCB creeps at peak load during the hold cycle. Creep during unloading will act to increase the slope of the unloading curve and, therefore, the apparent stiffness of the contact in the nanoindenting experiment. This will lead to an overestimation of the modulus.

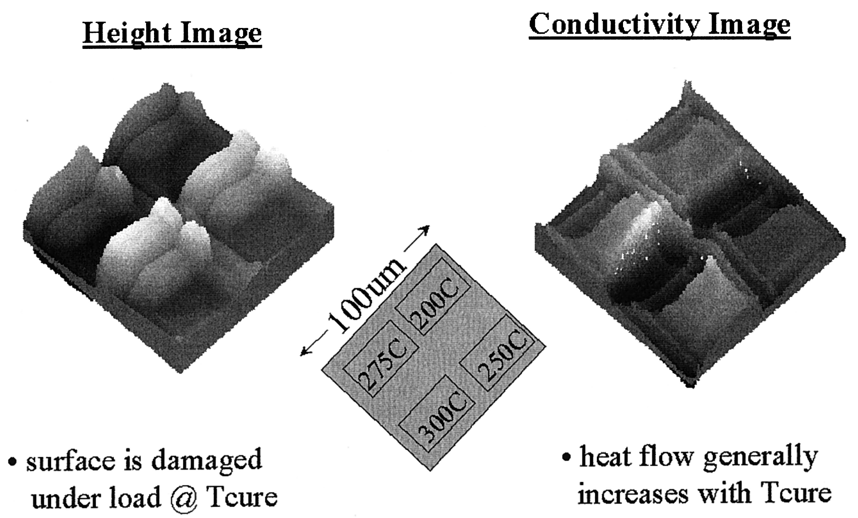
Measurements of creep following unloading can also be used to distinguish between BCB materials. One first obtains a load vs. depth profile, which provides a measure of the final depth of penetration. Subsequent AFM imaging of the indent allows one then to follow recovery of the indent with time. For example, two minutes after making 1000 uN indents (40 uN/second loading rate), the indent recovers by 63% for a thermally cured "dry-etchable" resin such as CYCLOTENE™ 3022 but only 53% for a thermally cured photodefinable resin such as CYCLOTENE™ 4024. Indents made on a fused silica standard showed a recovery of only 16% after two minutes. This method may therefore have some potential for future development. However, its sensitivity and reproducibility have not been evaluated for use in these systems.

Scanning Thermal Microscopy (SThM)

Over the last few years we have been investigating the potential of scanning thermal microscopy (SThM) to provide new property information regarding polymer surfaces with the Pollock group in the UK10). In the SThM experiment, a small bridge-balanced Wollaston thermistor tip is used as a contact mode AFM tip. The tip is used both as a heat source and a heat sensor. Differential heat flow and deflection measurements are made with respect to a reference probe that is mounted in air in close proximity to the scanning tip. The heat to the scanning tip can be modulated and the material's response can be monitored during imaging via lock-in techniques. The frequency of the modulation will affect the penetration depth of the thermal wave into the polymer surface. We have taken advantage of this capability to detect the presence or absence of BCB residues after wet development of vias over a conductive copper bond pad11).

In an unscanned mode, the tip can be positioned on the surface for local spectroscopic (local DTA or local modulated temperature-DTA) and TMA measurements. We have used the tip as a heat source to cure BCB while using the *same* tip as a local probe to monitor changes in the glass transition as that cure progresses.

Fig. 8 shows the layout of the heating experiment. We began with a 1 μm thick BCB film that had been hot plate baked at 125°C for 1 minute. A 100 μm x 100 μm area was scanned in four smaller areas with the tip heated at 200°C, 250°C, 275°C and 300°C under N_2. BCB is normally cured in an oxygen free, N_2 environment so, for this experiment, the microscope and sample were blanketed with N_2. The original large area was then imaged in both height and conductivity modes. These images are shown in the upper left and right, respectively, of Fig. 8. Note that the scanning with the heated probe led to some surface deformation but note also that the conductivity images appear brighter in the areas that saw higher temperature.



Height Image

Conductivity Image

- surface is damaged under load @ Tcure

- heat flow generally increases with Tcure

Fig. 8: Topographic (left) and conductivity (right) images of a CYCLOTENE™ 5021 thin film after curing the surface using the SThM tip heated to the temperatures indicated in the center schematic. The BCB had been initially hot plate baked at 125°C for 1 min. in N_2.

Next, the tip was moved into each heated area where two local thermal analysis measurements were made (ambient to 350°C @ 5°C/sec.). Representative differential heating curves for each patch are shown in Fig. 9. The derivative of the heat flow was plotted against the programmed tip temperature. The inflection point can be taken as a measure of the T_g. Note the gradual broadening and decrease in intensity of the transition with increasing tip temperature used to cure the surface. The measured T_g is always below the applied tip temperature. This may reflect problems with the accuracy of the calibrated temperature scale. More likely is it because of the short contact time of the tip in each region, keeping the extent of cure low[12)].

The extent of surface cure using the heated probe tip can be estimated from correlation of glass transition temperature with bulk cure measured by IR or DSC[13)] and wafer stress[14)] for BCB. The extent of cure achieved using the SThM tip is certainly no more than 80% at the highest applied temperature and well below the point of vitrification given the short contact times during scanning.

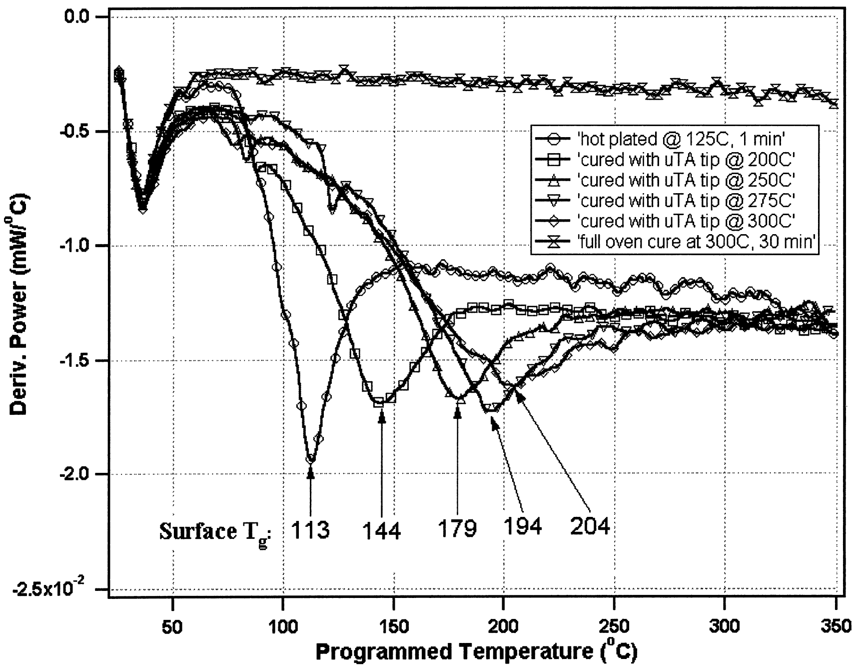


Fig. 9: The scanning thermal tip was used to cure the CYCLOTENE™ 5021 surface under N_2 at different temperatures. The resulting heat flow data from local thermal analysis (LTA) measurements using the same tip shows increasing surface T_g with increasing cure temperature.

Fig. 9 also shows the differential heat flow to a fully cured BCB that thermally cured in an N_2 environment. The heat flow does not change up to a tip temperature of 350°C, consistent with a bulk $T_g > 350°C$. The tip induced cure surfaces never achieve this level of cure. In fact, the BCB in these heated areas is still soluble in mesitylene and is readily removed by rinsing.

Conclusions

Various modes of scanning probe microscopy have been explored to provide new information about benzocyclobutene polymer thin films used in electronic applications. We have found that power spectral density analysis of TMAFM height images can be used to identify plasma processing treatments. Phase detection can be used to monitor changes in surface chemistry as a result of these processes. Microproperty characterization tools can now be applied locally and results compared to bulk measurements. Depth sensing nanoindentation can be used to measure surface mechanical properties of BCB following cure. Discrepancies between surface and bulk measurements appear to be related to viscoelastic effects. It would appear that the viscoelastic properties are different for photodefineable and "dry-etchable" resins after both have been subjected to the same thermal cure process. The reason is not known. Lastly, it was shown that thermal imaging and local thermal analysis using a scanning thermal microscope enabled us to follow the curing process of these resins by monitoring only in the near surface region. In fact, the probe itself was used to induce curing and then to measure the extent of that cure.

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