Synthesis of Polymer films with low Dielectric Constant (κ)

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Abstract. The semiconductor industry and Microelectronics based devices are in urgent need of materials having low dielectric constant (κ). Efforts are being made, world over, to develop low dielectric (say κ < 2.0) materials for microelectronic applications. It is thus of interest to develop materials having low dielectric constant (κ). Polyimide is widely used as packaging material in microelectronic devices packaging due to its good thermal and mechanical properties and good adhesion to metal surfaces. However, the dielectric constant of normal PI is high (κ ~3.4) as per the requirement of advance insulator material and for microelectronics. We have synthesized polyimide–silica composite films and it is shown that such films have much lower dielectric constant as compared to the normal PI films. The above polymer films were prepared by modifying the pristine polymer at the precursor stage of synthesis. We report the results of FTIR, XRD and dielectric studies of films which have been prepared using PMDA-ODA (Poly Amic acid in DMAc) as precursor and Tetra Ethoxy Silane (TEOS)/Silicic acid as modifier. It is seen that crystallinity and the dielectric of the composite films depend on SiO₂ concentration.

1 Introduction

Microelectronics based devices are of interest for several different applications. The fabrication of these devices and their smooth functioning is greatly hindered by the resistance–capacitance (RC) delay and the cross-talk noise between metal interconnects, especially when one reduces the sizes of the devices. It is thus of interest to develop materials having low dielectric constant (κ). This paper deals with synthesis and characterization of suitably modified Polyimides (PIs) films which are among the most promising candidates for use as next-generation interlayer dielectrics. The semiconductor industry is in urgent need of materials having low dielectric constant (κ). Efforts are being made, world over, to develop low dielectric (say κ < 2.0) materials for microelectronic applications. In addition to low dielectric constant, the above materials should have high-thermal stability, chemical stability and good adhesion to metals. Polyimides (PIs) are among the most promising candidates, which meet above requirements and can be used in microelectronic devices. Normal PI is, however, of not much use as it has dielectric constant of about 3.4. Fluorinated PIs having dielectric constant κ of about 2.4 are better than normal PIs for above applications. However, fluorinated PIs give out fluorine vapors at high temperatures and hence, they have poor mechanical properties at high temperature. We have synthesized nanocomposite PI films having nano-pores or silica nanoparticles embedded in them. These films are expected to have κ < 2, especially as it is known that porosity in a material leads to reduction in dielectric constant [1-3].
There are several different routes for synthesis of low-κ PI films [4, 5], though most of above approaches result in loss of one or more of the desired features (mechanical strength, thermal stability etc). We have generated silica nanostructures using a Siloxane Interacted Polyimide Precursor (SIPP) technique [6, 7]. This involves chemical modification of Polyimide i.e PAA poly (Amic acid) backbone chain at precursor stage and subsequent thermal imidization. It is possible to control nanostructures of the films by choosing appropriate time temperature protocol for thermal treatment. A number of thin polyimide silica composite films were synthesized using different modifiers with in-situ generation of siloxane interacted nanostructures The films have been characterized for their thermal stability, structure and dielectric behaviour using techniques such as TGA, FTIR, XRD and AFM and impedance analyzer.

2 Experiment

2.1 Material and method

Tetraethoxysilane (TEOS) 99% pure and Silicic acid 99% pure was procured from Lancaster, USA and used as silica generating precursor. Polyamic acid (PAA), which is marketed as ABR ON S-10, was procured from M/s ABR Organics Ltd., Hyderabad, India with 11.44% solid content in dimethylacetamide (DMAC) and was used as received. AR grade Tetrahydrofuran (THF), Supplied by Merck was used as co-solvent for the preparation of precursor solution. AR grade methanol, supplied by Merck was used as solvent for the removal of DMAC from the Polyimide silica composite films.

2.2 Preparation of PI/TEOS/Silicic acid blends

The silica generating precursor solutions were prepared by adding TEOS and silicic acid in THF. Appropriate concentrations of TEOS were taken in a known volume of THF and added to the calculated quantity of the PAA solution so that films having the ultimate desired concentration of TEOS (1% and 20 wt. %) and silicic acid (1% and 20 wt. %) could be obtained; they are designated as PITEOS-1, PITEOS-20, PIHS-1 PIHS-20. The unmodified polyimide is designated as PI. The blends were stirred for half an hour on magnetic stirrer. The films were casted on glass plate using method of spin coating.

The above casted were subjected to curing (thermal imidization) for conversion of PAA into polyimide silica films following a time temperature protocol of 70°C 1 hr., 100°C 1 hr. 150°C 1 hr. 200°C 1 hr. 250°C 1 hr. 300°C 1 hr. and 350 for 2hrs.

2.3 Characterization of the films

The Fourier Transform Infrared Spectrum (FT-IR) of Neat PI, and polyimide– silica composite films were recorded using Lambda BX instrument, Perkin Elmer, and dynamic thermo gravimetric analysis was performed using Perkin-Elmer TGA-7 instrument. The rate of heating was kept at 10°C/min in an inert atmosphere. The above studies were carried out at SAIF IIT Bombay.

The AFM (Atomic Force Microscopy) analysis of above films was carried out using Nanoscope III, Digital Instruments, (working in contact mode) at UGC-DAE CSR, Indore.

The XRD measurements were carried out using Bruker D8 Advance X-ray diffractometer. The x-rays were produced using a sealed tube and the wavelength of x-ray was 0.154nm (Cu K-alpha). The x-rays were detected using a fast counting detector based on Silicon strip technology (Bruker LynxEye detector) at UGC-DAE CSR, Indore.
The dielectric behaviour of the films was studied using Impedance Analyzer (Novocontrol model Alpha AT) at UGC-DAE-CSR, Mumbai Centre, BARC.

3 RESULTS and Analysis
The most important analysis of the films was FT-IR analysis as it reveals the chemical structure of the film. Moreover, it confirms the formation of imide unit and absence of certain unwanted chemicals. Figure 1 shows FT-IR absorption spectra of the pure PI and PI incorporated Silica composite films and the characteristic absorption spectra of the imide unit at 1776, 1777, 1724, 1374 and 722 cm\(^{-1}\) are clearly seen, both, for pure PI films and PITEOS composite films [8-9]. It is interesting to note that 1650 cm\(^{-1}\) peak, corresponding to PAA, has completely disappeared. The broad absorption spectrum around 1083 cm\(^{-1}\) seems to be arising from the asymmetric stretching of Si-O-Si units [10-12]. It is not surprising that intensity of this peak increased with the TEOS concentration. The absorption spectrum at 3400 cm\(^{-1}\) arises from OH groups [13-14].

Figure 1 FT-IR spectrum of pure (1) PI, (2) PIHS 1%, (3) PITEOS 20% films.

Figure 2 shows X-ray Diffraction Study of the prepared polyimide– silica Composite films. The XRD patterns of the polyimide-SiO\(_2\) composite films with various contents of SiO\(_2\), prepared according to processing conditions in Section 2.2. In Figure 2, there is a peak at 17.83 in the diffractogram of the polyimide (Neat PI) as the non-Gaussian distribution pattern that reveals a semi-crystalline structure polymer. This peak was also depicted in the all diffractogram of polyimide composite films.
As the loading of Silicic acid increased in the PAA precursor the peaks shoulder is at $\theta = 17.68$ suggesting that this could be due to the formation of SiO$_2$ particles and increase of SiO$_2$ particles in PI matrix.

The AFM topographic image of pure PI and PITEOS and PIHS composite films are shown from Figure 3. It is seen that while films containing higher concentration of TEOS and Silicic acid, show aggregation of silica particles (sizes in range of 200-400 nm), the low concentration films show dispersion of silica particles (sizes in range of 80-100 nm) within PI matrix.

Table 1 reports the decomposition temperature for neat PI and PITEOS and PIHS composite films. The decomposition temperature of the nano-composite films, especially having higher TEOS content, has been found to be lower than that for neat PI. The initial weight loss for the film occurs at about 517°C, which shows that nano-composite films are thermal stable at room temperature [15-8].

The high decomposition temperature of films having low concentration of TEOS and Silicic acid, suggests a favourable reinforcing effect and a uniform dispersion of in-situ formed silica particles within the PI matrix. The above studies clearly show that we have successfully incorporated silica particles in polyimide composite films.

Table 1- Thermal Stability of PI and PITEOS and PIHS films.

| S.No. | Initial Decomposition Temperature | Final Decomposition Temperature |
|-------|----------------------------------|---------------------------------|
| 1     | Neat PI                          | Silicic acid 1%                 |
| 2     | 17.83                            | 17.68                           |

Figure 2 XRD graph of pure PI and (2) PIHS 1%, films

Figure 3 AFM images of Neat PI (a), PIHS 1% (b) and PITEOS 20% (c) films
The dielectric studies have been carried on four films (neat PI and PI containing 1% and 20% silicic acid as modifier). All the samples had thickness of about 100µm and they were cured at 350°C for 2 hrs. The measured dielectric constants at different frequencies are shown in Table 2. It is noted that measured value of $\kappa$ for neat PI is 3.26, which is in reasonable agreement with the literature value of $\kappa= 3.2 -3.4$ at 1 KHz for commercially available PI films [19-21]. Further it is seen that the dielectric constant of samples containing 1% silicic acid is definitely lower than that for neat PI samples at all frequencies.

Table 2. Effect of frequency on dielectric constant of PI and PITEOS and PIHS films.

| Frequency Hz | Neat PI | PITEOS-20 | PIHS-1 | PIHS-20 |
|--------------|---------|-----------|--------|---------|
| 5000         | 3.35    | 2.71      | 2.07   | 3.92    |
| 1000         | 3.21    | 2.65      | 2.00   | 3.76    |
| 100          | 3.23    | 2.75      | 2.02   | 3.78    |
| 10           | 3.25    | 2.95      | 2.07   | 3.80    |
| 1            | 3.26    | 3.17      | 2.14   | 3.82    |
| 0.1          | 3.28    | 3.39      | 3.82   | 3.84    |

4 Conclusions
The new method of preparing siloxanes interacted PI films by using silica precursors like TEOS and silicic acid has been reported and their relationship to silica contents were investigated. Incorporation of both the precursors within PI matrix has been proven to be effective. The controlled incorporation of 1% PIHS showing promising result for dielectric constant at 1KHz while the lower concentration of silica content also showing good Thermal properties which is a requirement for low dielectric. Thus this study further needs detailed analysis over wide frequency range for dielectric behaviour and the effect of varying concentrations of modifiers and precursors for Dielectric constant of the PI films.

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