

Multilayer Electron-Beam Curing of Polymer Dielectric for Electrical Interconnections

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Electron-beam curing of a low dielectric constant polymer was investigated as an alternative process to conventional thermal curing for microelectronic interconnection applications. Electron-beam irradiation was used to cross-link polynorbornene, which was formulated so that no thermal cross-linking occurred. It was found that the electron-beam exposure made the polymer solvent resistant, and improved surface planarity in a multilayer structure. Further, it was also shown that electron-beam curing resulted in films with properties similar to those of thermally treated films. The degree of cross-linking was estimated.
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Manuscript received January 15, 2000. Available electronically March 7, 2000.

Thin film, organic-based, polymer dielectrics are potential candidates for use as interlevel dielectrics in integrated circuit and electronic packaging applications.¹ In order to be used in electrical interconnections, these polymers must possess suitable chemical, electrical, and mechanical properties. Another critical attribute required of these polymers is the ability to sequentially build up alternating layers of polymer and metal wiring. Several polymer systems, which satisfy many of these requirements, are currently available. In some cases, the polymer dielectric is prepolymerized with a specific molecular weight distribution, for optimum properties. The polymer is dissolved in a solvent along with several additives and then solvent cast (typically spin coated) to obtain a thin film of the polymer. Polymer curing at elevated temperature is necessary to carry out chemical reactions, which give the polymer film specific desirable properties. One of the important properties is solvent resistancy, which is necessary for fabrication of multilayer structures. Interaction between the cured polymer film and the solvent from the freshly cast second layer can lead to polymer swelling. Swelling of the existing polymer layer can distort already fabricated structures and can also lead to nonplanar surfaces. The planarizing ability of spin-cast polymers makes the processing of subsequent metal/polymer layers easier. Solvent resistance of underlying layers can be achieved through intermolecular reactions (*e.g.*, cross-linking of the polymer chains) or intramolecular reactions (*e.g.*, conversion of polyamic acid to a polyimide). The reactions are carried out during thermal curing and often require the addition of chemical additives to the polymer or polymer solution, which act as reactants or catalysts in the process. The control of the chemical additives and effects of the chemical by-products can be problematic to the polymer properties. In addition, the thermal curing can degrade the properties of the other materials present.

In this study, we have used electron-beam (E-beam) flood exposure of a polymer film to initiate the cross-linking of a polymer. The polymer, polynorbornene, was chosen because no chemical reaction occurred at the temperatures used in this study. Of specific interest is the ability of the E-beam exposure to rapidly stimulate cross-linking so as to impart the polymer film with acceptable properties, such as solvent resistancy. The use of E-beam initiated polymerization may provide a means for using new materials as dielectrics in microelectronics; those materials where thermal cross-linking is not desirable. Polynorbornene, a low dielectric constant, olefinic-based polymer, was used in this study as demonstration material and was provided by BFGoodrich Co. (Brecksville, OH). This polymer has been shown to possess excellent mechanical, electrical, and chemical properties.² It was formulated so that thermal cross-linking would

not occur. The effect of E-beam exposure on multilayer processing and some of the critical chemical, mechanical, and electrical properties in this polymer are reported here. This proof-of-concept study demonstrates that polymer backbones which are not easily thermally cured (*e.g.*, cross-linked) may be considered for interconnection dielectric materials.

The polymer backbone consists of 10 mol % triethoxy silyl norbornene and 90 mol % butyl norbornene units. The chemical structures of the monomer units are shown in Fig. 1. These two monomer units are randomly copolymerized and dissolved in mesitylene to obtain a polymer solution.² The polymer sample used in this study has a polydispersity index (M_w/M_n) of 2.8 and a weight average molecular weight (M_w) of 283,000. E-beam curing was conducted

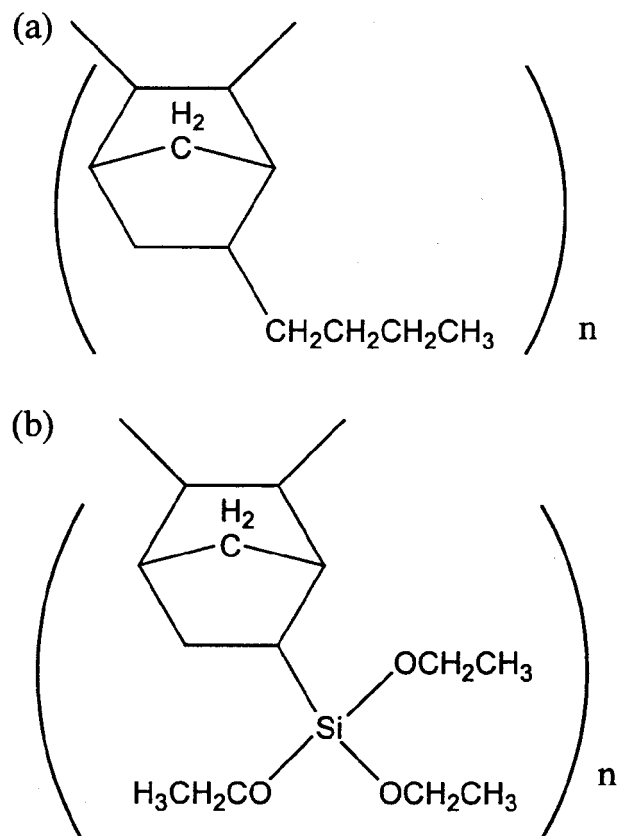


Figure 1. Monomer repeat units in polynorbornene (a) butyl norbornene (b) triethoxy silyl norbornene.

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Table I. Refractive index and thickness before and after mesitylene soak.

Dose ($\mu\text{C}/\text{cm}^2$)	n_{TE} after cure	n_{TM} after cure	Thickness (μm) $\pm \sigma$ after cure	n_{TE} after solvent soak	n_{TM} after solvent soak	Thickness (μm) after solvent soak	Fractional thickness remaining after solvent soak
Thermal cure	1.5069	1.5051	9.63 ± 0.45	NA	NA	NA	0.00
25	1.5103	1.5105	9.23 ± 0.35	1.5112	1.5099	6.12 ± 0.55	0.66
50	1.5114	1.5104	9.49 ± 0.47	1.5117	1.5133	7.30 ± 0.32	0.77
75	1.5138	1.5137	9.02 ± 0.36	1.5166	1.5128	7.98 ± 0.28	0.88
100	1.5133	1.5127	8.67 ± 0.52	1.5150	1.5133	8.00 ± 0.19	0.92
250	1.5171	1.5158	8.60 ± 0.53	1.5166	1.5141	8.11 ± 0.23	0.94
500	1.5218	1.5208	8.65 ± 0.53	1.5215	1.5200	8.73 ± 0.53	NA
1000	1.5257	1.5244	8.55 ± 0.46	1.5251	1.5241	8.50 ± 0.31	NA

n_{TE} is the in-plane index and n_{TM} is the through-plane index.

Charlesby-Pinner Plot for e-beam cured polynorbornene

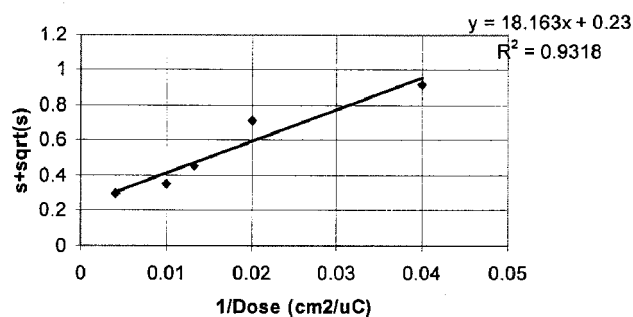


Figure 2. Charlesby-Pinner plot for E-beam cured polynorbornene.

using an Electroncure 30-200-AT system (Honeywell Electron Vision, San Diego, CA). Uniform flood exposure can be achieved across 6 in. diam substrates. Details of the E-beam tool can be found elsewhere.^{3,4} Nitrogen was used as the process gas in the E-beam chamber and the samples were back heated to 200 or 250°C, during E-beam exposure. The polynorbornene films were spin-coated to a final thickness of 10 μm . The accelerating voltage on the cathode was set at 28 keV in order for the electrons to penetrate through the entire film thickness.⁵ The polynorbornene properties were measured as a function of the E-beam dose, as given in microcoulombs per square centimeter, $\mu\text{C}/\text{cm}^2$.

Table I shows the thickness and refractive index (in-plane and through-plane) for E-beam and thermally cured polynorbornene films. These were measured on film-cured metallized silicon wafers. The silicon wafers were sputter coated with Ti (100 Å)/Au (1000 Å)/Ti (100 Å) metal stack, the polymer film spin coated and cured, and the thickness and refractive index were measured using a prism coupler (model 2010 Prism Coupler, Metricon Corp., Pennington, NJ) at a wavelength of 632.8 nm. Each value is an average of five individual measurements. The E-beam cured polynorbornene films were compared to a thermally heated sample (referred to as “Thermal cure” in Table I). The thermal treatment was carried out at 200°C for 30 min in a nitrogen purged oven. This thermal treatment was used to mimic a thermal cure process; however, in this case no cross-linking reaction was built into the polynorbornene. As seen from Table I, E-beam exposure leads to a decrease in the film thickness and increase in index of refraction. The thickness decreased from 9.63 μm (for the thermal treatment sample) to 8.60 μm for the highest dose E-beam cured film (cured at a dose of 250 $\mu\text{C}/\text{cm}^2$). The decrease in thickness may be due to a combination of mass loss

due to E-beam irradiation and increase in density due to cross-linking. The increase index of refraction is an indicator of the density change.

After curing and measurement of thickness and index, each film was soaked in mesitylene for 48 h, vacuum dried for 12 h, and the thickness and index value were then remeasured, as shown in columns 5-7 in Table I. This was done to study the effect of E-beam radiation on the dissolution properties of the film. The last column in Table I shows the fractional thickness remaining after mesitylene soak (ratio of the final thickness after soaking to thickness after curing). The mesitylene soak completely removed the thermally treated film because no cross-linking took place and there was little resistance to solvent dissolution. This is expected, because in this experiment no cross-linking agent was added to the polymer to provide solvent resistance in the cured film. For the E-beam cured films, the thickness of the polymer decreased only slightly during solvent soaking. For the film cured at a dose of 25 $\mu\text{C}/\text{cm}^2$, the thickness of the film decreased from 9.23 to 6.12 μm during the solvent soak and vacuum dry step. As the E-beam dose increased from 25 to 250 $\mu\text{C}/\text{cm}^2$ the thickness of the film remaining on the wafer increased. The highest E-beam dose resulted in 94% of the polymer remaining on the wafer after soaking. This shows that E-beam irradiation levels of >100 $\mu\text{C}/\text{cm}^2$ gave significant solvent resistancy to the films.

The Charlesby-Pinner model^{6,7} was used to estimate the cross-link density in the E-beam cured polynorbornene films. This model can be used to relate the soluble weight fraction (s) of a film, to the E-beam dose (r), as shown in

$$s + \sqrt{s} = (p_0/q_0) + (1/q_0)u_1r \quad [1]$$

where p_0 is the dislinking density [number of dislinks (scission events) per monomer repeat unit, per $\mu\text{C}/\text{cm}^2$ dose], q_0 is the cross-linking density (number of cross-links per monomer repeat unit, per $\mu\text{C}/\text{cm}^2$ dose), u_1 is the number of monomer repeat units per number averaged molecule ($u_1 = M_n/M_0$, M_0 = molecular weight of the monomer repeat unit). In order to estimate the cross-link density, q_0 , it is necessary to experimentally obtain the soluble fraction, s , as a function of E-beam dose, r , using the data from Table I. The fractional thickness remaining on the wafer was taken as the gel fraction (gel fraction, $g = 1-s$) of the polymer. Figure 2 shows the Charlesby-Pinner plot for E-beam cured polynorbornene. The ratio of chain scission to chain cross-linking (obtained from the intercept value in Fig. 2 and Eq. 1) was 0.23. This implies that cross-linking is more favorable than chain scission upon E-beam irradiation of the film. This is also confirmed by the improved solvent resistance in the film upon exposure to E-beam radiation. This value of p_0/q_0 compares well with that observed for linear polyethylene irradiated in vacuum

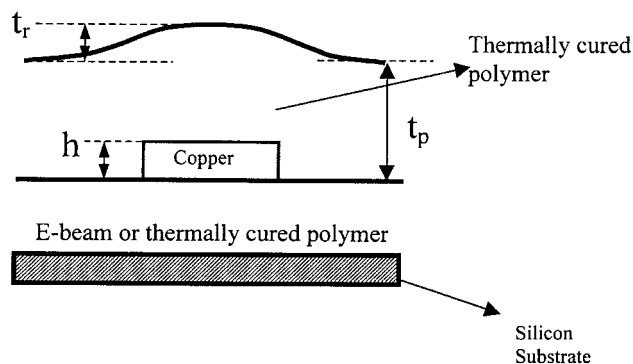


Figure 3. Test structure for evaluation of degree of planarization.

(0.29).⁶ The cross-link density (q_0) can be evaluated from the slope of the line in Fig. 2 (Eq. 1) and the initial molecular weight distribution of the polymer. The average molecular weight of the monomer repeat unit, M_0 , is 157.8 g/mol, as calculated from the chemical structures, Fig. 1. Since the number average molecular weight of the polymer is known ($M_n = 283,000/2.8 = 100,000$), the number of repeat units per number averaged molecule ($u_1 = M_n/M_0$) is 634. Using this value and the slope of the line in the Charlesby-Pinner plot (Fig. 2), the estimated cross-link density is 8.68×10^{-5} cross-links per repeat unit, per $\mu\text{C}/\text{cm}^2$. At an E-beam dose level of $1000 \mu\text{C}/\text{cm}^2$ (at 28 keV), this corresponds to approximately one cross-link per 12 polymer repeat units (monomer units). At a dose of $1000 \mu\text{C}/\text{cm}^2$, there is one incident electron per 794 polymer repeat units. Thus, on average, each incident electron is responsible for initiating 66 polymer cross-linking events as the 28 keV electron dissipates its energy through elastic and inelastic collisions. The polymer dislinking caused by E-beam irradiation is responsible (at least in part) for the loss of mass, as seen in the final thickness.

In order to evaluate the beneficial effects of E-beam induced cross-linking in the film, multilayer test structures were fabricated. The test structures consisted of two layers of polymer. The base layer of the polymer was either thermally cured (thermal treatment) or E-beam cured with one of three different doses: 500, 750, or $1000 \mu\text{C}/\text{cm}^2$. Copper lines were fabricated on top of the first polymer layer (prior to deposition and processing of the second polymer layer) using standard lithography, seed layer sputtering, electroplating, and etchback (semiadditive process). The copper layer had lines of four different widths: 25, 50, 75, and $100 \mu\text{m}$. The spacing between the lines was the same as the linewidth. Details of this process has been published previously.⁸ The test structures were characterized by measuring the height of the copper line, h , using a surface profilometer. The surface profile of the second layer of polymer (on top of the metal lines) was measured using a surface profilometer to obtain the relief height, t_r , of the polymer on top of the metal line. A drawing of the structure is shown in Fig. 3. The degree of planarization (DOP) was calculated using

$$DOP\% = [1 - (t_r/h)] \cdot 100 \quad [2]$$

It was not possible to fabricate a two-polymer layer for the thermal-only first layer because the non-cross-linked polymer dissolved in the solvent from the second layer of polymer. When the base layer was E-beam cured, the multilayer structure was uniform and showed no visible signs of first-layer dissolution or swelling.

The DOP was evaluated on the test structures using Eq. 2. In the test structures fabricated on a thermally cured base layer of the polymer, DOP could not be evaluated as the surface profile of the second layer of the polymer was irregular. The DOP values for the test structures, where the base layer of the polymer was cured at the three dif-

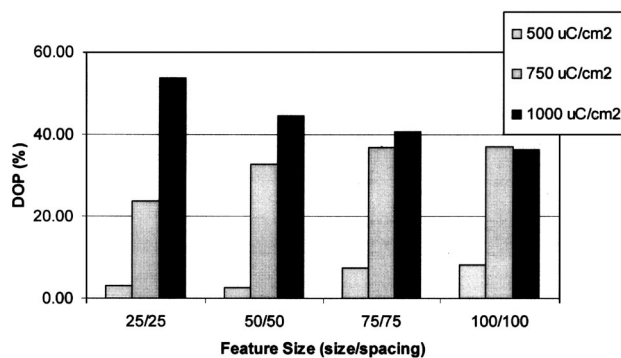


Figure 4. DOP as a function of E-beam dose for E-beam and polynorbornene films.

Table II. Summary of properties for e-beam cured and thermally cured polynorbornene films.

Measured value	Thermal cure	E-beam cure $1000 \mu\text{C}/\text{cm}^2$, 200°C
Residual stress on a $\langle 100 \rangle$ Si wafer (MPa)	21	17.65
Through-plane relative permittivity (10 kHz)	2.43	2.46
Loss tangent (10 kHz)	0.0008	0.0016
Solvent resistance	< 1 min	>10 days
n_{TE}/n_{TM}	1.5069/1.5051	1.5257/1.5244
Cure time	~3 h	~ 15 min

ferent E-beam cure doses, is shown in Fig. 4. The DOP is shown for each of the copper linewidths ($25 \mu\text{m}$ lines/ $25 \mu\text{m}$ spaces, etc). The DOP value was relatively independent of copper linewidth, but highly dependent upon the E-beam dose of the first polymer layer. The highest DOP, 53%, was found for the $25 \mu\text{m}$ features with the polymer cross-linked at $1000 \mu\text{C}/\text{cm}^2$. The improvement in the surface planarity with E-beam dose, can be attributed to increased cross-linking in the underlying polymer layer. As the base layer of the polymer was more tightly cross-linked, the solvent from the second layer of the polymer could no longer swell or dissolve the underlying layer.⁸ Thus, the planarization was dramatically improved.

The properties of the thermally treated and E-beam cured films were measured in order to evaluate the effect of E-beam exposure on other properties in polynorbornene films. Standard methods of testing were used, as described elsewhere.^{2,4} Table II contains a summary of properties measured in a thermally treated film and an E-beam cured film ($1000 \mu\text{C}/\text{cm}^2$). The properties of the two films are comparable, as can be seen in Table II. Fourier transform infrared (FTIR) spectra of the E-beam and thermally cured film were collected. FTIR spectrum of the E-beam cured film was identical to that obtained from a thermally cured film indicating that the bulk chemical structure in the E-beam cured film is similar to that in a thermally cured film, to the resolution and sensitivity of FTIR.

Conclusions

In this study, E-beam curing of polynorbornene films was investigated as an example of E-beam cross-linkable polymer for micro-electronic, interconnection dielectric. E-beam processing avoids the long, thermal treatment necessary for curing many materials, and enables the use of polymers which otherwise would not have sufficient cross-linking, or avoids the use of thermally activated cross-linking chemicals. The ability of the E-beam radiation to create

cross-links in the film and hence improve surface planarity in multilayer structures has been demonstrated. Further, it was also shown that E-beam curing results in films with properties similar to those of thermally cured film. Thus, excellent multilayer processing of certain polymer systems can be achieved via E-beam curing.

Acknowledgments

The authors gratefully acknowledge the MCM-D consortium (Prime no. MDA 927-94-3-0035, contract no. 000104) and the National Science Foundation Engineering Research Center in electronic packaging at Georgia Tech. BFGoodrich's Electronic Materials Division donated the polymer samples. The assistance and discussions with Daniel Kovach, The Boeing Corporation, Bill Livesay, and Peter Ludlow are acknowledged. The contributions of Punit Chiniwalla, Brian Dusch, and Stephanie Register concerning measurements and discussions on cross-link density are recognized.

The Georgia Institute of Technology assisted in meeting the publication costs of this article.

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