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Ferrocene Containing Polyimides as a Route to Low-κ Dielectric Materials

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Polyimides incorporating the ferrocene unit were prepared by *in situ* curing of poly (amic acid) macromolecules with ferrocene, for the molecular-level design of low dielectric constant (low-κ) materials. The effects of ferrocene on dielectric properties of polyimide are investigated in detail in this study. Ferrocene containing polyimides exhibit a number of desirable properties including low-water absorption and admirable thermal stability. Systematic studies demonstrate that proper insertion of ferrocene into a polyimide backbone can give rise to a reduction in the material's dielectric constant. All composites were subjected to DSC measurements for the purpose of examining Tg from all composition. Scanning electron microscopy (SEM), X-ray diffraction (XRD) and the other conventional techniques were used for structural characterization.

Keywords: ferrocene; hybrid materials; low dielectric constant; micro electronics; polyimide; synthesis

Introduction

Materials having low dielectric constant comprise the benefit of facilitating manufacture of higher performance integrated circuits (IC) instruments with decreasing feature size of the chip.[1] On the other hand, inter level dielectric materials must meet severe material property necessities for flourishing integration into the common interconnect structures. These requirements are based on electrical properties, thermal stability, thermo mechanical, thermo stress properties, and moisture uptake. The desired electrical properties are low dielectric constant, low dielectric loss, and high breakdown voltage. However, the propagation delay and cross-talk are primary problems which have been concerned in dielectric materials. Ongoing improvement in device's performance has significantly affected its dimensional requirement. These enhancements have to reduce in the wiring pitch and increase in the number of wiring leave to fulfill demands for density and performance improvement, especially at high frequency operations in the hundreds of megahertz or even gigahertz range. As device dimensions shrink to less than 0.18 mm process (even 0.13 mm or smaller), it is necessary to reduce either the resistance of the metallization or the dielectric constant of the IMD (inter-metal dielectrics) material or both.[1,2]

In addition to the low dielectric constant, materials must also exhibit high thermal stability (T_g and T_d), low thermal expansion coefficient, low moisture uptake, good chemical stability and electric properties for practical applications.[1,3]

Numerous methods have been developed to lower the material dielectric constant.[7–14] It is well-known that the integration of fluorinated substitutes into a polymer is able to reduce its dielectric constant because of small dipole and the low polarizability of the C–F bond.[15] Moreover, polymer free volume is also increased by replacing methyl groups by trifluoromethyl groups.[17–20]

Polyimides (PI) have been widely used in the microelectronic industry for their excellent tensile strength and modulus, low

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thermal expansivity and dielectric constant, and good resistance to organic solvents. Molecular chain modification by introducing a flexible linkage or a pendant group can make PI soluble. However, it is difficult to adjust PI thermo physical properties by changing their chemical structure.] Polyimides (PIs) have been widely used as dielectric and packaging materials in the microelectronics industry because of their good mechanical, thermal, and dielectric properties.[21–23] However, with κ of about 3.4, most of PIs are insufficient in meeting the requirement of $\kappa < 2.5$ for the dielectrics of the near future,[24] and the ultra-low κ of less than 2.2 for the technology nodes below 130 nm.[25–32] In the present study, we implement a novel approach by using organic-inorganic composites with well-defined architectures to tether ferrocene groups to the main chains of pre-synthesized polyimide to form films. This approach can be an effective way to lower κ while maintaining certain thermal properties of the resulting composites.

Experimental Part

Polyimide Synthesis

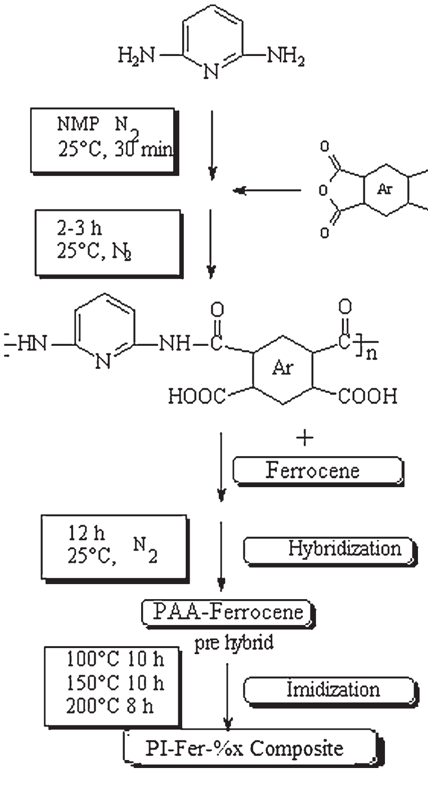
Poly (amic acid) synthesis was performed as follows: 2,6-diaminotriazine (1.11 g, 5 mmol) was dissolved in N-methyl-2-pyrrolidone (NMP) (15 mL) in a 50 mL Schlenk tube equipped with a nitrogen line, overhead stirrer, a xylene filled Dean-Stark trap, and a condenser. Pyromellitic dianhyrides (PMDA) (1.09 g, 5 mmol) was added to the amine solution and stirred overnight to give a viscous solution. After being stirred for 3h, the solution was heated to reflux at 145 °C for 15 h. During polyimidization process, the water generated from the imidization was allowed to distill from the reaction mixture together with 1–2 mL of xylene. After being allowed to cool to ambient temperature, the solution was diluted with NMP and then slowly added to a vigorously stirred solution of 95% ethanol. The precipitated polymer was collected via filtration, washed with ethanol, and dried under reduced pressure at 150 °C. The polymer was isolated with 93% yield.

Sample Preparation

HNO_3 treated positively charged ferrocene was added into the poly (amic acid) solution at 145 °C with fixed ratio, and the synthesis process lasted for 4 h. As shown in Scheme 1, polyimide-ferrocene composites with different ratios of ferrocene unit (1, 3, 5, % weight percent). The mixture was stirred and allowed to evaporate slowly at 25 °C for 12 h and cure at 200 °C for 8 h under vacuum to ensure total imidization of the poly (amic acid) to polyimide. After curing, smooth, stiff and hazel to brown film was obtained.

Measurements

Infrared spectra were obtained using an ATI UNICAM systems 2000 Fourier-



Scheme 1.
Synthetic pathway for the preparation of PI-Fer-x % (x = 1 to 5 wt%).

transform infrared spectrophotometer (FT-IR). Inherent viscosities ($\eta_{inh} = \ln\eta_r/c$ at a polymer concentration of 0.5 g/dL) were measured with an Ubbelohde suspended-level viscometer at 30 °C using NMP as the solvent. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out using a Shimadzu TGA 60 and Shimadzu DSC 60 with a heating rate of 10 °C min^{-1} under air and nitrogen, respectively. Dielectric constants were measured by Agilent Technologies 4294A Precision Impedance analyzer at 1-1000 kHz. Chemical composition analysis by EDAX was performed with an EDAX Hitachi-S-4700 analyzer associated to a scanning electron microscope (SEM, Hitachi Ltd. S-4700). Incident electron beam energies from 3 to 30 keV had been used. In all cases, the beam was at normal incidence to the sample surface and the measurement time was 100 s. Capacitances were determined with a HP4294A at a frequency between 1 kHz to 1 MHz. All chemicals were purchased from Aldrich and used after purification. NMP was distilled over CaH_2 under reduced pressure and stored over 4 Å molecular sieves.

Results and Discussion

The preparation of polyimides is summarized in Scheme 1. The intermediates and polymers were characterized by FT-IR spectra. The results are in agreement with the proposed structures. Thus, the FT-IR spectra of all polyimides in Figure 1 showed distinct features that clearly indicate imide ring formation and the disappearance of the poly (amic acid) peak during the thermal cyclization step.

The characteristic absorption bands of amic acid and carboxyl groups in the 3240 to 3320 cm^{-1} and 1500 to 1730 cm^{-1} regions and those of the imide ring appear near 1770 cm^{-1} (asym. C=O stretching) and 1720 cm^{-1} (sym. C=O stretching), 1373 cm^{-1} (C–N stretching) 1053 cm^{-1} and 723 cm^{-1} imide (ring deformation).

The peak assignments are listed in Table 1. The characteristic absorption bands of the imide group near 1775, 1722, 1377, 1119, and 721 cm^{-1} were observed in the cured samples. The characteristic band of the amide carbonyl at 1650 cm^{-1} was not present indicating that the imidization reaction was complete

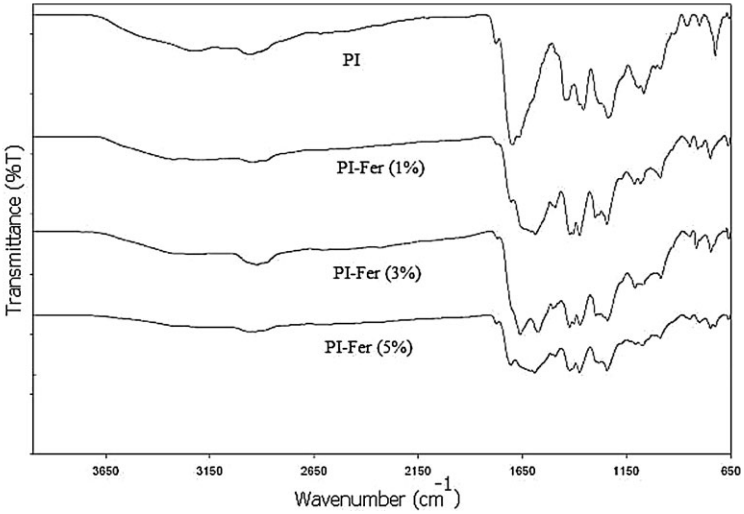


Figure 1.
FT-IR spectra of pure PI, and PI-ferrocene composites with different loadings of ferrocene in polymer (1 to 5%) (b).

Table 1.
FTIR Peak Assignment for PI and PI-Ferrocene Films.

Peak position (cm^{-1})	Assignment
3480(w)	ν (OH),
1775(s)	ν (C=O), in-phase, imide
1722(s)	ν (C=O), out-of-phase, imide
1506(s)	ν (C_6H_4)
1377(s)	ν (CNC), axial, imide
1167(m)	ν (C_6H_4) or ν(C_6H_2)
817(m)	ν (CH in ferrocene)
882(m)	ν (C_6H_2) and ferrocene
823(m)	ν (C_6H_4))

s, strong; m, medium; w, weak

Dielectric Properties

The dielectric constant κ is directly related to the polarizability of a material; therefore, it is strongly dependent on its chemical structure. Saturated hydrocarbons are significantly lower polarizable than species that are unsaturated, conjugated, or have polarizable phenyl groups. This effect is demonstrated by comparing the dielectric constants of an aromatic PI with different percent ferrocene loadings. In general, the κ value can be lowered by breaking off the conjugated system or decreasing the number of phenyl group in the monomer. However, these alterations have to compromise with lower thermal stability. Strong electron-withdrawing inductive effect decreases the electronic polarizability. For this reason in this study, we incorporated ferrocene groups between the backbones of polyimides during the poly (amic acid) forming step.

As shown in Figure 2, PI-Ferrocene composites possessed low dielectric constants of 2,93 to 3.04 at 1 MHz. Incorporation of ferrocene into the backbone of polyimides (DTA-Fer-1% to DTA-Fer-5%) decreased the dielectric constant of the polymer by nearly 0. 80. These examples illustrate the effect of adding ‘‘internal free volume’’ from ferrocene into the polymer film. This can be attributed to the ferrocene unit with the homogeneity nanopore increasing in the free volume. Figure 2 constitutes the major findings of the present work, that is, the figure displays the effective measured dielectric constant κ of PI dispersed with various particles. When PI is dispersed with particles of ferrocene 1% wt,κ, increases as embedded particle contents is increased. Since the dielectric constant of pure PI and is 3.24 the decrease of κ with embedded particle contents is not surprising and may be accounted for in terms of, for example, the Maxwell-Garnett model.[33] As was already pointed out, the particles with zero coercivity are expected to show rapid responses to the induced internal magnetic field at high frequencies leading to a reduced dielectric constant.

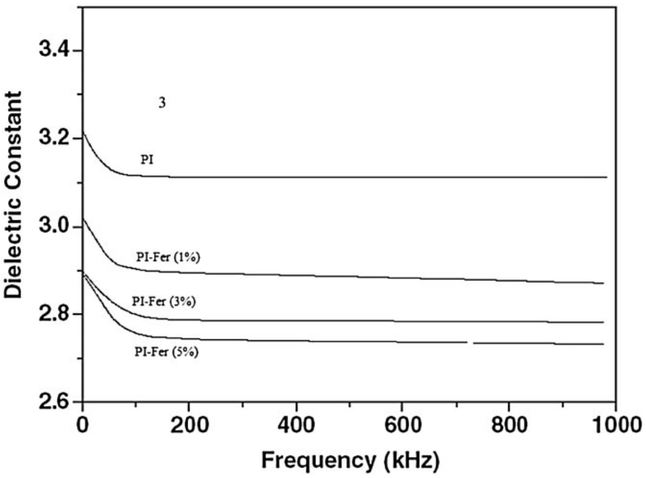


Figure 2.
Dielectric constants of PI-ferrocene composites with different loadings of ferrocene in polymer (1 to 5%).

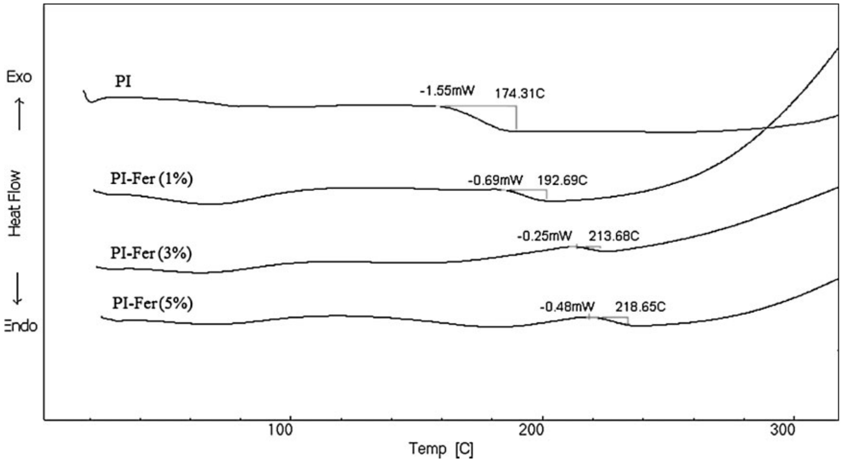


Figure 3.
DSC of pure PI and PI-ferrocene composites with different loadings of ferrocene in polymer (1 to 5%).

Thermal Properties

The glass transition temperature is an important property of a dielectric film. Exceeding T_g the polymer may cause a large decrease in Young's modulus and typically results in a shift in the dielectric properties. All composites were subjected to DSC measurements for the purpose of examining miscibility.

Figure 3 shows the DSC thermograms of all composites exhibiting only one T_g from all composition. A single T_g strongly implies that all these composites are homogenous. Figure 3 shows the dependence of the T_g on the composition of these copolymers, increasing the ferrocene content results in T_g increase than average values. The results indicate that the ferrocene moiety improves the thermal stability over current polyimides used in the microelectronic applications.

A successful interlayer dielectric must possess a number of other desirable properties in addition to a low κ, and other relevant properties, such as the dimensional and chemical stability of the materials to

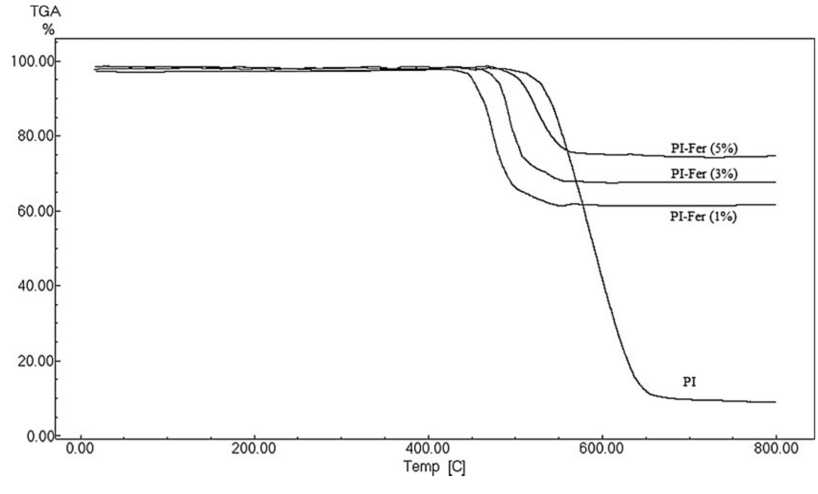


Figure 4.
TGA of pure PI and PI-ferrocene composites with different loadings of ferrocene in polymer (1 to 5%).

high temperatures is highly critical. TGA analysis of PI-ferrocene composites were given in Figure 4. Their thermal decomposition temperatures (T_d = temperature at 5% mass loss) were measured via thermogravimetric analysis (TGA) and showed that the introduction of ferrocene into polymer backbones increased thermal stability.

Figure 5(a) shows the SEM image of pure PI respectively. The film shows some pores, which are usually observed due to some deformation of polymer film during casting. The SEM images of PI- Ferrocene (1 wt % g-Ferrocene) observed in Figure 5(b) showed particle agglomerates under both the resolutions. The agglomerates of the ferrocene particles appear to be submicron. The high concentration of the ferrocene might have contributed to the particle agglomeration during film formation. Also, the dispersion of the ferrocene particles is not uniform, which again has been caused by its high concentration.

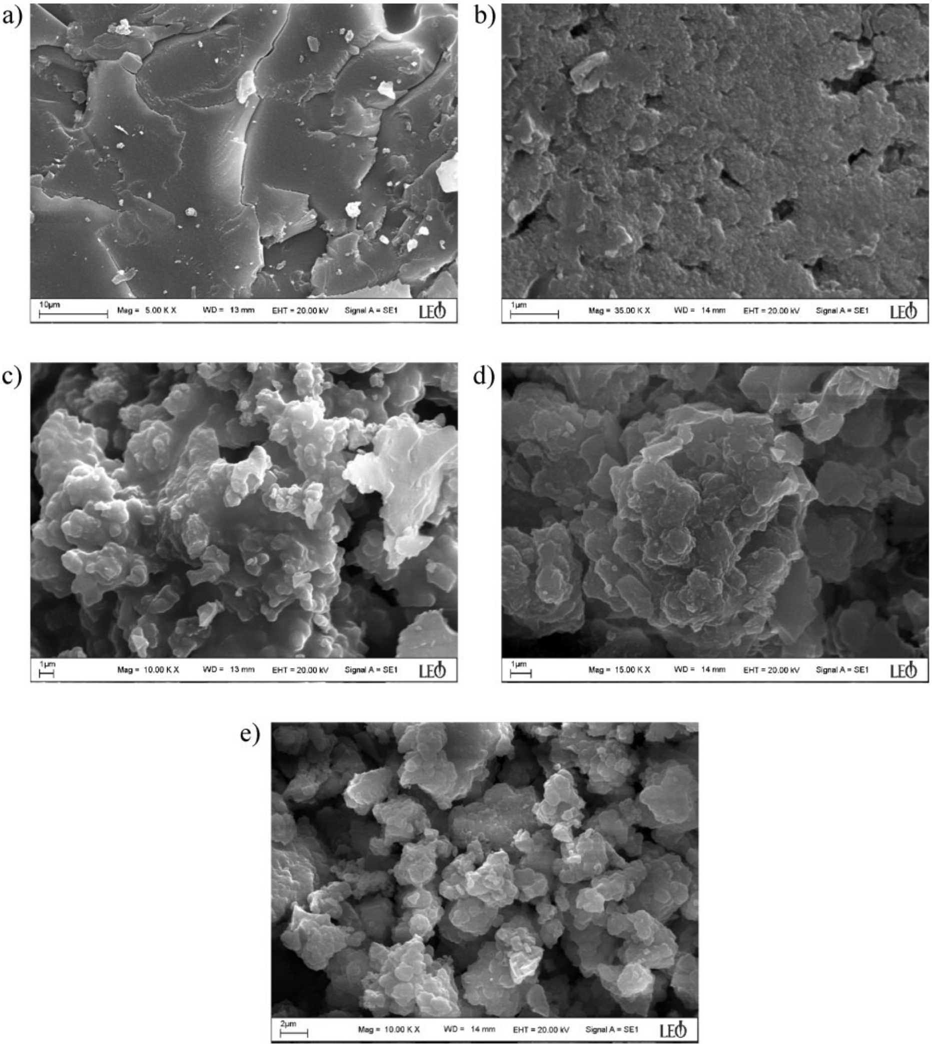


Figure 5.
SEM image of pure PI, and PI-ferrocene composites with different loadings of ferrocene in polymer (b) 1%, (c) 3%, (d) 5%.

Figure 5(d) shows SEM image of PI-Ferrocene (5 wt % Ferrocene). The dispersion looks more dense when compared with its predecessor (1 wt %); however, some submicron agglomerates are also noticed along with some pores of the original polymer film. The SEM image of PI-Ferrocene (10 wt % Ferrocene) shown in Figure 5(e) had dispersion of the ferrocene particles in the polymer even covering the pores observed in the polyimide film. The films look more homogenous; however, particle agglomerates cannot be ruled out in this case also.

Conclusion

Ferrocene particles were dispersed into polyimide (PI) in order to investigate their influence on the dielectric constant of PI. Tethering ferrocene group into the backbone of the PI lower the dielectric constant by a factor of 0.8. We implement a novel approach by using organic-inorganic composites with well-defined architectures to tether ferrocene groups to the main chains of pre-synthesized polyimide to form films. This approach can be an effective way to lower κ while maintaining certain thermal properties of the resulting composites.

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