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Photoinitiated Cationic Polymerization of 1,3-Diisopropenylbenzene: A Novel Spin-on Polymeric Dielectric

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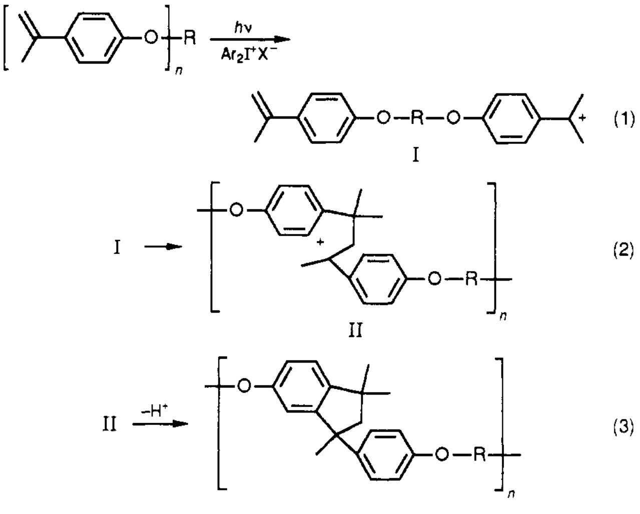
The cationic photopolymerization of 1,3-diisopropenylbenzene proceeds rapidly under UV irradiation catalyzed by diaryliodonium salt photoinitiators to give hard, transparent films. Investigations have shown that the polymerization proceeds mainly by a condensation followed by intramolecular ring-closure process to yield indane structures along the polymer backbone. The inclusion of a small amount of linear poly(indane) as a film-forming agent along with the monomer gives solutions which can be spin coated onto silicon wafers. Measurements made on the photopolymerized coatings give a dielectric constant of 2.6. These coatings also display excellent thermal stability and a low coefficient of thermal expansion.

Introduction

Low dielectric constant insulators are critical components in on-chip interconnect and first-level package-integrated circuit applications. Such materials fulfill several functions.[1] First, they provide electrical and electronic isolation of one discrete chip component from another and permit high component densities by eliminating crosstalk between the discrete components. Second, they function to planarize the topography of a chip during many fabrication steps. Last, they act as barriers to contaminants and corrosive agents and to low energy α-partical penetration. Because of their importance, much past and current research has been directed towards the development of novel low dielectric constant insulators in general and to organic dielectric materials in particular. The focus on organic dielectrics has derived mainly from the ability of these materials to be easily prepared and applied using solution or vapor deposition techniques. Besides having a low dielectric constant, an organic dielectric must also possess good thermal stability, a low coefficient of thermal expansion, adhesion to various substrates which are present on the chip, low water absorption, and a high glass transition temperature.

Few organic dielectric materials have all of the above stated desired properties. For example, polyimides show excellent processibility, thermal and adhesion properties, but have dielectric constants in the range of 3.5–3.6.[2] Furthermore, polyimides undergo considerable water absorption which gives rise to even higher dielectric constants when stored under conditions of high relative humidity. As mentioned above, the density of packing of discrete electronic devices depends largely on the magnitude of the impedance of the components which decreases as the dielectric constant is reduced. For the past 2 decades, the trend has been toward an increase in the density of discrete devices as the size of the devices shrinks. Consequently, polymeric alternatives to polyimides with lower dielectric constants are being sought which also possess comparable processing, mechanical, and thermal characteristics.

In the past few years, research in this laboratory has centered on the area of photoinitiated cationic polymerization. In a recent publication,[3] we reported that the photopolymerization of monomers possessing two isopropenyl aryl groups proceeds mainly by a condensation-ring closure process to form poly(indanes). A general mechanism for this reaction is given in eqs 1–3.



Photopolymerization proceeds by the initial photolysis of the iodonium salt to yield reactive cations, radical cations. These species subsequently react with traces of water and the monomer itself to generate a strong Brøsted acid, HX, which protonates one of the propenyl groups of the monomer. In the steps which follow, the carbenium ion, I, which is formed in the initial reaction attacks a second monomer molecule leading to carbenium ion containing species, II, which undergoes an intramolecular ring closure to generate indane groups along the backbone of the polymer with the simultaneous release of a chain carrying proton.

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* To whom correspondence should be addressed.

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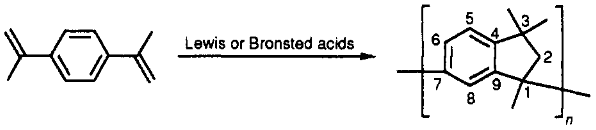
The similar acid-catalyzed condensation-ring closure reaction was previously reported by D'Onofrio[4] and by Nuyken[5-7] et al. for 1,4-diisopropenylbenzene to lead to poly(*p*-indane) (poly[1,7(1,3,3-trimethyl)indanyl]):



(4)

Polyindanes prepared by either catalytic method exhibit excellent thermal characteristics. Poly(*p*-indane) synthesized from 1,4-diisopropenylbenzene has a glass transition temperature of 210 °C and shows no weight loss below 450 °C in air.[6] Because of the excellent characteristics of this polymer and since its hydrocarbon structure suggested that the dielectric constant of this polymer may also be below 3.0, it was decided to consider this as well as other monomers as potential substrates for photopolymerizable low dielectric constant films.

Experimental Section

Materials. 1,3-Diisopropenylbenzene was purchased from the Aldrich Chemical Co. and used without further purification. The preparation of the photoinitiator, (4-octyloxyphenyl)-phenyliodonium hexafluoroantimonate, has been described previously.[8]

Gel permeation chromatographic (GPC) analyses were carried out using a Waters 600E HPLC equipped with a refractive index detector, $CHCl_3$ was used as the eluent at a flow rate of 1.0 mL/min. Polymer molecular weights were determined using polystyrene standards. Gas chromatographic analyses were performed on a Hewlett Packard HP-5840A Gas Chromatograph equipped with 6 ft × $^1/_8$ in. OV-17 phenylsilicone columns and a flame ionization detector. Infrared spectra were recorded on a Perkin-Elmer 1800 Fourier transform infrared spectrophotometer. ^1H NMR spectra were obtained using a Varian XL-200-MHz spectrometer at room temperature in $CDCl_3$ solvent.

Synthesis of Poly[1,6-(1,3,3-trimethylindanyl)] [Poly(*m*-indane)]. 1,3-Diisopropenylbenzene was polymerized in dichloromethane using 1 mol % $TiCl_4$ at −78 °C for 8 h (yield, 13%). Polymerization was also carried out by allowing a solution of the monomer containing 1 mol % of the photoinitiator, (4-octyloxyphenyl)phenyliodonium hexafluoroantimonate, to stand in vial in laboratory light at room temperature for 72 h. The viscous polymerization mixture was diluted with chloroform and then precipitated into methanol. After filtering and drying the resulting solid white polymer, poly(*m*-indane), was obtained in 95% yield having a M_w = 19 170 g/mol, M_w/M_n = 4.04.

Differential Scanning Photocalorimetric Studies. The photoinitiated cationic polymerization of 1,3-diisopropenylbenzene was monitored using a Perkin-Elmer DSC-7 differential scanning calorimeter equipped with a DPC-7 photocalorimeter module fitted with a 100-W high-pressure Hg arc lamp. Polymerizations were conducted isothermally at 30 °C on 2–3-mg samples of the monomer–photoinitiator solutions.

Photopolymerization on Silicon Wafers. A mixture containing 0.15 g of poly(*m*-indane), 1 g of 1,3-diisopropenylbenzene, and 0.02 g (0.5 mol % based on 1,3-diisopropenylbenzene) of (4-octyloxyphenyl)phenyliodonium hexafluoroantimonate was spin coated onto 4-in. aluminum metal vapor deposited silicon wafers. Clear, uniform, smooth coatings were obtained using a Solitec 1110 wafer spinner operating at 2100 rpm for 10 s. The coatings were applied and photopolymerized in a class 100 clean room to avoid contamination.

Photopolymerization was carried out by irradiating the coated wafers for 30 s at a distance of approximately 6 in. from a General Electric H-3T7 200-W medium-pressure Hg arc lamp. After irradiation, the coatings were completely dry and could be further handled for dielectric measurement. After photopolymerization, polymer was insoluble in all solvents.

The thickness of the poly(*m*-indane) coating at various spots on the wafer was measured by first scratching through the coating and then measuring the step height using a Tencor Instruments, Alpha-Step 200. The thickness of the coating was also measured using a Rudolph Research Autoel II ellipsometer and a Nanometrics Nano Spec/AFT. There was good agreement between all three measurements. The average thickness was 2.2 μm.

Dielectric Constant Measurements. The aluminized silicon wafers spin coated with the photopolymerized poly(*m*-indane) were covered with a contact mask having numerous circular holes 0.237 998, 0.515 62, and 1.008 cm in diameter. The wafers were placed in a Airco Temescal CV-8 vacuum chamber and aluminum metal vapor deposited by electron-beam evaporation at 10^{-6} Torr. In this manner, circular capacitors with three different diameters were fabricated.

Capacitance measurements were carried out with the aid of a Hewlett-Packard, 4280 A 1-MHz C meter/C–V plotter. Contact was made to the back side of the wafer and via a surface probe to one of the aluminum contacts. Then, the capacitance was measured using a 1-MHz ac signal. The capacitance of 50 individual capacitors were measured and the results averaged. From this capacitance data, the dielectric constants were calculated and averaged.

The dielectric constants were calculated using the equation

$$\epsilon = dC/A\epsilon_0$$

in which ϵ is the dielectric constant, d is the thickness, C is the capacitance, A is the area and ϵ_0 is the permittivity in a vacuum.

Thermogravimetric Analysis. Thermogravimetric analysis data were obtained using a Perkin-Elmer TGA-7 thermogravimetric analyzer. The analyses were carried out on 4–6-mg samples of the cured polymer film which contained 0.5 mol % of (4-octyloxyphenyl)phenyliodonium hexafluoroantimonate as the photoinitiator. Samples were heated to 600 °C in a nitrogen atmosphere at a rate of 10 °C/min.

Coefficient of Thermal Expansion Measurements. A Perkin-Elmer TMA 7 was employed to measure the coefficient of thermal expansion.

Results and Discussion

In these studies, it was decided to investigate the use of cationic photopolymerizations for the deposition of low dielectric constant coatings. Photopolymerization appeared to have many advantages for applying dielectric materials in the process of integrated circuit fabrication. First, a liquid photopolymerizable monomer could be conveniently spun onto silicon wafers at various stages of integrated circuit fabrication and used to planarize the surface over any existing topography. Second, since cationic photopolymerizations are typically very rapid, coatings can be produced quickly by irradiating the wafer in-line for a few seconds using UV light. Since solvents are not required in the photopolymerization, such a process is essentially pollution-free. Last, if desired, the photosensitive monomer could be patterned by an imagewise exposure using a mask.

While it has been shown that poly(*p*-indane) can be prepared by the cationic polymerization of 1,4-diisopropenylbenzene and that the resulting polymer has many potentially desirable properties as a low dielectric constant material, it has several drawbacks which make its use impractical. For example, only low molecular weight

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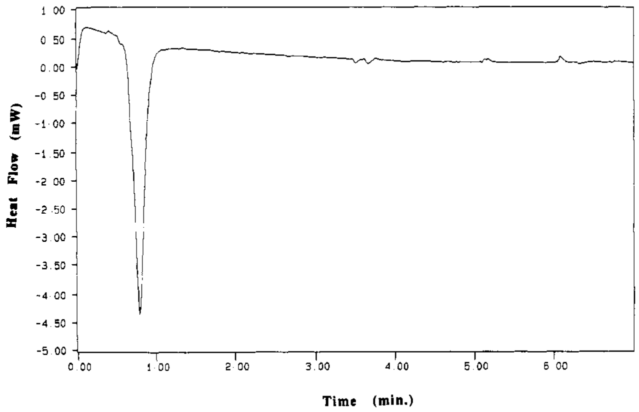
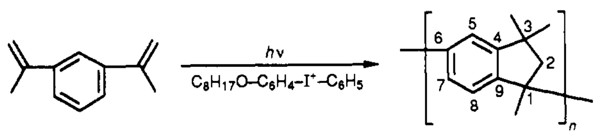


Figure 1. Differential scanning photocalorimetry curve of the photopolymerization of 1,3-diisopropenylbenzene in the presence of 0.5 mol % (4-octyloxyphenyl)phenyliodonium hexafluoroantimonate. Shutter opened at 0.5 min.

polymers have been thus far obtained which is likely due to the poor solubility of the polymer in the monomer during polymerization. Further, 1,4-diisopropenylbenzene is a solid and cannot easily be directly spun onto a silicon wafer or photopolymerized without the use of a solvent.

In contrast, the isomeric 1,3-diisopropenylbenzene is a free-flowing, colorless, mobile liquid with a high boiling point (231 °C). A preliminary study of the cationic photopolymerization of this monomer using 0.5 mol % of (4-octyloxyphenyl)phenyliodonium hexafluoroantimonate as the photoinitiator is shown in the differential scanning photocalorimetry curve of Figure 1. Immediately on opening the shutter, photopolymerization proceeds rapidly and exothermically. As indicated by the sharpness of the curve, the monomer is very reactive and polymerization is essentially complete after approximately 30 s of irradiation. When films of the same solution were drawn onto glass plates and irradiated using a 200-W medium-pressure mercury arc lamp, dry, tack-free films were obtained within 20 s of irradiation. On the basis of these as well as on earlier results,[3-7] are overall photopolymerization can be depicted as shown in eq 5 to give poly(*m*-indane) (poly[1,6(1,3,3-trimethyl)indanyl]).



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These results suggested that this system might be directly useful as a spin-on low dielectric constant coating. However, when the same monomer–photoinitiator solutions were spun onto either bare silicon wafers or aluminum-coated wafers, very poor coatings resulted. It was determined that the problem was due to the very low viscosity of the solutions and their lack of the required viscoelastic properties necessary to give good spreading and film-forming characteristics.

In an effort to circumvent these problems, it was decided to incorporate a small amount of a film-forming polymer into the spin coating solution. In addition to good film forming characteristics, the polymer must itself have good thermal and dielectric properties. In addition, the polymer must not possess functional groups which interfere with the cationic photopolymerization of the monomer. Several candidate polymers were contemplated and prepared. However, the best material for this purpose was found to be linear, low molecular weight poly(*m*-indane) (M_W = 19 170 g/mol) prepared by the slow cationic photopolymerization of 1,3-diisopropenylbenzene. A solution of the monomer containing 13% by weight of this poly(*m*-indane) and 0.5 mol % of the diaryliodonium salt photoinitiator (based on 1,3-diisopropenylbenzene) was found to have good spin-coating characteristics. To determine the best irradiation conditions for the photopolymerization, a film of the above solution was applied to a NaCl plate and the sample irradiated using a 200-W medium-pressure mercury arc lamp. Infrared spectra were recorded at various irradiation times to monitor the course of the photopolymerization. The results are shown in Figure 2. The decrease in the double bond absorption bands at 3100 and 1600 cm^{-1} are particularly evident. Figure 3 shows the differential scanning photocalorimetry curve of the monomer polymer mixture.

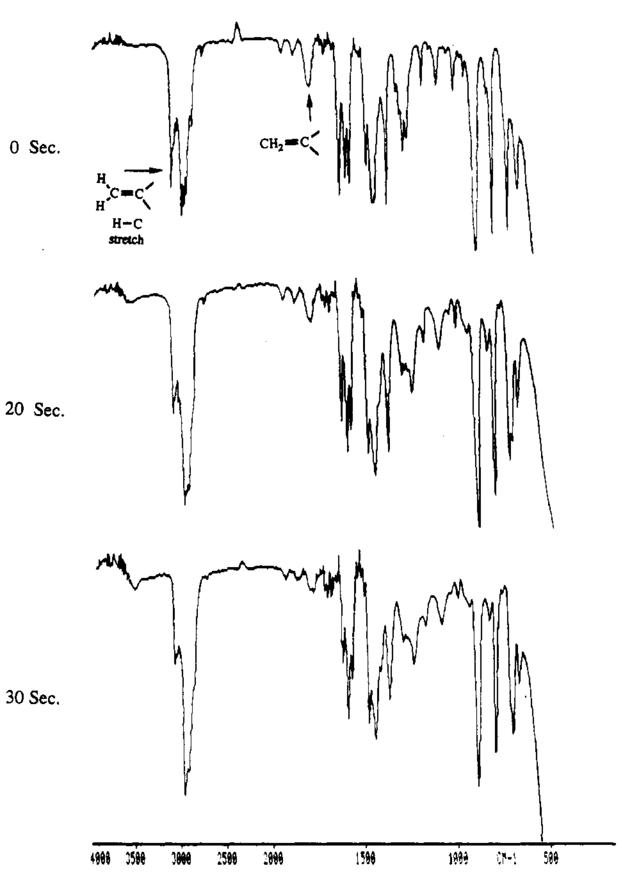

Figure 2. Infrared study of the photopolymerization of 1,3-diisopropenylbenzene containing 13% poly(*m*-indane) in the presence of 0.5 mol % (4-octyloxyphenyl)phenyliodonium hexafluoroantimonate.

The above photopolymerizable solution was then spin coated onto vapor deposited aluminum-coated silicon wafers and photopolymerization of the monomer–polymer mixture was initiated by the irradiation of the wafers for 30 s using a 200-W medium pressure mercury arc lamp. The thickness of the photopolymerized coating was measured and found to be 2.2 μm. Thereafter, an array of circular aluminum pads of three different diameters were evaporated onto the polymerized coating and then the capacitance measured at various points over the surface of the wafer. The dielectric constant was then calculated and found to be 2.6 from an average of 50 measurements.

These dielectric constant results were very encouraging. It is especially notable, that although the photoinitiator is an ionic material and might be expected to have a

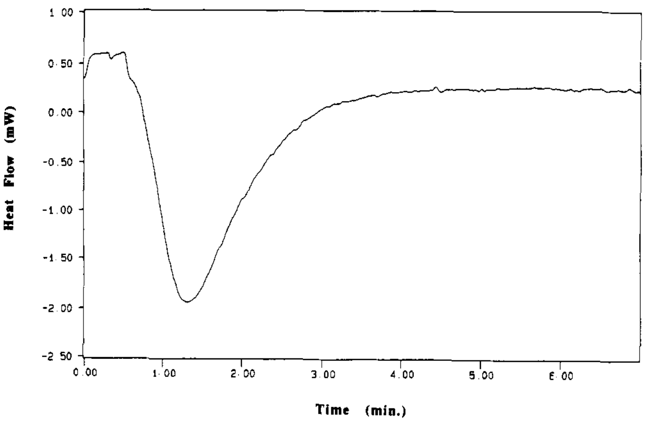

Figure 3. Differential scanning photocalorimetric study of the photopolymerization of 1,3-diisopropenylbenzene containing 13% poly(m-indane) in the presence of 0.5 mol % (4-octyloxyphenyl)-phenyliodonium hexafluoroantimonate.

considerable elevating effect on the dielectric constant, apparently, little effect is observed. The magnitude of the dielectric constant of poly(*m*-indane) appears to be what might be predicted from other related materials. For example, polystyrene is an analogous aromatic hydrocarbon polymer with a dielectric constant of 2.55 that is used for many dielectric applications.[9] However, polystyrene is limited by both its low glass transition temperature (T_g = 90 °C) and its tendency to thermally decompose at approximately 300 °C. In contrast, no glass transition temperature for the poly(*m*-indane) produced by cationic photopolymerization was recorded below 350 °C. This suggests that due to the rigidity of the chain backbone and to some crosslinking, that the T_g may lie near to the thermal decomposition temperature. The thermal stability of the photopolymerized poly(*m*-indane) was measured using thermogravimetric analysis under nitrogen at a heating rate of 40 °C/min. Figure 4 gives the TGA curve of the dielectric coating which shows that this material undergoes a weight loss of 5% at approximately 450 °C. This stability would appear adequate for most downstream wafer-processing requirements, including wave soldering.

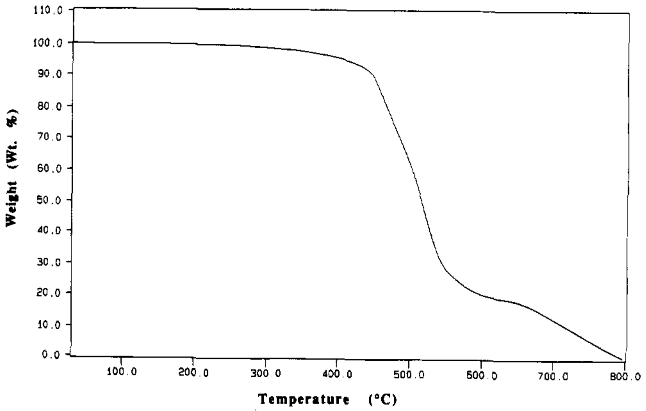

Figure 4. Thermogravimetric analysis of photopolymerized poly(*m*-indane) at 40 °C/min in nitrogen.

Another property of critical importance for a given dielectric material in integrated circuit fabrication is its coefficient of thermal expansion. Using a Perkin-Elmer TMA-7, the coefficient of thermal expansion (CTE) was measured in the range 25–250 °C and found to be 20 × 10^{-6} ppm/°C. For comparison, the CTE for polyimides is generally in the range 50 × 10^{-6} ppm/°C.[1] The low CTE measured for the spin-on photopolymerized poly(*m*-indane) is a highly desirable characteristic and comes closer than many other organic polymers to matching the CTE values for other integrated circuit materials such as silicon, molybdenum, aluminum and copper (CTE (3–30) × 10^{-6} ppm/°C).

Conclusions

Low dielectric constant coatings can be prepared for use in integrated circuits by directly photopolymerizing 1,3-diisopropenylbenzene in the presence of a diaryliodonium salt photoinitiator and a small amount of a film forming polymer. The poly(*m*-indane) which is produced has a dielectric constant of 2.6 as well as a low coefficient of thermal expansion and a high thermal stability.

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