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Design of hydrophobic polydimethylsiloxane and polybenzoxazine hybrids for interlayer low k dielectrics

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Spectral data of

4, 4´-diaminodiphenylmethane benzoxazine (DDM-Bz)

FT-IR (KBr, cm^{-1}): 3065 (=CH), 2940-2850 (aliphatic CH, CH_2 stretching), 1612 (C=C stretching), 1465 (aliphatic CH bending), 1242 (C-O-C), 930 (N-C-O) and 750 (ortho-substituted benzene ring).

^{1}H NMR (400MHz, CDCl3) δ (ppm): 7.14-6.62 (m, Ar), 6.12-6.09 (m, =CH), 5.41 (s, O-$\underline{CH_2}$-N), 5.17-5.12 (m, =CH_2), 4.65 (s, Ar-$\underline{CH_2}$-N), 3.85 (s, Ar-$\underline{CH_2}$-Ar) and 3.52-3.42 (m, Ar-$\underline{CH_2}$-CH).

2, 2´-diaminoethane benzoxazine (DAE-Bz)

FT-IR (KBr, cm^{-1}): 3064 (=CH), 2943-2847 (aliphatic CH, CH_2 stretching), 1641 (C=C stretching), 1462 (aliphatic CH bending), 1220 (C-O-C), 930 (N-C-O) and 750 (ortho-substituted benzene ring).

^{1}H NMR (400MHz, CDCl3) δ (ppm): 7.05-6.85 (m, Ar), 6.07-6.00 (m, =CH), 5.11-5.07 (m, =CH_2), 4.97 (s, O-$\underline{CH_2}$-N), 4.08 (s, Ar-$\underline{CH_2}$-N), 3.39-3.37 (d, Ar-$\underline{CH_2}$-CH) and 3.01 (s, N-$\underline{CH_2}$-$\underline{CH_2}$-N).

4, 4´-diaminobutane benzoxazine (DAB-Bz)

FT-IR (KBr, cm^{-1}): 3062 (=CH), 2942-2850 (aliphatic CH, CH_2 stretching), 1640 (C=C stretching), 1462 (aliphatic CH bending), 1222 (C-O-C), 930 (N-C-O) and 750 (ortho-substituted benzene ring).

^{1}H NMR (400MHz, CDCl3) δ (ppm): 7.06-6.81 (m, Ar), 6.05-6.01 (m, =CH), 5.10-5.05 (m, $=CH_2$), 4.90 (s, O-$\underline{CH_2}$-N), 4.00 (s, Ar-$\underline{CH_2}$-N), 3.37-3.36 (d, Ar-$\underline{CH_2}$-CH), 2.79-2.77 (m, N-$\underline{CH_2}$-CH_2) and 1.65-1.63 (m, N-CH_2-$\underline{CH_2}$).

6, 6´-diaminohexane benzoxazine (DAH-Bz)

FT-IR (KBr, cm^{-1}): 3060 (=CH), 2945-2852 (aliphatic CH, CH_2 stretching), 1642 (C=C stretching), 1462 (aliphatic CH bending), 1220 (C-O-C), 930 (N-C-O) and 750 (ortho-substituted benzene ring).

^{1}H NMR (400MHz, CDCl3) δ (ppm): 7.02-6.83 (m, Ar), 6.06-5.99 (m, =CH), 5.10-5.05 (m, $=CH_2$), 4.90 (s, O-$\underline{CH_2}$-N), 4.00 (s, Ar-$\underline{CH_2}$-N), 3.37-3.36 (d, Ar-$\underline{CH_2}$-CH), 2.76-2.73 (m, N-$\underline{CH_2}$-CH_2), 1.61-1.59 (m, N-CH_2-$\underline{CH_2}$-CH_2) and 1.41-1.39 (m, N-CH_2-CH_2-$\underline{CH_2}$).

Polydimethylsiloxane-4, 4´-diaminodiphenylmethane benzoxazine pre-polymer (PDMS-DDM-Bz)

FT-IR (KBr, cm^{-1}): 2962-2860 (aliphatic CH, CH_2 stretching), 1612 (C=C stretching), 1465 (aliphatic CH bending), 1256 (CH_3-Si-CH_3), 1087, 1028 (Si-O-Si asymmetric stretching), 930 (N-C-O) and 800 (CH_2-Si-O).

^{1}H NMR (400MHz, CDCl3) δ (ppm): 7.01-6.79 (m, Ar), 5.30 (s, O-$\underline{CH_2}$-N), 4.55 (s, Ar-$\underline{CH_2}$-N), 3.77 (s, Ar-$\underline{CH_2}$-Ar), 2.58-2.55 (m, Ar-$\underline{CH_2}$), 1.61-1.59 (m, Ar-CH_2-$\underline{CH_2}$), 0.62-0.57 (m, $\underline{CH_2}$-Si), 0.1-0.09 (m, $\underline{CH_3}$-Si-$\underline{CH_3}$).

Polydimethylsiloxane-2, 2´-diaminoethane benzoxazine pre-polymer (PDMS-DAE-Bz)

FT-IR (KBr, cm^{-1}): 2960-2855 (aliphatic CH, CH_2 stretching), 1640 (C=C stretching), 1462 (aliphatic CH bending), 1257 (CH_3-Si-CH_3), 1087, 1028 (Si-O-Si asymmetric stretching), 933 (N-C-O) and 800 (CH_2-Si-O).

^{1}H NMR (400MHz, CDCl3) δ (ppm): 7.02-6.85 (m, Ar), 4.95 (s, O-$\underline{CH_2}$-N), 4.07 (s, Ar-$\underline{CH_2}$-N), 2.99 (s, N-$\underline{CH_2}$-$\underline{CH_2}$-N), 2.57-2.54 (m, Ar-$\underline{CH_2}$), 1.62-1.58 (m, Ar-CH_2-$\underline{CH_2}$), 0.62-0.57 (m, $\underline{CH_2}$-Si), 0.12-0.10 (m, $\underline{CH_3}$-Si-$\underline{CH_3}$).

Polydimethylsiloxane-4, 4´-diaminobutane benzoxazine pre-polymer (PDMS-DAB-Bz)

FT-IR (KBr, cm^{-1}): 2962-2860 (aliphatic CH, CH_2 stretching), 1642 (C=C stretching), 1462 (aliphatic CH bending), 1256 (CH_3-Si-CH_3), 1087, 1028 (Si-O-Si asymmetric stretching), 933 (N-C-O) and 800 (CH_2-Si-O).

^{1}H NMR (400MHz, CDCl3) δ (ppm): 7.00-6.81 (m, Ar), 4.88 (s, O-$\underline{CH_2}$-N), 3.99 (s, Ar-$\underline{CH_2}$-N), 2.74-2.71 (m, Ar-$\underline{CH_2}$), 2.61-2.59 (m, N-$\underline{CH_2}$), 1.62-1.58 (m, Ar-CH_2-$\underline{CH_2}$), 1.38-1.36 (m, N-CH_2-$\underline{CH_2}$), 0.65-0.61 (m, $\underline{CH_2}$-Si), 0.10-0.08 (m, $\underline{CH_3}$-Si-$\underline{CH_3}$).

Polydimethylsiloxane-6, 6´-diaminohexane benzoxazine pre-polymer (PDMS-DAH-Bz)

FT-IR (KBr, cm^{-1}): 2962-2860 (aliphatic CH, CH_2 stretching), 1640 (C=C stretching), 1462 (aliphatic CH bending), 1256 (CH_3-Si-CH_3), 1087, 1028 (Si-O-Si asymmetric stretching), 933 (N-C-O) and 800 (CH_2-Si-O).

^{1}H NMR (400MHz, CDCl3) δ (ppm): 7.00-6.79 (m, Ar), 4.86 (s, O-$\underline{CH_2}$-N), 3.99 (s, Ar-$\underline{CH_2}$-N), 2.76-2.57, 1.91-1.90, 1.63-1.61, 0.65-0.61 (m, Aliphatic CH_2), 0.10-0.09 (m, $\underline{CH_3}$-Si-$\underline{CH_3}$).

Polybenzoxazine (PBz)

FT-IR (KBr, cm^{-1}): 3460 (free OH), 3000-2838 (aliphatic CH, CH_2 stretching), 1614 (C=C stretching), 1515 (aliphatic CH bending), 1264 (C-O stretching), 1408 (tetra substituted benzene ring).

Polydimethylsiloxane - polybenzoxazine polymer (PDMS-PBz)

FT-IR (KBr, cm^{-1}): 3500 (free OH), 2965-2834 (aliphatic CH, CH_2 stretching), 1644 (C=C stretching), 1465 (aliphatic CH bending), 1408 (tetra substituted benzene ring), 1264 (CH_3-Si-CH_3), 1094, 1026 (Si-O-Si asymmetric stretching).

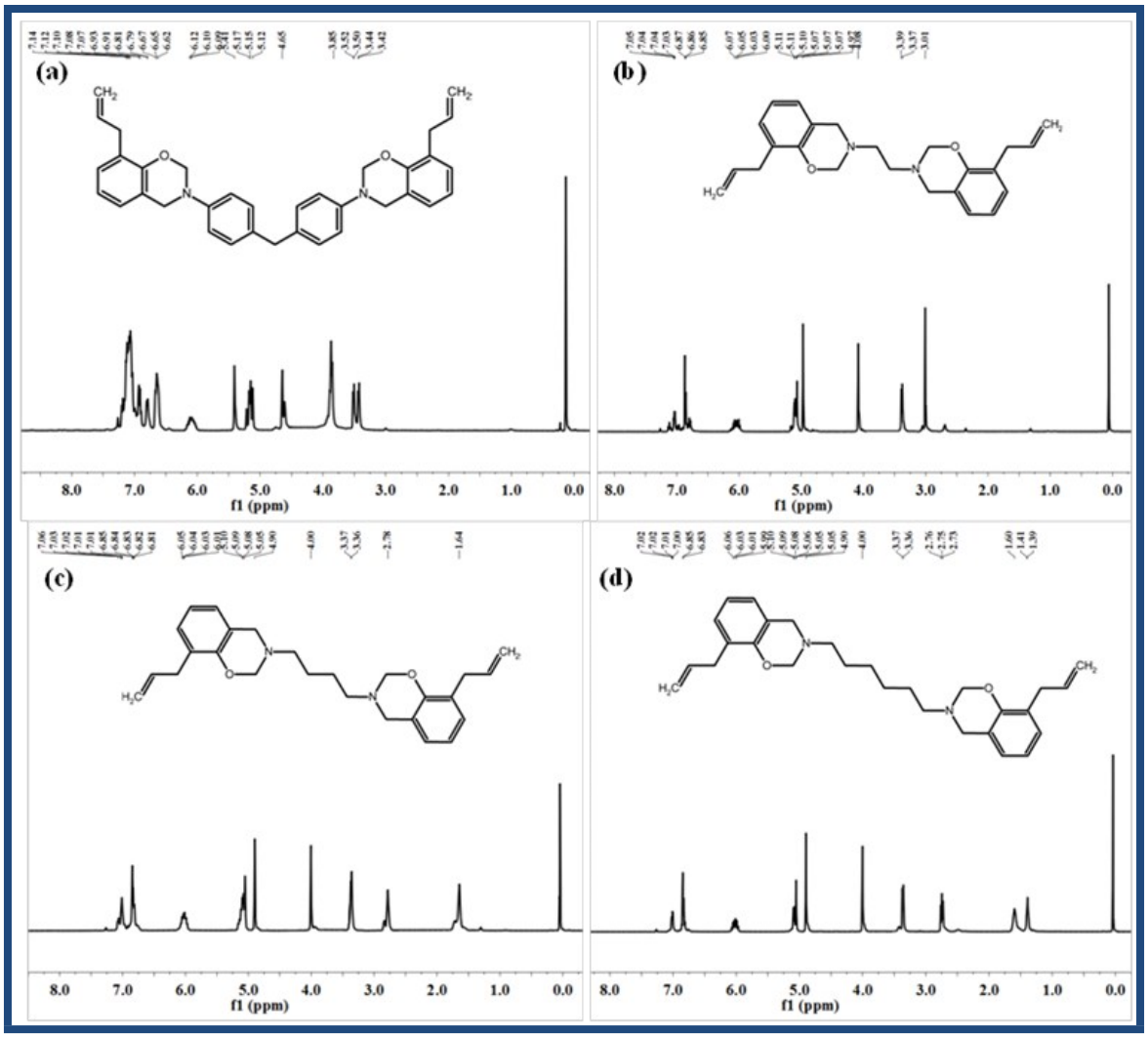

Fig. S1 ^{1}H NMR spectra of DDM-Bz (a), DAE-Bz (b), DAB-Bz (c), and DAH-Bz monomer.

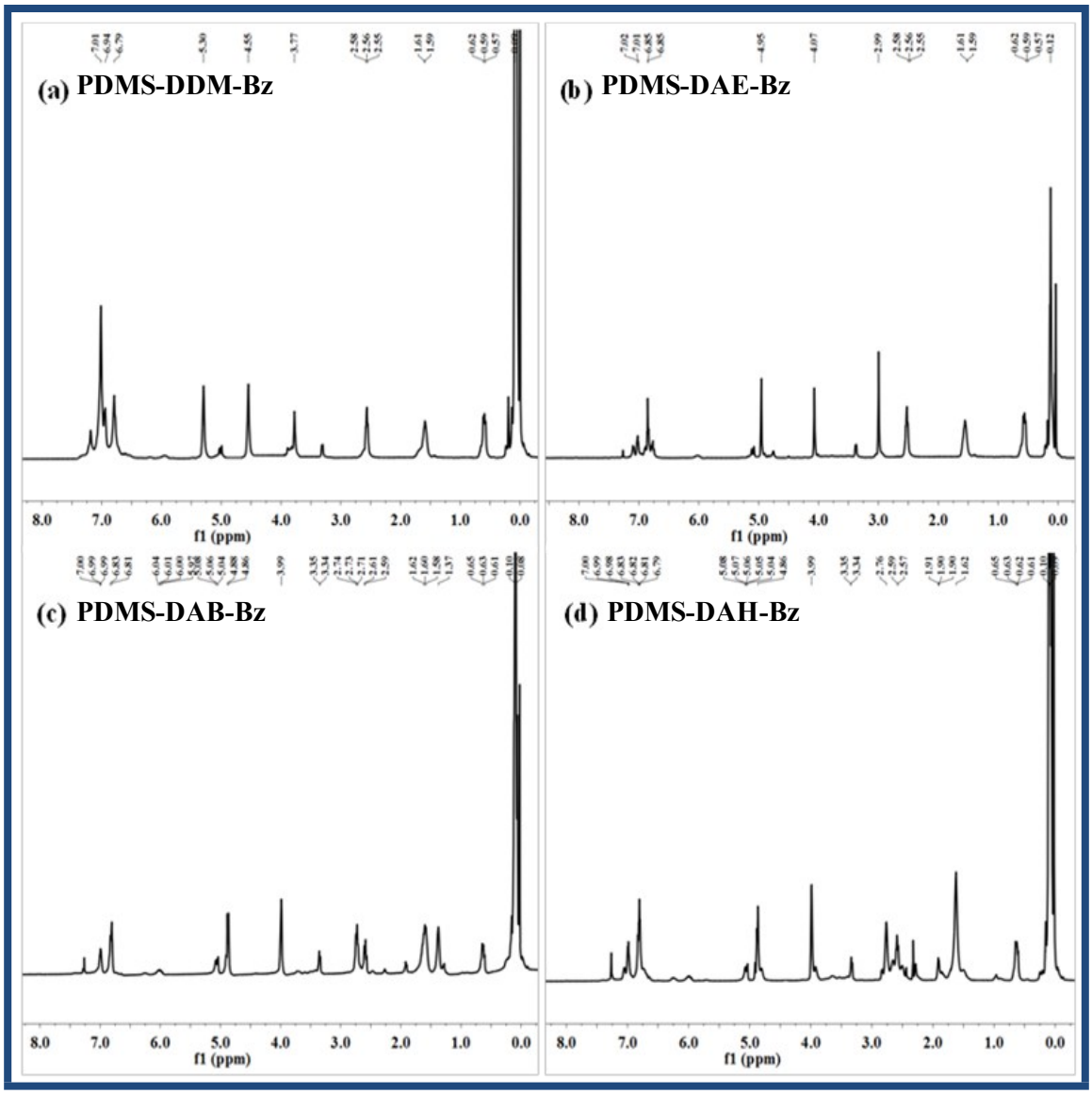

Fig. S2 ^{1}H NMR spectra of PDMS-DDM-Bz (a), PDMS-DAE-Bz (b), PDMS-DAB-Bz (c), and PDMS-DAH-Bz (d) pre-polymer.

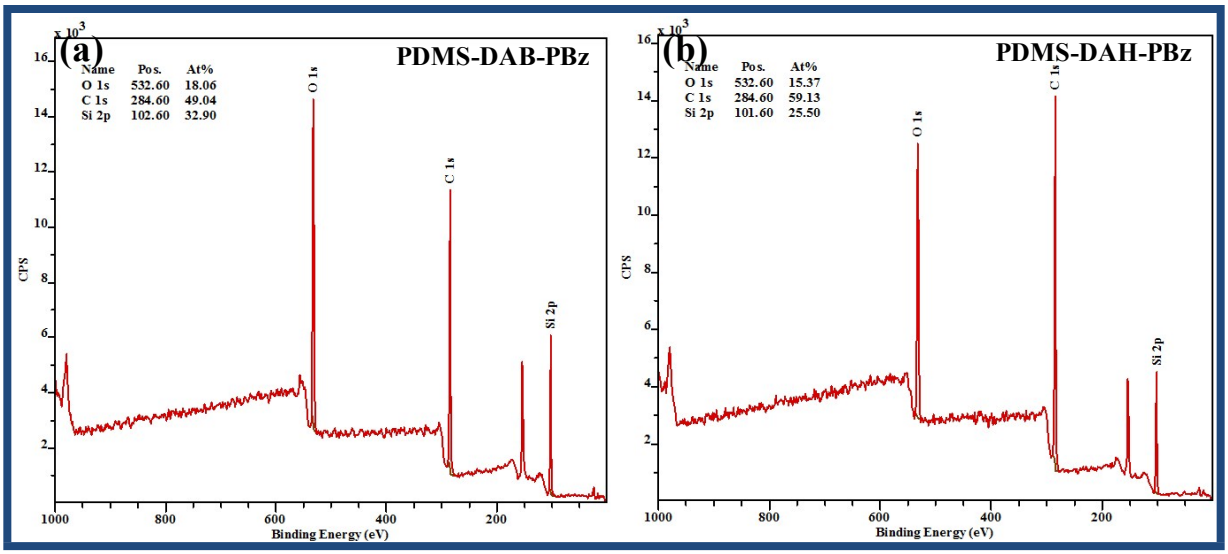

Fig. S3 XPS spectra of PDMS-DAB-PBz (a) and PDMS-DAH-PBz (b).

Table S4 The weight of PDMS and benzoxazine monomer.

Sample name	PDMS (1 equivalent, g)	benzoxazine monomer (1.08 equivalent, g)
PDMS-DDM	4.1	5.06
PDMS-DAE	4.1	3.70
PDMS-DAB	4.1	3.98
PDMS-DAH	4.1	4.25

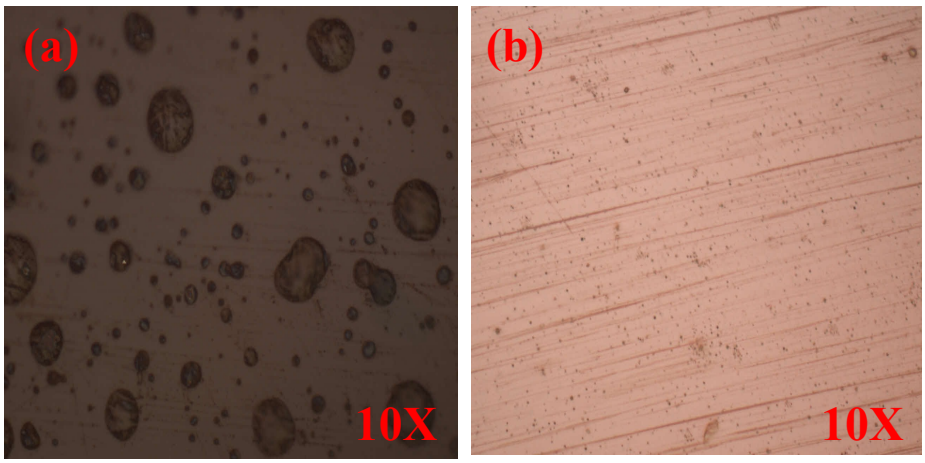

Fig. S5 Optical images of PDMS-PBz (a) and PDMS-DAH-PBz (b)