New High Strength Low-*k* Spin-On Thin Films for IC Application

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ABSTRACT: To achieve successful integration of low dielectric constant materials with copper lines, it is critical to develop a low dielectric constant material with good mechanical properties. A new high strength spin-on low dielectric constant polymer, poly((*m*-diethynylbenzene)-*co*-(triethynylbenzene)), has been developed. Its oligomer showed good solubility, high thermal stability, low moisture pickup, and strong UV absorption. The cured polymer thin film displayed a dielectric constant of 2.7 at 1 MHz and a dielectric breakdown strength larger than 230 V/μm. It had an extraordinarily high Young's modulus of 16.8 GPa and a hardness of 3.5 GPa. Compared to polyimide, it had stronger adhesion to Si and tantalum. By use of polystyrene as a porogen, a dielectric constant as low as 1.9 was obtained while still maintaining an acceptable high Young's modulus of 7.7 GPa and hardness of 2.0 GPa.

Introduction

Continuous miniaturization in integrated circuits (IC) requires using a low dielectric constant (low-*k*) material to lower the RC delay, power dissipation, and cross-talk.[1] As early as 1999, the International Technology Roadmap for Semiconductors (ITRS) called for low-*k* materials with a dielectric constant of 2.7. In April 2000, IBM announced its intent to use SiLK (Dow Chemical Co.), a spin-on aromatic thermosetting polyphenylene.[2] Then, Texas Instruments stated its intension to use Black Diamond (Applied Materials), a chemical vapor deposition (CVD) dielectric. A battle between spin-on dielectrics (SODs) and CVD low-*k* materials commenced.[3] In general, SODs have better extendibility to lower *k* values but have lower mechanical properties which might cause lower production yield and reliability issues. SiLK, which has a Young's modulus of 2.2 GPa and a hardness of 0.5 GPa, is the most widely used SOD since it was successfully integrated with copper lines in IBM 130 nm devices in 2000. However, some industry sources said IBM had been struggling with the yield problems and reliability issues of SiLK.[4] In late 2003, SiLK took a public relation hit when IBM revealed that it would switch back to CVD materials in its 90 nm chips.[5] On the contrary, CVD materials are more compatible with existing integration processes, but their extendibility to next-generation low-*k* materials, especially *k* value below 2.2, is questionable. In February 2004, Applied Materials held a press conference to trumpet the use of its Black Diamond low-*k* film by several firms in 90 and 130 nm semiconductors.[5] Although SODs might have lost ground to CVD materials in the current technology generation, the battle is far from over. In fact, with increasing porosity in CVD materials to achieve a lower *k* value, many properties, such as mechanical properties and thermal conductivity, will decrease. Obviously, to win this battle, SODs researchers need to develop a high strength low-*k* SOD, which is able to integrate with copper lines having high production volume and reliability.

Poly(*m*-diethynylbenzene), discovered initially in the early 1960s by Hay and co-workers,[6] was chosen in this study as a starting material because of its high thermal stability, low moisture pickup, low dielectric constant, and possible lithographic sensitivity.[7,8] Moreover, it can form a highly condensed aromatic structure after curing, which would provide high Young's modulus and hardness.[9] However, its low solubility and crystalline nature make it difficult to form a stable thin film.[10] Several studies have been carried out to solve this problem. Stille and Whitesides incorporated a solubilizing aliphatic side group.[11−13] Miller et al. synthesized several copolymers containing aromatic diacetylenes.[7] Although the solubility was improved, the dielectric constant of the materials was increased.

In this study, oligomer *m*-diethynylbenzene (DEB) and co-oligomer (*m*-diethynylbenzene)-*co*-(triethynylbenzene), DEB-*co*-TEB, were synthesized. The following sections will discuss synthesis and physical properties of oligomer DEB and DEB-*co*-TEB. Then focus will be on dielectric properties and mechanical properties of a cured poly(DEB-*co*-TEB) thin film.

Experimental Section

Materials. *m*-Diethynylbenzene monomer was purchased from Lancaster Synthesis Inc. (Pelham, NH). 1,3,5-Triethynylbenzene was obtained from Alfa Aesar (Ward Hill, MA). Polyimide (PI-2808) was purchased from HD MicroSystems (Parlin, NJ). Other chemicals were purchased from Aldrich (Milwaukee, WI). All chemicals were used as received except for abietic acid which was purified by heating to 260 °C under vacuum twice and then only collecting the portion at 260 °C.

Synthesis of Oligomer *m*-Diethynylbenzene (DEB). Oligomer *m*-diethynylbenzene (DEB) was synthesized following the previously reported method.[14]

Synthesis of Oligomer (*m*-Diethynylbenzene)-*co*-(Triethynylbenzene) (DEB-*co*-TEB). 14.0 g (0.11 mol) of *m*-diethynylbenzene (DEB), 5.56 g (0.037 mol) of 1,3,5-triethynylbenzene (TEB), extra phenylacetylene, and 8.3 mL of an acetone/pyridine mixture (50:50 volume ratio) in 200 mL of acetone was added into a vigorously stirred catalyst solution containing 13.3 g (0.13 mol) of Cu_2Cl_2, 8.3 mL of the acetone/pyridine mixture (50:50 volume ratio), and 700 mL of acetone. The catalyst solution was preoxidized by bubbling O_2 through for about 10 min before addition. The O_2 flow was continued throughout the rest of the reaction. 16.6 mL of the acetone/pyridine mixture was added over a period of 10 min. The reaction was conducted in the dark by covering the reaction flask

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with aluminum foil for 12 h. The reaction mixture was poured into HCl/methanol solution. The precipitate was collected, washed with methanol, and dissolved in chloroform. The solution was washed with HCl and deionized water, dried with $MgSO_4$, filtered, and precipitated from methanol. The solid was vacuum-dried at 50−55 °C overnight to afford 10.2 g of a light-orange powder. An FT-IR spectrum of DEB-*co*-TEB showed an acetylene υ(C≡C) stretch at 2220 cm^{-1} and no ethynyl C−H stretch at 3300 cm^{-1}, indicating all ethynyl groups reacted to form diacetylene groups. ^1H NMR of DEB-*co*-TEB (THF-d_8, 400 MHz Bruker) displayed δ 7.3−7.5 (m, 46H, Ar−H), 7.5−7.6 (m, 40H, Ar−H), and 7.7−7.8 (m, 15H, Ar−H).

Fabrication of Dense Thin Film. A 25−35 wt % DEB-*co*-TEB oligomer in cyclohexanone solution was spin-coated onto a silicon wafer to form a thin film. The thin film was soft-baked at 110 °C for 1 min in air, cured at 200 °C for 30 min, and heated at 450 °C for 30 min in a vacuum annealer.

Fabrication of Porous Film. Low molecular weight polystyrene (M_w = 780) was used as a porogen and dissolved in THF to provide a 25 wt % solution A. Another type of solution A was prepared by replacing polystyrene with abietic acid and selecting acetone as a solvent. Solution B was prepared by dissolving DEB-*co*-TEB into cyclohexanone at a 25 wt % concentration. Solutions A and B were mixed at various weight ratio to form a new solution by stirring at room temperature for 2 h and then allowing to sit for over 12 h. The resulting solutions were spin-coated onto Si wafer dices or metal (gold)-deposited Si wafer dices and soft-baked on a hot plate at 110 °C for 1 min to remove most of the solvent. The wafer was then cured in a vacuum annealer under controlled heating. A typical curing recipe for forming a porous film was as follows: ramp at 5 °C/min to 200 °C, hold at 200 °C for 30 min, ramp at 5 °C/min to 250 °C and hold for 30 min, ramp at 5 °C/min to 350 °C and hold for 30 min, and then ramp at 5 °C/min to 450 °C and hold for 30 min to burn out the porogen. The film was then cooled to room temperature at 5 °C/min. When abetic acid was used, air was bled into the annealer through a needle value while holding at 450 °C.

Characterization. ^1H NMR measurements were carried out using a Varian Unity 400 NB NMR system with THF-d_8 as a solvent. GPC was performed using a 3x Plgel 10 μm mixed B LS column, THF as a solvent, and polystyrene as a standard. FT-IR spectra, 64 scans at 4 cm^{-1} resolution, were obtained using a Nexus 670 FT-IR E. S. P. (Thermo Nicolet) and analyzed by Origin software. FT-IR samples were prepared by forming pellets with KBr powder. Differential scanning calorimetry (DSC) was run at a heating rate of 10 °C/min in a nitrogen atmosphere from 30 to 400 °C. The thermal stability was investigated by thermogravimetric analysis (TGA) using a TA Instruments Hi-Res TGA 2950 and involved heating the samples from room temperature to 600 °C with a ramp rate of 10 °C/min under nitrogen or air. The thermal conductivity was measured by a picosecond time-domain thermoreflectance using a 3ω method. UV spectra were obtained in a Shimadzu 2100 UV−vis spectrophotometer. A Hitachi S-4700 scanning electron microscope (SEM) was used to observe the pore structure of a thin film at an accelerating voltage of 10 kV. The sample was sputtered with a 10 Å thick platinum/gold coating before loading into the SEM chamber. Transmission electron microscopy (TEM) was carried out on a Philips CM-12 microscope operated at 120 kV. The dielectric breakdown strength measurements were performed using a B&L probe station and a HP 4339B high-resistance meter. DC voltages were applied to the sample stepwise from −100 to 100 V. The dielectric constant and dielectric loss were measured using a probe station and a HP 4284A Precision LCR meter. The frequency was 1 MHz, and both the capacitance and dielectric loss were recorded. The size of the electrode pad and the thickness of the thin film were measured using a surface profilometer (Tencor Alpha Step 200). Digital Instruments (DI) MultiMode AFM was used to measure the average surface roughness of a thin film on a Si wafer. A commercially available TriboScope 1-D transducer and Nanoscope IIIa controller from Hysitron Inc. (Minneapolis, MN) were attached to the DI MultiMode AFM to measure the Young's modulus and the hardness of the polymer thin film. A cornered cube diamond tip was used. These measurements were quantified using a published method, where the tip shape and system compliance were calibrated.[15] The tests were conducted under 150 μN maximum loading force and a loading/unloading rate of 10 μN/s. The experiments were carried out at room temperature under an air atmosphere. When the TriboScope 2-D transducer was used instead of the 1-D transducer, the instrument was also used to carry out a nanoscratch test. A 60° included angle conical diamond probe tip with a 1 μm spherical radius was used, and the correct transducer constants were obtained by performing an air indent.

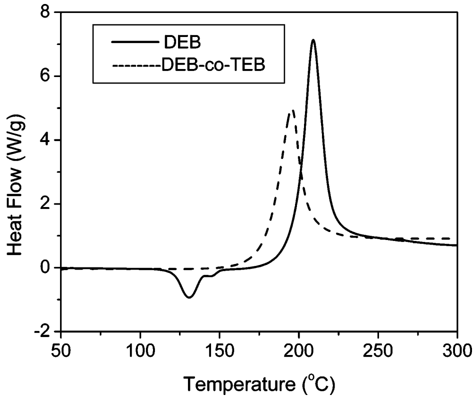

Figure 1. DSC curves of DEB and DEB-*co*-TEB oligomers.

Table 1. Solubility of DEB and DEB-*co*-TEB in Some Common Spin-Coating Solvents (in wt %)

solvent	DEB	DEB-*co*-TEB
THF	~10	>20
cyclohexanone	~5	~40
N-methylpyrrolidone (NMP)	<5	>30
phenylacetylene	<5	>30

Results and Discussion

Properties of Oligomer *m*-Diethynylbenzene. According to the result of gel permission chromatography (GPC), the average number molecular weight (M_n) of this oligomer was 710 and the average degree of polymerization was 4. The polymerization dispersity was 1.2. The solubility of this oligomer in common spin-coating solvents was low (see Table 1). The DSC curve of DEB in Figure 1 displayed a melting peak at around 130 °C.

Physical Properties of Co-oligomer DEB-*co*-TEB. To improve the solubility of DEB, an oligomer (*m*-diethynyl benzene)-*co*-(triethylnylbenzene), DEB-*co*-TEB, was copolymerized by an oxidative coupling reaction. Compared to DEB, oligomer DEB-*co*-TEB showed greatly improved solubility in common spin-coating solvents (see Table 1). No melting peak was observed for DEB-*co*-TEB sample in its DSC curve (see Figure 1), which indicated that oligomer DEB-*co*-TEB had an amorphous structure (further confirmed by X-ray diffraction analysis). This might explain its improved solubility. The curing reaction of DEB-*co*-TEB occurred at around 195 °C, which was about 10 °C lower than that of DEB and with a smaller exotherm. TGA showed that DEB-*co*-TEB is stable up to 480 °C in N_2 with 5.6% weight loss at 600 °C. The cured thin film only had around 1.5% age of weight loss after 8 h at 425 °C. The UV testing indicated that the DEB-*co*-TEB oligomer had strong UV absorption at 226 and 342 nm. The normal-to-plane thermal conductivity of the cured poly(DEB-*co*-TEB) thin film is 0.31 W cm^{-1} K^{-1}.

Dielectric Properties of Poly(DEB-*co*-TEB) Thin Film. The dielectric constant and the dissipation factor of cured poly(DEB-*co*-TEB) were 2.7 and 0.03 (both at 1 MHz), respectively. The

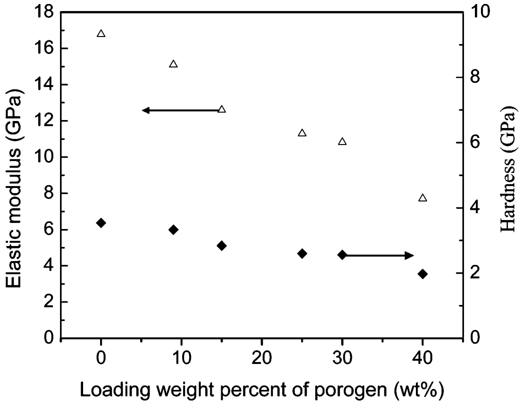

Figure 2. Effects of porogen (PS) loading on the elastic modulus and the hardness of cured poly(DEB-*co*-TEB) thin film with a thickness of 700 nm.

Table 2. Effects of Porogen Loading on Dielectric Properties of Poly(DEB-*co*-TEB) Film

porogen (wt %)	dielectric constant	dielectric loss	breakdown strength (V/μm)
0	2.70	0.03	>235
9	2.59	0.02	>232
15	2.43	0.04	>222
20	2.39	0.03	>211
25	2.26	0.02	>196
30	2.13	0.02	>192
35	2.03	0.03	>217
40	1.85	0.02	>220

breakdown strength was larger than 230 V/μm. The dielectric constant of cured poly(DEB-*co*-TEB) thin film showed little or no change when exposed to the ambient environment (relative humidity was from 40% to 60%) for several weeks, indicating its low moisture pickup. The effects of porogen (polystyrene, PS) loading on the dielectric constant, dissipation factor, and breakdown strength are shown in Table 2. The *k* value of the poly(DEB-*co*-TEB) can be lowered to 1.9 by adding 40 wt % PS. The breakdown strength and dissipation factor did not display significant change.

Mechanical Properties of Poly(DEB-*co*-TEB) Thin Film. Sufficient elastic modulus and hardness are essential for low-*k* materials to withstand stresses occurring during processing. The nanoindentation test was performed on the cured thin film with a thickness of around 700 nm and average roughness of 0.5 nm. The Young's modulus and hardness of the cured polymer thin film were around 16.8 and 3.5 GPa, respectively. As a control, a 700 nm thick polyimide (PI) thin film on Si wafer was also measured using the same method. Its Young's modulus and hardness were around 3.8 and 0.4 GPa, respectively. The dependence of the elastic modulus and hardness of the cured poly(DEB-*co*-TEB) thin film on the loading amount of porogen (PS) is shown in Figure 2. The elastic modulus and hardness gradually decreased with the increased loading amount of the porogen. By adding 40 wt % PS, the porous polymer film displayed an average elastic modulus of 7.7 GPa and hardness of 2.0 GPa, which are about 46% and 57% of that of the dense polymer film, respectively.

The adhesion between various layers in multilevel metallization is also crucial for the reliability of ICs.[16] Since the dielectric layer directly contacts the diffusion barrier layer for Cu (such as tantalum (Ta) layer) and Si substrate in the interconnect structure, it requires that low-*k* materials have good adhesion to these two layers. In nanoscratch tests, the critical force causing the delamination of a thin film from a substrate can be used to compare the adhesion of the thin film. Table 3 indicates that poly(DEB-*co*-TEB) when compared to polyimide had stronger adhesion to the Si substrate and Ta layer.

Table 3. Critical Forces (μN) in Nanoscratch Tests[a]

substrates	poly(DEB-*co*-TEB)	polyimide
Si	600	50
Ta	1000	250

[a] Thickness of the polymer films was 700 nm.

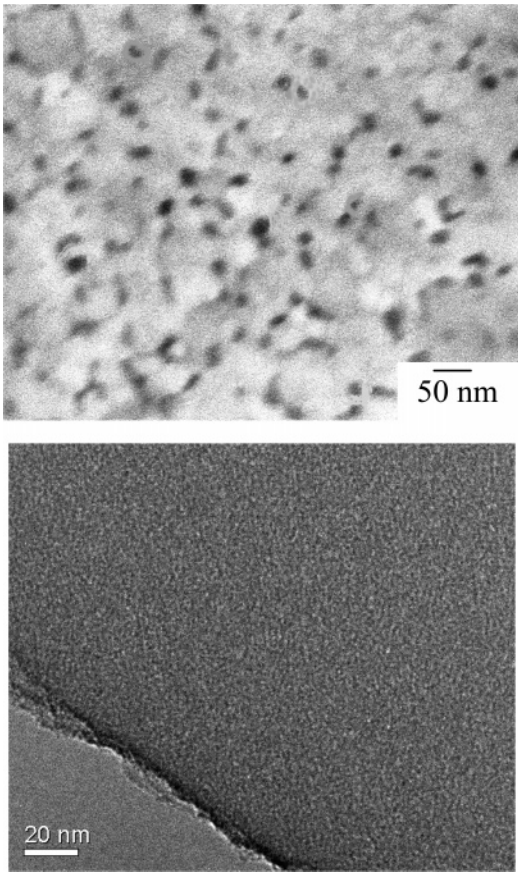

Figure 3. SEM image (top) of cross section of the porous poly(DEB-*co*-TEB) film, using PS as a porogen (loading content was 35 wt %). TEM image (bottom) of cross section of the porous poly(DEB-*co*-TEB) film, using abietic acid as a porogen (loading content was 35 wt %).

Pore Structure of Poly(DEB-*co*-TEB) Thin Film. The SEM image in Figure 3 shows the pore structure of the porous poly(DEB-*co*-TEB) thin film with 35 wt % PS loading. Most of the pores were closed with the pore size in the range 10−30 nm. Using purified abietic acid as a porogen, we successfully decreased the pore size to less than 5 nm (see TEM image in Figure 3).

Conclusions

A new aromatic thermosetting copolymer, poly(DEB-*co*-TEB), was developed as a good insulating material which has high elastic modulus and good adhesion for use in the multilayer interconnect structures of microelectronic devices. Its amorphous structure makes it easy to form submicron thin film by spin-coating technique. The copolymer displayed good thermal stability, low moisture pickup, relatively high thermal conductivity, and patterning potential due to its strong UV absorption. The Young's modulus and hardness of the cured thin film were 16.8 GPa and 3.5 GPa, respectively, significantly higher than those of the commercial polymeric low dielectric constant thin films. The poly(DEB-*co*-TEB) thin film had a dielectric constant of 2.7 at 1 MHz and breakdown strength larger than 230 V/μm and a weight loss of only 1.5% at 425 °C after 8 h. When polystyrene was used as a porogen, its k value can be lowered to 1.9 by forming a porous structure with 40 wt % porogen loading. This porous thin film had a Young's modulus of 7.7 GPa and a hardness of 2.0 GPa. SEM and TEM images showed that the pores were mostly closed and the pore size can be decreased to less than 5 nm by using abietic acid as a porogen. We believe that this material is a very promising low-k material for current and future interconnect structures.

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References and Notes

(1) Peercy, P. S. *Nature (London)* **2000**, *406*, 1023−1026.
(2) Martin, S. J.; Godschals, J. P.; Mills, M. E.; Shaffer II, E. O.; Townsend, P. H. *Adv. Mater.* **2000**, *12*, 1769−1778.
(3) Peters, L. *Semicond. Int.* **2000** (June), 108−124.
(4) Murphy, T. *Electron. News* **2002 (**April 1**)**.
(5) Mccoy, M. *Chem. Eng. News* **2004**, *82* (June), 18−24.
(6) Hay, A. S. *J. Org. Chem.* **1960**, *25*, 1275.
(7) Miller, T. M.; Kwock, E. W.; Baird Jr., T.; Hale, A. *Chem. Mater.* **1994**, *6*, 1569−1574.
(8) Kwock, E. W.; Baird Jr., T.; Miller, T. M. *Macromolecules* **1993**, *26*, 2935−2940.
(9) Neenan, T. X.; Callstrom, M. R.; Scarmoutzos, L. M.; Stewart, K. R.; Whitesides, G. M.; Howes, V. R. *Macromolecules* **1988**, *21*, 3525−3528.
(10) Dawson, D. J.; Fleming, W. W.; Lyerla, J. R.; Economy, J. *ACS Symp. Ser*. **1985**, *282*, 63−79.
(11) Callstrom, M. R.; Neenan, T. X.; Whitesides, G. M. *Macromolecules* **1988**, *21*, 3528−3530.
(12) Rutherford, D. R.; Stille, J. K. *Macromolecules* **1988**, *21*, 3530−3532.
(13) Rutherford, D. R.; Stille, J. K.; Elliott, C. M.; Reichert, V. R. *Macromolecules* **1992**, *25*, 2294−2306.
(14) Economy, J.; Jung, H.; Gogeva, T. *Carbon* **1992**, *30*, 81−85.
(15) Oliver, W. C.; Pharr, G. M. *J. Mater. Res.* **1992**, *7*, 1564−1585.
(16) Lanckmans, F.; Brongersma, S. H.; Varga, I.; Bender, H.; Beyne, E.; Maex, K. *Mater. Res. Soc. Symp. Proc.* **2000**, *612*, D1.4.1.

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