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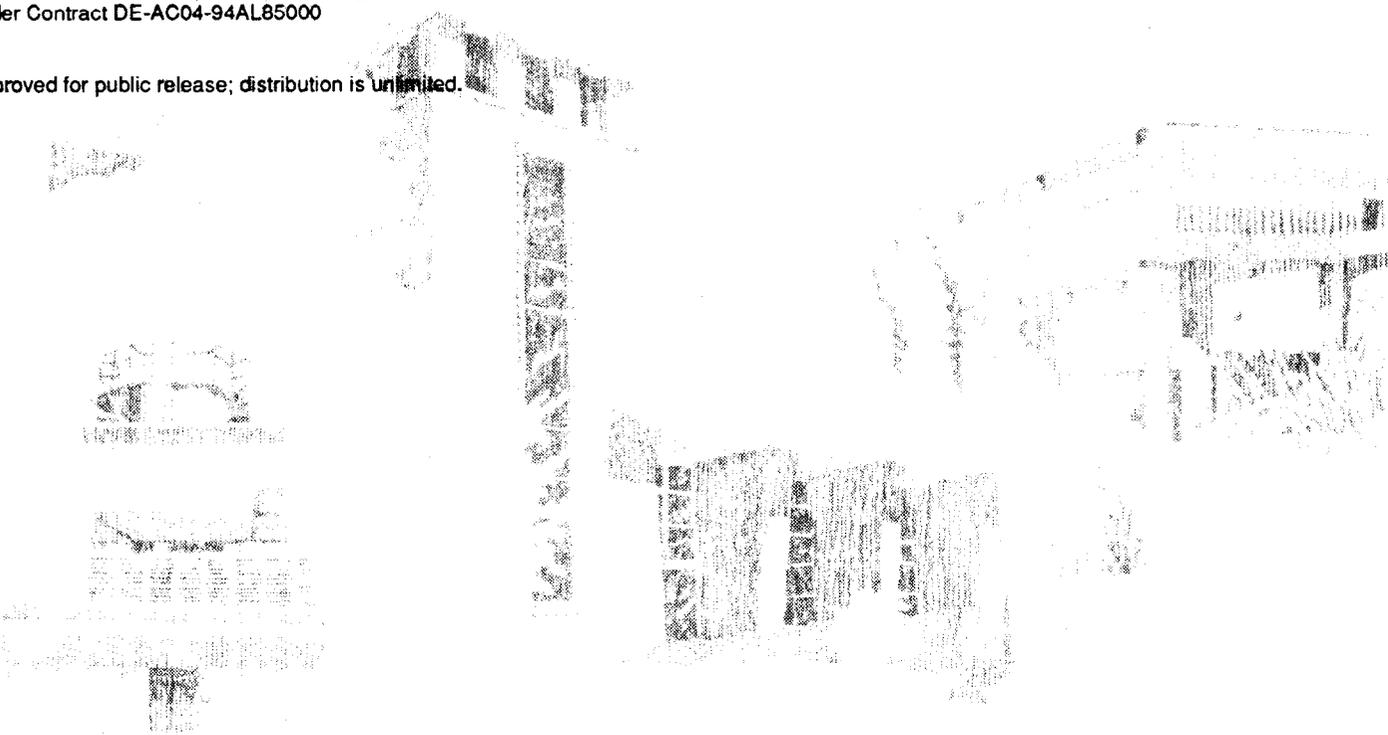
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Microporous Polyimide Films for Reduced Dielectric Applications

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Abstract

With all the advances in the microelectronics industry, a limiting factor to computer chip speed and size is becoming the dielectric constant of the interlayer insulating materials. Dielectric constants of these layers have been reduced in going from inorganic to organic type materials. A further reduction in dielectric constant, coupled with better mechanical properties are still required for these types of materials. We have developed a technique involving spincoating in conjunction with a thermodynamic process called "Non-solvent Induced Phase Separation" (NSIPS) to create microporous polyimide films that exhibit both a lower dielectric constant and better stress reduction properties compared to their solid film counterparts. In this technique, we spincoat a soluble polyimide solution in 1,3-dimethoxybenzene solvent onto a silicon wafer, and then immediately submerge the "wet" polymer film into a non-solvent bath, typically toluene. Phase separation of the polymer occurs on a micron size scale and the resulting microporous structure becomes locked in by the high glass transition temperature of the polyimide. We have determined the factors affecting the film morphology, thickness, pore size, and percent porosity; these factors include the polymer concentration, spin speed, and the type of non-solvent used. The different morphologies obtained for the varying non-solvents are explained in terms of thermodynamics and kinetics of phase separation and diffusion, using an idealized ternary phase diagram. One particular film having a porosity of 68%, thickness of 22 microns and pore size of 1.4 microns had a measured dielectric constant of 1.88 and dielectric loss of 0.002. Stress measurements indicated that the microporous film reduced surface stress on the wafer by more than a factor of 10 when compared to the analogous solid polyimide film.

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Microporous Polyimide Films for Reduced Dielectric Applications

Introduction

In the microelectronics industry, significant advances have been made in lithographic and related technologies. These advances have translated into fabrication of smaller and faster devices. However, the extent to which these technologies can be implemented is limited by the dielectric constant of the insulating medium used in the devices. The signal propagation speed along a wire in a chip is inversely proportional to the square root of the dielectric constant of the surrounding insulator. Therefore a decrease in the dielectric constant will result in faster propagation speeds.¹ The dimensions of a device are also affected by the insulator dielectric constant. A material with a relatively large dielectric constant will cause more noise to be heard between adjacent wires - a phenomena referred to as "cross-talk". A lower dielectric constant in the insulating medium reduces the amount of cross-talk, and thus allows the wires to be placed closer together. These smaller dimensions allow for shorter wire lengths, which directly translates into a faster cycle time for a device.¹ Therefore a decrease in the dielectric constant of the insulating medium both increases the overall speed of a device, as well as decreasing its dimensions.

One recent approach to lower dielectric constants has been to switch from using inorganic type insulators (dielectric constant of 4.5 - 11) to organic type insulators, with polyimides being the organic polymer of choice (dielectric constant of 3 - 4).² However, polyimides suffer in that they usually have inferior mechanical properties, such as larger thermal expansion coefficients and lower thermal conductivities, compared to their inorganic counterparts. More specific efforts have been to develop polyimides with even lower dielectric constant by breaking up the linearity of the polymer chain.³ Typically, trifluoromethyl substituents are used. The problem usually associated with these newer polyimides is that they tend to have lower thermal stability than the classical ones.

Our work has involved developing a technique that will both reduce the dielectric constant and improve some of the mechanical properties of the insulating layers of a microelectronic device. Our approach is to make a polyimide film into a microporous structure and simultaneously incorporate it into the electronic device. Due to the porosity, a significant amount of the film will be filled with air. Since the dielectric constant of air is close to 1, the film will have a substantially reduced dielectric constant. The foam structure will have a smaller overall thermal expansion coefficient than its

solid counterpart because of less material present, and it will also be able to reduce the surface stress felt by the substrate, and thus cause fewer interface failures.

To make these microporous films, we use spincoating in combination with a thermodynamic technique called "Non-Solvent Induced Phase Separation" or NSIPS for short.^{4,5} NSIPS involves dissolving a polymer in a solvent, and then exposing the polymer solution to a non-solvent. The non-solvent causes the polymer to phase separate out of solution on a micron size scale, creating a microporous structure.

Experimentals

All organic solvents and non-solvents were obtained commercially and used without further purification. Ultem[®] 1000, a soluble polyimide, was graciously provided by General Electric Co. Spincoating was performed on a Headway Research Inc. Photo-Resist Spinner. Dielectric constant and loss were measured on a Hewlett Packard 4194A Impedence/Gain-Phase Analyzer.

Microporous film formation procedure:

A general procedure for the fabrication of microporous films is as follows: The Ultem polyimide is dissolved at the desired concentration in a suitable solvent, such as 1,3-dimethoxybenzene. The solution is poured onto a glass slide that is placed in the spincoating apparatus. The slide is then spun at the desired rpm for a specified length of time. The glass slide, having a uniform polymer/solvent film on it, is immediately submersed in a bath of non-solvent, such as toluene. After about five minutes, the resulting microporous film is removed and air-dried over night. The microporous polymer film is floated off the glass slide in water, and fractured through the middle for Scanning Electron Microscopy (SEM) analysis. SEM is used to determine film thickness and average pore size. Porosity is inferred from density measurements, which are calculated from the dimensions of the glass slide, and the thickness and weight of the polymer film.

The most successful solvent for solvating the polyimide and giving uniform spincoated films was 1,3-dimethoxybenzene (DMB). All of the results will involve this organic as the solvent. The first experiments involved determining the effect on the microporous structure of using different non-solvents to induce the phase separation. Ultem was dissolved in DMB at 20wt%, spincoated at 2000 rpm for 20 s, then submersed in the desired non-solvent. The non-solvents tested were: methanol, isopropanol, acetone, acetonitrile, ether, toluene, and supercritical CO₂. Figure 1 shows the cross-section of the films, as observed by SEM, for each of these non-solvents that were tried.

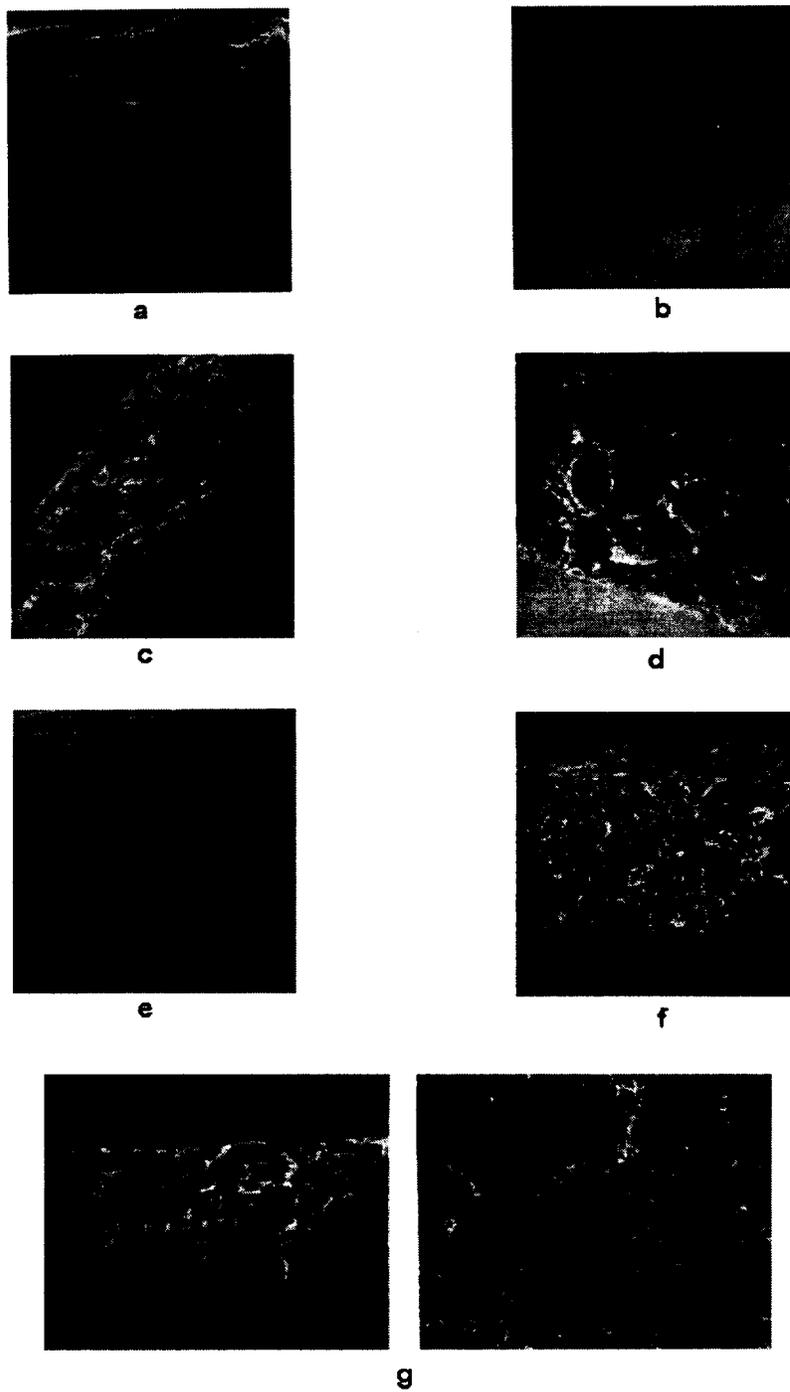


Figure 1. Microporous Polyimide Films Created with DMB as Solvent and with the Following Non-Solvents: a) Methanol b) Isopropanol c) Acetone d) Acetonitrile e) Ether f) Toluene g) Supercritical Carbon Dioxide (Edge View and Surface View)

The remaining studies were conducted with DMB as a solvent, and toluene as a non-solvent. In order to determine the effect of concentration and spin rate on the resulting microporous film thickness, pore size, and pore structure, three concentrations of polyimide in DMB were made: 15%, 20% and 25%. The solutions were then spincoated onto a glass slide at 1000, 2000, 3000, or 4000 rpm, and then immediately submersed in a bath of the non-solvent toluene.

Results

The results of the thickness vs. spin rate are shown in figure 2. The results of pore size vs. spin rate are shown in figure 3. It is also important to determine percent porosity for all these samples. We determined this by knowing the dimensions of the glass slide (the films were typically the same length and width as the glass slide), the thickness, and the weight of the polymer film. The results of percent porosity vs. spin rate are shown in figure 4.

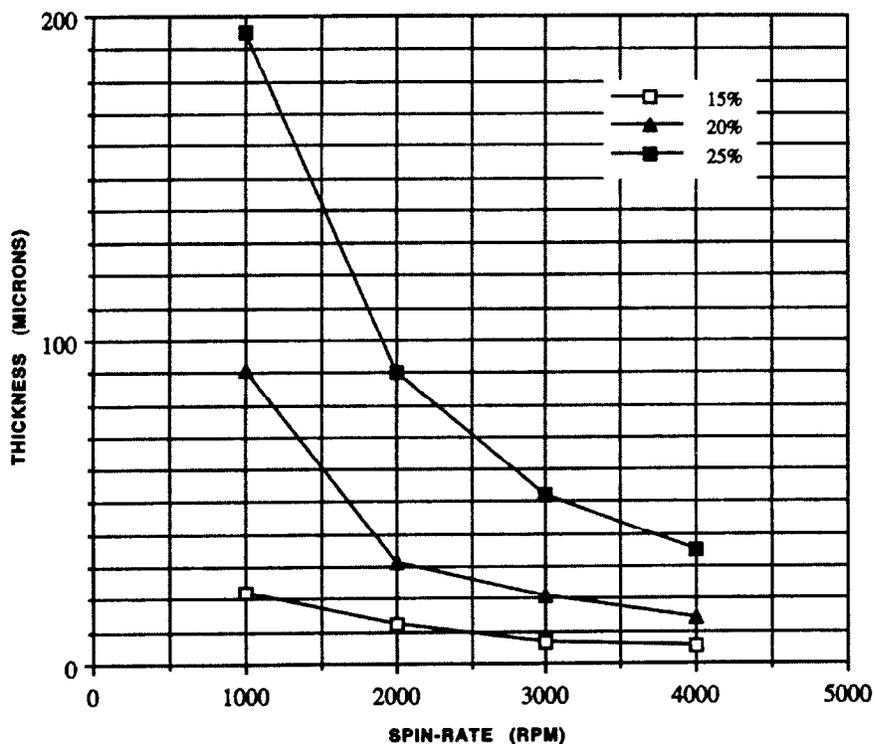


Figure 2. Thickness of Microporous Film Vs. Spin-Rate for 15, 20, and 25wt% solutions of Ultem in DMB.

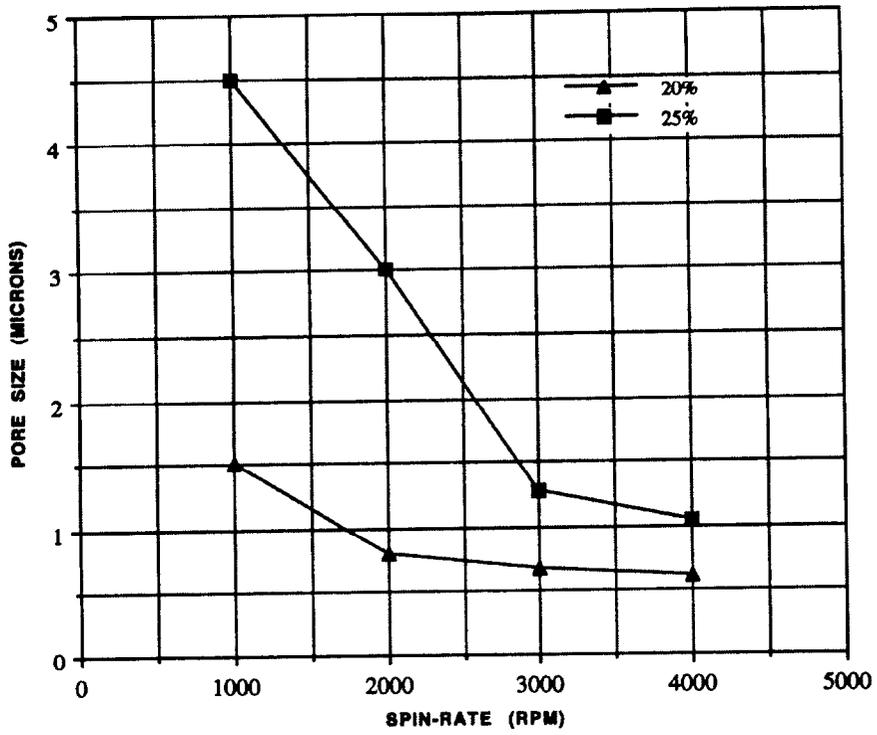


Figure 3. Pore Size Vs. Spin-Rate for 20 and 25wt% solutions of Ultem in DMB.

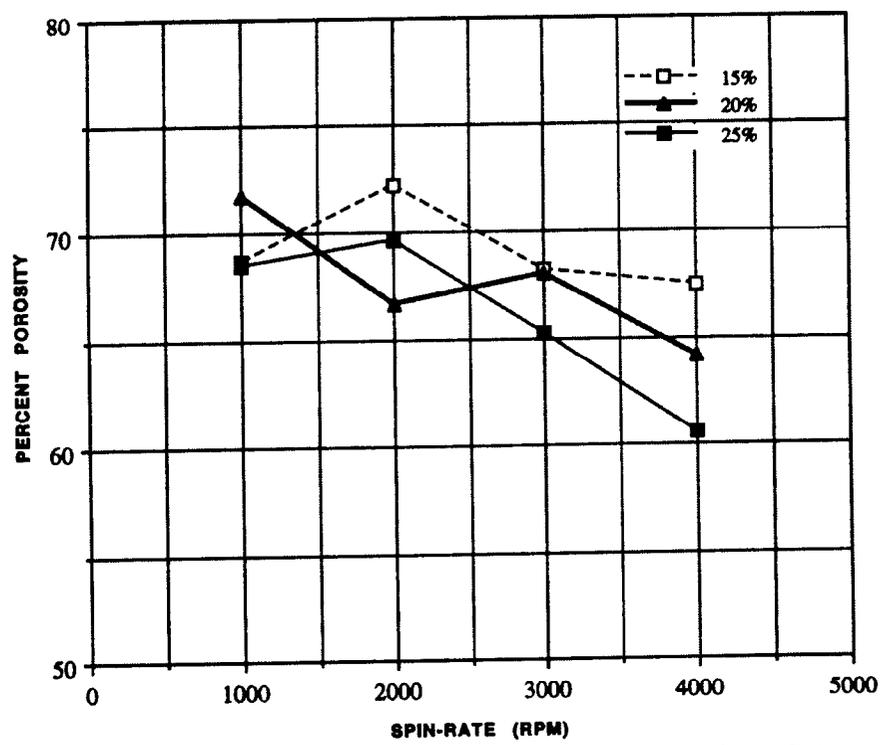


Figure 4. Percent Porosity Vs. Spin-Rate for Initial Ultem Solutions in DMB of 15, 20, and 25wt%.

Dielectric measurements were performed on one sample having a film thickness of 22 mm, pore size of 1.4 mm, and porosity of 68%. The result at 1 kHz was a dielectric constant of 1.88 and a dielectric loss of 0.002.

Stress measurements show this microporous polyimide film to create a surface stress of 1.9 MPa, and an analogous solid polyimide film to create a surface stress of 20.6 MPa.

Discussion

In the NSIPS process, thermodynamic and kinetic effects play an important role in determining the pore size and morphology of the microporous polyimide film. Figure 5 shows a general ternary phase diagram involving polymer, solvent, and non-solvent. Line A-B-C shows a typical pathway for the process.

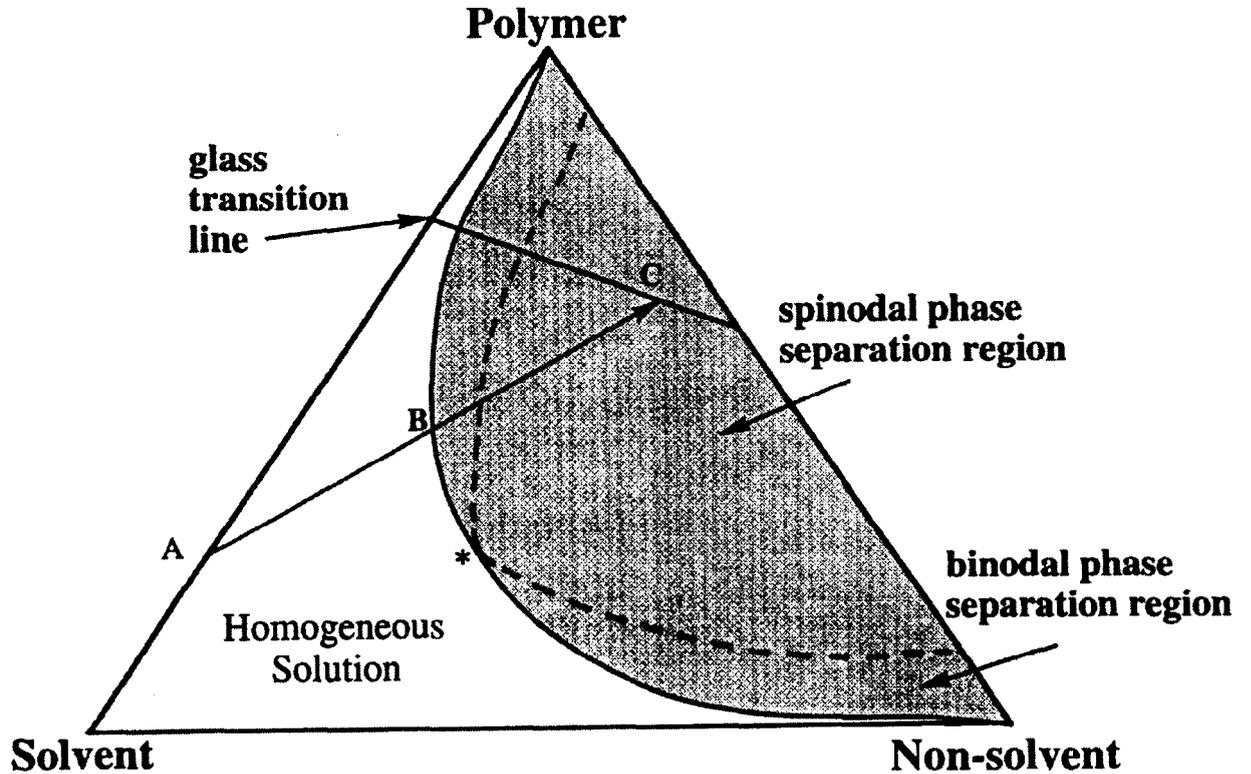


Figure 5. Ternary Phase Diagram of Polymer, Solvent, and Non-Solvent.

Point A in the diagram represents the polymer concentration in the "wet" solvent/polymer film immediately after spincoating. When this film is placed in the non-solvent bath, the film moves quickly along the line to point B. At this point, the system hits the phase separation envelope, and will go through a binodal or a spinodal phase separation

process, depending on where point B is on the envelope. As the system continues to move toward equilibrium, it reaches the glass transition line, designated by point C, at which time the polymer rich phase turns glassy and locks in the microstructure that had been developing up to that time. Two types of phase separation can occur: binodal, or spinodal phase separation, as indicated in the figure. Binodal phase separation involves a nucleation followed by a propagation process. Above the critical point (*) small "islands" of phase separated solvent/non-solvent are formed by nucleation. During propagation more solvent/non-solvent adds to these islands, and eventually islands are joined together to form a network, leaving behind a polymer rich phase that forms its own network. Binodal phase separation involving polymer "islands" can also occur with processes moving through the binodal region below the critical point. Spinodal phase separation involves a dynamic process whereby concentration fluctuations occur in a wave-like fashion. These fluctuations grow unstable and result in polymer rich areas and polymer poor areas throughout the solution. This type of phase separation is sometimes referred to as spontaneous phase separation, and usually results in much smaller pore sizes than in the binodal process. Kinetic factors affecting the morphology mostly include diffusion rates of polymer, solvent, and non-solvent. The length of time that the system is forced to remain in the phase separated region before hitting the glass transition is directly related to these diffusion rates. A slower diffusion process causes the system to be in the "non-glassy" phase separated region longer, which allows for more phase coarsening to occur. The more that phase coarsening is allowed to occur, the greater will be the final pore size of the microporous structure.

The SEM pictures in figure 1, involving the different non-solvents, are interpreted in light of the discussion above. In all of the different non-solvent systems, we interpret the SEM results to show a binodal phase separation process involving solvent/non-solvent "islands". When methanol, toluene, or supercritical CO₂ are used, a uniform pore structure results throughout the thickness of the film. This implies that the diffusion is sufficiently fast that every point in the film is at the same location in the phase diagram at the time that glassiness locks in the structure. The film exposed to ether or isopropanol as a non-solvent shows a dense, non-porous skin that spans about 20-50% of the thickness of the film. This skin occurs on the side of the film that first comes in contact with the non-solvent. The remaining portion of the film has a relatively uniform pore structure. This indicates that the polymer is highly insoluble in the non-solvent, and the surface of the film forms a skin instead of a porous structure. The fact that the remaining thickness is porous indicates that the skin sets up a diffusion barrier that allows a small amount of non-solvent to diffuse in and gives some time for phase coarsening to occur. In the case of acetone or acetonitrile as a non-solvent, large pore sizes are observed along with the usual small pores. This indicates that in these systems, a certain amount of phase coarsening of the phase separated polymer domains occurs before these regions turn glassy. It is likely that a small amount of non-solvent remains in the phase separated "walls" of the pore, and effectively plasticize them. These plasticized walls can then coalesce further until a high enough polymer concentration exists to turn the walls glassy. In the case of supercritical CO₂ as a non-solvent, cracks are observed in the film. This indicates the process is very effective in removing solvent, and therefore the film cannot

be plasticized at all. A residual amount of solvent still remains in the porous film. It is not enough to plasticize the polymer, and subsequent drying creates stresses in the film that cause cracks.

The overall implication of the non-solvent results is that the porous film morphology and pore size can be manipulated into a desired structure by varying the polymer concentration, the type of solvent, and the type of non-solvent.

The most uniform films were formed using DMB as a solvent and toluene as a non-solvent. We decided to study this system extensively. Figure 2 shows the effect on microporous film thickness of spincoating three different concentrations of polyimide at different spin rates, followed by exposure to toluene. As would be expected, higher concentrations led to thicker films. As concentration of polyimide in DMB increases, the viscosity of the solution increases. This viscosity determines the thickness that can be obtained by the "wet" polymer film during a spin coating process, which determines the thickness of the final microporous film. Another expected result is that higher spin rates result in thinner microporous films. This is determined by the ratio of inertial to viscous forces. At higher spin rates, inertial forces become more dominant due to higher centrifugal acceleration. This allows more material to be "thrown off" during the spinning process, thus leading to less solution on the substrate, resulting in thinner films.

Figure 3 shows the results of pore size vs. spin rate for the 20% and 25% solutions. For the 15% solution of Ultem in DMB, a bimodal pore size distribution was observed, much like what was seen with the acetone and acetonitrile non-solvent systems. In the figure it is seen that higher spin speeds result in smaller pore sizes. At first, this was thought to be caused by evaporation of the solvent at the higher spin rates, which would concentrate the polymer and possibly lead to smaller pore sizes. Nuclear Magnetic Resonance (NMR) samples were taken from the wet polymer films immediately after spinning at various speeds. The NMR results indicated that the polymer concentration remained roughly the same regardless of the spin speed, and were essentially the same as the concentration before spinning. This indicates that kinetic effects are causing the differences in pore size vs. spin rate. A uniform pore structure suggests that the non-solvent is diffusing in quickly, causing the phase separation. Larger pore sizes suggest that the DMB solvent is having a harder time diffusing out, and thus more time is allowed for phase coarsening to occur. As previously stated, the higher spin speeds created thinner films. These thinner films would less likely be affected by the DMB solvent diffusion rate, and thus less time is allowed for phase coarsening to occur, resulting in smaller pore sizes. The higher concentrations result in thicker films, and again the diffusion through thicker films is slower, allowing for phase coarsening and larger pore size formation to occur.

Finally, the percent porosity was determined for various polymer concentrations at various spin speeds, as shown in figure 4. Again, an unexpected result is that for spin speeds less than 4000 rpm, there was no correlation of percent porosity vs. concentration. All the samples exhibited a porosity between 65 and 72%. At a spin speed of 4000 it

became evident that higher concentrations resulted in lower porosities of the microporous film, which is the expected result.

To date, one dielectric measurement has been performed on a microporous Ultem film. A 20% solution of Ultem in DMB was spincoated onto a silicon wafer that had a gold electrode deposited onto it. After spincoating, the silicon wafer containing the wet solvent/polymer film was submersed in a toluene bath, and the usual microporous structure resulted. After drying overnight, another gold electrode was deposited on top of the film. The microporous film had a porosity of 68%. The value for the dielectric constant was determined to be 1.88, and for dielectric loss was 0.002 (at 1 kHz). The dielectric constant of solid Ultem polyimide is 3.15 at the stated frequency. This result clearly indicates that the presence of the microporous structure significantly reduces the dielectric constant of the film. As a rough approximation, a dielectric constant can be estimated assuming a linear relationship between a system with 100% air and one with 100% polymer. On this basis, a microporous Ultem film with 68% porosity should have a dielectric constant of 1.69. More accurate models would predict an even lower value. The fact that our measured dielectric constant is higher suggests two possibilities. One is that there may still be residual solvent in the film, which could contribute to raising the dielectric constant. NMR verified the presence of residual solvent in the "dry" microporous film. The other possibility is that there is a significant amount of water adsorbed into the microporous structure thus increasing the dielectric constant. The relatively high surface area present in these microporous films would certainly lend strength to that explanation.

Stress measurements were performed that showed the above microporous polyimide film to create a surface stress of 1.9 MPa. Stress measurements on a solid Ultem polyimide film showed it to create a surface stress of 20.6 MPa. Therefore the microporous film reduced the stress by more than a factor of 10. This verifies our initial hopes that the microporous structure would improve some of the mechanical properties of the film.

Conclusion and Summary

In the course of this work it was determined that polyimide films with a variety of morphologies, pore sizes, and thicknesses could be created. The ability to vary the solvent, non-solvent, polymer concentration, and spincoating speed lead to tremendous control over the obtained pore morphology and size. Furthermore, it was implied that both thermodynamic and kinetic effects were factors in determining the final structure of the microporous films. This phenomena has been studied and verified by other researchers.⁶⁻⁹ Finally, the hypothesis that a microporous polyimide film should have a lower dielectric constant and better stress characteristics was verified by our experiments. These experiments are significant in that they suggest that a microporous dielectric film can be fabricated, and could be used as the insulating material in computing chips. The

ultimate result is a smaller and faster computer chip. Future studies will be to determine the complete ternary phase diagram for our system, and also the dependence of the dielectric constant on porosity, and on the presence of residual solvent and water. We also wish to conduct stress measurements to determine if these microporous films effectively reduce the stress at the interface, and we will investigate other possibilities of reducing pore size further in order to make these materials even more useful for the computer chip industry.

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