Materials Science and Engineering B 186 (2014) 7–14

Contents lists available at ScienceDirect

Materials Science and Engineering B

journal homepage: www.elsevier.com/locate/mseb

Borazine-containing arylacetylene resin as low dielectric constant materials

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ARTICLE INFO

Article history:
Received 26 October 2013
Received in revised form 27 February 2014
Accepted 4 March 2014
Available online 15 March 2014

Keywords:
Borazine
Low dielectric constant
Arylacetylene

ABSTRACT

A novel borazine-containing arylacetylene resin (PBZA) has been synthesized in high yield through condensation reaction between B,B′,B″-trichloroborazine and arylacetylene Grignard reagent, which are potential candidates as low dielectric constant material for microelectronic packaging and also radio and microwave frequency substrate. The PBZA is a brown viscous liquid and soluble in a variety of common solvents. PBZA could be cured by polymerization of alkynyl groups to form organic–inorganic hybrid structure containing borazine ring and aromatic rings with exothermic polymerization temperature in the 190–250 °C range and the structure exhibits great dependence on the substituent on borazine in PBZA. The cured PBZA exhibits high thermal stability with char yield up to nearly 80% at 1000 °C and great chemical stability. Especially, the cured PBZA shows low dielectric constant (ca. 2.7) and extremely low dielectric loss (<0.002). The cured PBZA under higer annealing temperatures exhibits lower dielectric constant and dielectric loss.

1. Introduction

With the rapid development of telecommunication industry, the demands for low dielectric constant materials have been increased dramatically for microelectronic packaging and also as radio and microwave frequency substrates [1–5]. The speed of the signal through the dielectric medium is in inverse proportion to the square root of the dielectric constant, and signal strength in the substrate material weakens with increasing frequency because the dielectric loss tangent becomes larger [2]. Thus, the dielectric constant and loss tangent of the base substrate play an important role for the design of high frequency circuits [2,5]. Reducing the dielectric constant of materials has been known crucial to minimizing resistive-capacitive (RC) delay, power consumption, and cross talk noise [5–7]. Besides, the materials need to meet good mechanical properties, thermal and chemical stability to ensure high device reliability in end use. Varieties of materials have been investigated for these purposes, but most of the offerings are not ideal for the application. For example, the Si-based materials lack sufficient toughness at the targeted low-dielectric-constant, F-containing materials are incompatible with common metal liners, some of the organic polymer systems are mechanically unsuitable at process temperatures because of low glass transition temperature and thermal stability, and some other polymer systems do not meet the process temperature requirements [8]. In order to obtain the satisfactory materials, molecular modeling was used to predict the dependencies of dielectric property and thermal stability on polymer repeating unit structure. Based on such method, Dow publicly announced what became known as SiLK low dielectric constant (ca. 2.7) material which was prepared from polyarylenes [9]. Polyarylacetylene could form three-dimensional network structures containing a lot of aromatic rings after curing. These structures endow SiLK with low dielectric constant, better mechanical and thermal ability, because aromatic rings are stable and have lower dielectric constant [8]. In addition the crosslinked structure in polymer has an important effect on dielectric constant of polymer. The cross-linking decreases the length of chain segments, restrains their motion, and reduces the dielectric constant. The dielectric constant of polymer is dominated by orientation polarization [10]. Therefore, the cross-linked polymer has a lower dielectric constant even though with strong polar group in polymer structures, such as phenolic resin and polyimide.

Borazine is a very stable molecule and called inorganic benzene because its structure consists of 6 elements with alternating boron and nitrogen groups. G.R. Dennis stated that borazine is less polarizable than benzene and the dielectric constant of a borazine molecule was calculated to be a very low 1.9 from simulation based on the molecular-orbit method [11,12]. Sei Tsunoda

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http://dx.doi.org/10.1016/j.mseb.2014.03.001
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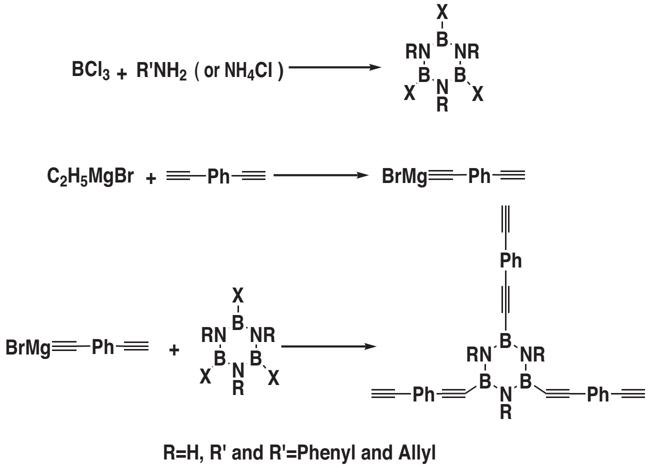

Scheme 1. Schematic illustration of the formation of borazine-containing arylacetylene resin (PBZA) via condensation reaction.

reported that a compound containing borazine ring backbone has small molecular polarizability [13] and low dielectric constant. Yuko Uchimaru invented a new borazine-silicon-based polymer with a low dielectric constant (ca. 2.5) [12,14]. Yong-peng Lei reported poly[(alkylamino)borazine]s for producing BN fibers with low dielectric constant [15,16].

Therefore, it is very interesting to gain a polymer containing borazine rings and cross-linked structures, which would have low dielectric constant and loss, good mechanical performance and high thermal stability. With this purpose in mind, our approach has been focused on borazine-containing arylacetylene resin (PBZA) as low dielectric material precursors, which can form three-dimensional network structure through polymerization of acetylene groups. In this paper, the PBZA is synthesized through the condensation reaction between B,B′,B″-trichloroborazine and arylacetylene Grignard reagent (Scheme 1). The synthesis, curing mechanism, and thermal and dielectric properties of the PBZA are investigated. B,B′,B″-trichloroborazine with hydrogen, allyl and phenyl has been chosen to prepare PBZA with different substituent, such as hydrogen on the borazine (PBZA-H), allyl group on the borazine (PBZA-V) and phenyl group on the borazine (PBZA-P). The substituent would be investigated on how to influence the structure, thermal property and dielectric properties of cured PBZA.

2. Experimental

2.1. Materials

Boron trichloride was purchased from BeiJing Multi Technology Co. Ltd. Diethynylbenzene was supplied by Fine Chemical Institute of East China University of Science and Technology and distilled on a vacuum line before use. Toluene, tetrahydrofuran, ethyl bromide, and magnesium powder were purchased from Sinopharm Chemical Reagent Co. Ltd. Tetrahydrofuran and toluene were refluxed over sodium and freshly distilled in nitrogen before use.

2.2. Instrumentation

NMR analyses were performed on a BRUKER AVANCE 400 (400 MHz) instrument, using teramethylsilane (TMS) as an external standard in $CDCl_3$ solution. Fourier transform infrared (FTIR) spectra were obtained using a Nicolet 550 spectrometer. Differential scanning calorimetric analyses (DSC) were performed on a NETZSCH 200 PC module. Thermogravimetric analyses (TGA) were performed on a TA Instruments SDT Q600 analyzer. All thermal analyses were conducted under nitrogen atmosphere at a heating rate of 10 °C/min. Dielectric constant measurement was carried out using a Concebt 40 broadband dielectric spectrometer (Novocontrol Technologies GmbH & Co., KG, Germany). A test sample of 20 mm in diameter and 1 mm in thickness was placed between the two copper electrodes; thus, a parallel plate capacitor was formed. The dependence of the dielectric constant and dielectric loss on the frequency of the applied field was studied within the frequency range of 0.1 Hz–10 MHz. The pyrolysis/gas chromatography/mass spectrometry (Py/GC/MS) analyses were conducted on a Frontier Lab Single-shot Pyrolyzer PY-2020i (PY Single-shot Pyrolyzer, quartz tube) and a Shimadzu GCMS-QP2010 chromatograph/mass spectrometer (chromatographic column, 30 m × 0.25 mm i.d. × 0.25 μm; carrier gas, helium gas; pressure, 34.0 kPa; total flow, 84.3 mL/min; column flow, 0.80 mL/min). Pyrolysis was carried out at 650 °C (>50 °C/ms) for 10 s. The temperature of column was held at 40 °C for 1 min, and then increased with a heating rate of 10 °C/min, and finally maintained at 650 °C.

2.3. Synthesis of PBZAs

All synthetic reactions described below were carried out in nitrogen atmosphere using Schlenk techniques. The B,B′,B″-trichloroborazine was prepared by allowing BCl_3 to react with NH_4Cl in toluene at 110 °C and purified by sublimation [17]. B,B′,B″-trichloro-N,N′,N″-triphenylborazine was obtained by the reaction of BCl_3 and aniline in the presence of triethylammonium in toluene and purified by recrystallization from toluene. B,B′,B″-trichloro-N,N′,N″-triallylborazine was obtained by the reaction of BCl_3 and allylamine in the presence of triethylammonium in toluene and purified by distillation [18]. The ethynylphenylethynylmagnesium bromide was prepared according to the reported literature [19].

Syntheisis of PBZA-H. The PBZA-H was obtained according to the following procedure. In a 250 mL four-necked flask equipped with condenser, thermometer, mechanical agitation, and funnel, ethynylphenylethynylmagnesium bromide (9.95 g, 0.03 mol) in 100 mL THF was added under a nitrogen atmosphere, then cooling the solution to 0 °C, B,B′,B″-trichloroborazine (1.84 g, 0.01 mol) in 70 mL toluene was dropwise added. After that, the mixture was allowed to heat up to 50 °C and stirring for an additional 4 h. Then the solution was cooled to room temperature. Dioxane was added to the solution until no more precipitation produced and then standing for 6 h. After isolating the white precipitation by filtration, the filtrate was evaporated on a rotary evaporator to remove the solvents, and the product was given as a brown viscous liquid (PBZA-H) in 79% yield. Anal: NMR ($CDCl_3$): δ (^{1}H, ppm) = 7.20–7.80 (m, Ar), 3.11 (s, $-C\equiv CH$), 5.60 (brs, NH).

Syntheisis of PBZA-P. The PBZA-P was prepared through the condensation reaction between the mixture of arylacetylene Grignard reagent (9.95 g, 0.03 mol) and B,B′,B″-trichloro-N,N′,N″-triphenylborazine (4.12 g, 0.01 mol) by following the procedure described above, in 75% yield. Anal: NMR ($CDCl_3$): δ (^{1}H, ppm) = 6.50–7.80 (m, Ar), 3.11 (s, $-C\equiv CH$).

Syntheisis of PBZA-V. The PBZA-V was prepared through the reaction of 9.95 g (0.03 mol) of arylacetylene Grignard reagent and 3.04 g (0.01 mol) of B,B′,B″-trichloro-N,N′,N″-triallylborazine according to the procedure described above, in 80% yield. Anal: NMR ($CDCl_3$): δ (^{1}H, ppm) = 7.20–7.80 (m, Ar), 3.11 (s, $-C\equiv CH$), 5.8–6.2 (m, $-CH=$), 4.9–5.3 (m, $CH_2=$), 4.3–4.5 (d, $-CH_2-$).

2.4. Thermal curing of the PBZAs

The precursor PBZA was thermally cured according to the procedure: 120 °C for 2 h, 150 °C for 4 h, 160 °C for 4 h, 180 °C for 2 h, 210 °C for 2 h, 250 °C for 2 h, and 270 °C for 2 h.