Characterization and dielectric property of polyimide-silica composite films prepared via sol–gel and thermal imidization process

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Organic/inorganic hybrid has been proved as a new type advanced material because it combines the respective advantages of organic component (e.g. flexibility, low dielectric constant and process ability etc.) and inorganic component (e.g. rigidity, strength, durability and thermal stability) [1–2]. In microelectronic and aerospace industries, aromatic polyimides (PIs) have been applied as important materials owing to their special chemical and physical properties including good resistance to organic solvent except acids, good film-forming characteristics and processability via precursor routes, high tensile modulus, low thermal expansion and low dielectric constant. Nowadays, it is difficult for the single polyimide to meet some ultimate requirements such as matching the thermal expansion coefficient between the constituent layers of semiconductor circuit multi-chip modules. Due to the lower thermal expansion and higher mechanical strength of the inorganic material, introducing proper inorganic component into the polyimide matrix is contributing a method to overcome this problem [3]. Concerning the dielectric constant of silica is lower than most of other inorganic materials, silica is adopted as an inorganic component in this work. The polyimide-silica hybrid films are prepared utilizing sol–gel reaction, and their structure, thermal stability and dielectric constant are investigated respectively.

The precursor solutions of poly(amic acid)s (PAA)s with 15% solid concentration in N,N'-dimethyl acetamide (DMAc) are synthesized by the reaction of dianhydride (e.g. 3,3',4,4'-benzophenone tetracarboxylic dianhydride, BTDA; and pyromellitic dianhydride, PMDA) and diamine (e.g. 4,4'-oxydianiline, ODA; 4,4'-diaminno diphenyl ether, MDA, and phenylene diamine PDA) for 18 hr at room temperature. After specific proportion of tetraethoxysilane (TEOS) and 3-Aminopropyl-triethoxysilane (APTEOS) are stirred into PAA solution, the calculated quantity of water diluted in DMAc is added, and the mixture is stirred for additional 4 hr at room temperature. After the precursor hybrid films are obtained by casting above mixture and evaporating solvent, they are heated at 100, 200, 300 °C consecutively in N_2 stream to give the final silica/PI hybrid films. Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FT-IR, BRUKER VECTOR 22) is employed to confirm the chemistry structure of silica/PI hybrids. Thermogravimetric analysis (TGA) are conducted on a Pyris 1DSC. The dielectric constants are measured on YD2810b LCR Bridge meter.

ATR-FTIR spectra of the BTDA-ODA polyimide-silica hybrids and pure polyimide films are shown in Fig. 1. The characteristic absorption of PAA at 1650 cm^{-1} disappears thoroughly, and the characteristic absorptions of imide unit at wave number of 1780, 1714, 1372 and 732 cm^{-1} are found for pure PI and hybrids [4]. It is approved that the addition of TEOS and APTEOS don't yield any negative effects on the imidization of PAA. On the other hand, the broad absorption around 1080 cm^{-1} is the asymmetric stretching of Si–O–Si units. The adsorption intensity of this peak increases with TEOS content. In the FT-IR spectra of SiO_2 reference, the characteristic absorptions at 1000–1100 cm^{-1} and 3400 cm^{-1} are generated from Si–O–Si bonds and –OH/–NH_2 groups respectively [5]. The absorption similarity of Si–O–Si between the hybrids and reference specimen indicates that the silica sources in form of TEOS and APTEOS are efficiently converted to Si–O–Si structures through the preparation of hybrid.

Fig. 2 shows the TGA curves of pure BTDA-ODA polyimide and hybrids containing SiO_2 in 15 wt% and 30 wt%. The decomposition temperature of hybrids is found a little lower than that of pure polyimide. These phenomena may be caused by elimination of water from the Si-OH groups at SiO_2 at higher temperature [6]. It is suggested that silicic acid hasn't been condensed completely in imidization process. With lifting temperature, the formation of Si—O—Si network proceeds continuously. Concerning a slow weight loss also occurred in TGA measurement of reference SiO_2, it could be considered that the decomposition of organo-groups in of APTEOS contribute another source for loss of hybrids below 600 °C. Fig. 3 shows the onset temperature of the composite films with different polyimide matrix. It is found that the decomposing onset temperatures of all samples are over 520 °C. Such thermal stability will not limit the possible applications of these hybrids as dielectric materials.

The dielectric properties of the series of pure polyimide and polyimide/silica hybrid films measured at 10 KHz are shown in Fig. 4. The dielectric constants of the composite films range from 3.4 to 6.0. With increase of silica content, the dielectric constant values increase gradually. This result is expectable for

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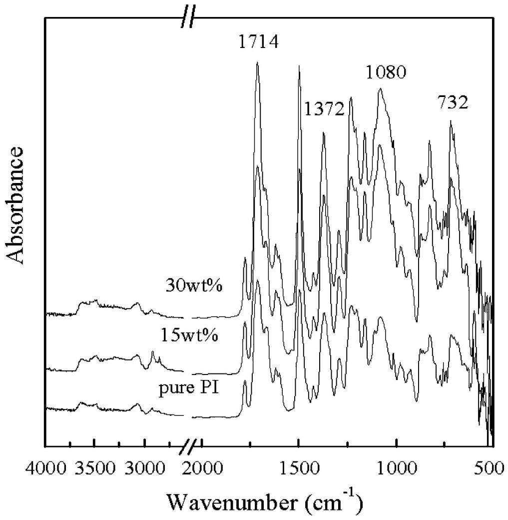

Figure 1 ATR-FTIR spectra of BTDA-ODA polyimide and corresponding polyimide-silica composite films.

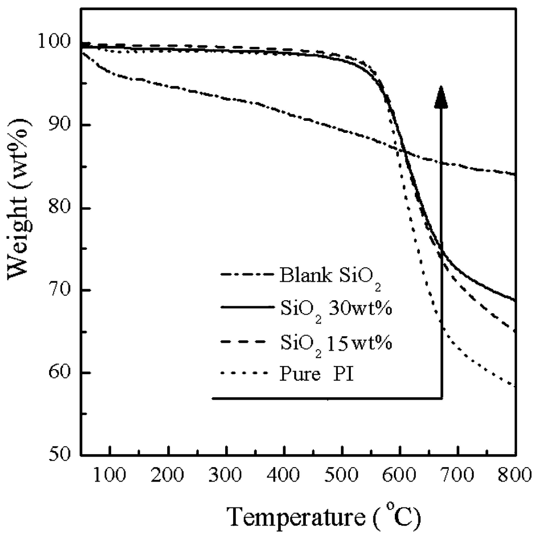

Figure 2 TGA curves of BTDA-ODA polyimide and corresponding polyimide-silica composites films.

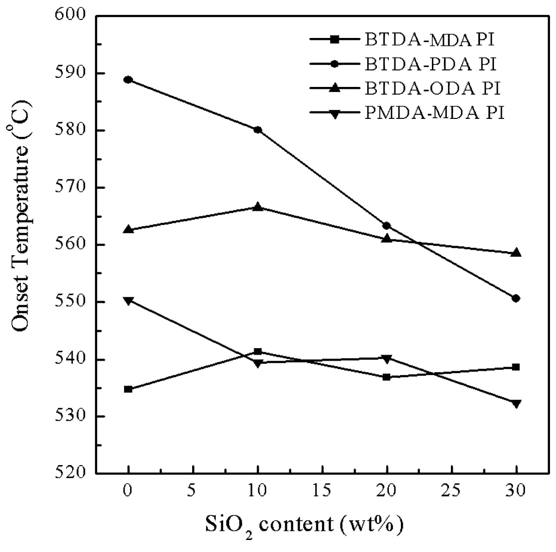

Figure 3 Decomposition onset temperature of different polyimide and polyimide-silica composite films.

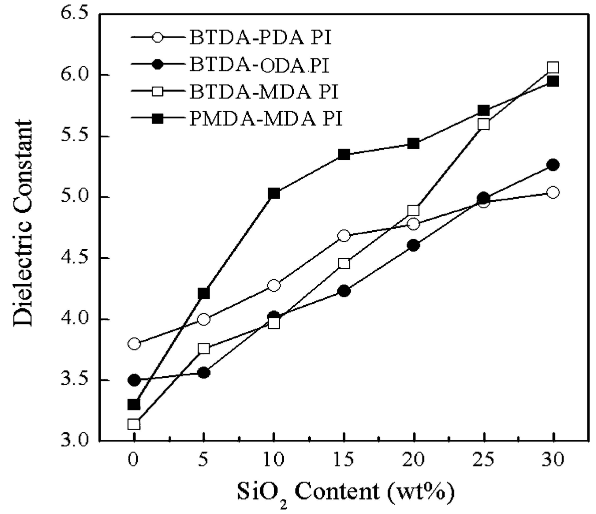

Figure 4 Influence of SiO_2 content on dielectric constant of polyimide-silica composite films.

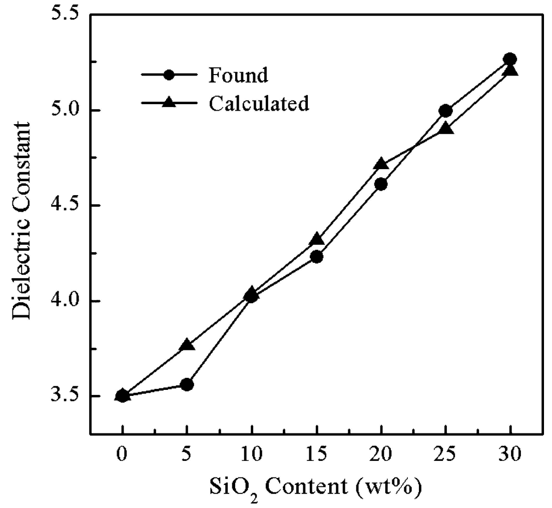

Figure 5 Comparison of experimental and theoretical values of dielectric constant at 10 KHz for BTDA-ODA polyimide-silica composite films with different silica content.

the dielectric constant of the filler (e.g. silica) is larger than that of polymer (e.g. polyimide) matrix [7]. The results comparing the experimentally observed values of BTDA-ODA polyimide-silica composite films and those evaluated values using Maxwell Garnett model [8] ($\varepsilon = v_1\varepsilon_1 + v_2\varepsilon_2$) are shown in Fig. 5. It shows that volumetric law of mixture model fit to the experimental data well.

In conclusion, the dielectric constant of polyimide-silica composite films is efficiently controllable through changing silica content. The thermal stable polyimide-silica composite films will be a kind of new promising high performance materials for dielectric application.

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