Dielectric and conduction properties of polyimide films

Conference Paper · October 2011

DOI: 10.1109/SMICND.2011.6095784

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DIELECTRIC AND CONDUCTION PROPERTIES OF POLYIMIDE FILMS

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Abstract–*Dielectric and conduction properties of polyimides were evaluated on the basis of dielectric constant, dielectric loss, electric modulus and AC conductivity, and their variation with frequency and temperature. Polyimide films exhibited good insulating properties with dielectric constants values in the range of 2.78 - 3.48 and dielectric loss comprised between 0.01 and 0.03 at 1Hz at room temperature.*

Keywords: *polyimide; dielectric constant; dielectric loss; AC conductivity; conduction mechanism.*

1. INTRODUCTION

In the past decade, miniaturized ultra large-scale integrated circuit (IC) chips and semiconductor devices with improving performance have become a main orientation in microelectronics industry and been pursued as a global trend [1]. The use of ultra-low dielectric constant (ultra-low k) interlayer materials can greatly reduce the RC time delay, cross-talk, and power dissipation in the new generation of high density integrated circuits [2, 3].

Polyimides (PI's) have been widely used as dielectric and packaging materials in the microelectronics industry because of their unique physicochemical properties: excellent thermal stability, good radiation and chemical resistance, good mechanical strength, low moisture adsorption, and good adhesion to semiconductor and metal substrates [4, 5].

The importance of polyimides for high-performance nanocomposites designed for electrical and dielectric applications requires a better understanding of the intrinsic dielectric and electric characteristics and their temperature dependence.

Consequently, the focus of this work is to investigate a series of polyimides having various structures by using dielectric spectroscopy to gain insight into the molecular mechanism determining its dielectric properties and kinetic characteristics. Particular attention is placed on elucidating the electric and dielectric properties in the domain of glass transition and sub-glass transition. The influence of absorbed water in the films is also discussed.

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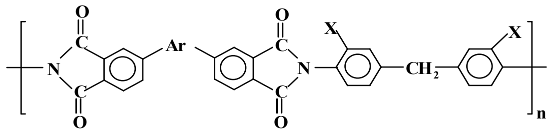
2. EXPERIMENTAL

The structure of the investigated polymers is presented in Scheme 1.



PIa: **Ar = - O-C_6H_4- $C(CH_3)_2$ - C_6H_4- O -; X = H ;**
PIb: **Ar = - O-C_6H_4- $C(CH_3)_2$ - C_6H_4- O -; X = CH_3**
PIc: **Ar = CO; X = H ;**
PId: **Ar = CO; X = CH_3**
PIe: **Ar = $C(CF_3)_2$; X = H ;**
PIf: **Ar = $C(CF_3)_2$; X = CH_3**

Scheme 1. Structure of the polymers.

The polyimide films were obtained by casting the polyamidic acid solution onto glass plates and drying at 60°C over 4 h to evaporate the solvent. The subsequent heating of the precursor films at 100, 150, 200, and 250°C consecutively (for 1h at each temperature) resulted in a final polyimide film.

Measurements

FTIR spectra were recorded with a FT-IR VERTEX 70 (Bruker Optics Company).

Dielectric measurements were performed with Novocontrol Dielectric Spectrometer, Concept 40. The measurements were run at constant temperature by taking frequency scans (1 Hz to 1 MHz) every 5°C between -120°C and + 250°C. In order to distinguish the influence of heating on the samples, two cycles of dielectric measurements were performed in this temperature range. Polyimide films with thicknesses comprised between 30 and 50 μm were placed between two round electrodes and tested.

3. RESULTS AND DISCUSSION

3.1. Dielectric Constant and Dielectric Loss

Polyimide films exhibited good insulating properties with dielectric constants values in the range of 2.78 - 3.48 and dielectric loss comprised between 0.01 and 0.03 at 1Hz at room temperature (table 1)

Table 1. Dielectric constant and dielectric and dielectric loss at 1 and 10^4 Hz and 25^0C

Polymer	Dielectric constant, ε'		Dielectric loss, ε'' $x10^{-2}$	
	1 Hz	10^4 Hz	1 Hz	10^4 Hz
PIa	3.25	3.16	2.09	1.03
PIb	3.08	2.99	2.93	1.23
PIc	3.48	3.40	2.58	1.33
PId	3.32	3.22	2.56	2.24
PIe	2.89	2.84	2.02	0.943
PIf	2.78	2.73	1.36	0.763

3.2. Relaxation Processes

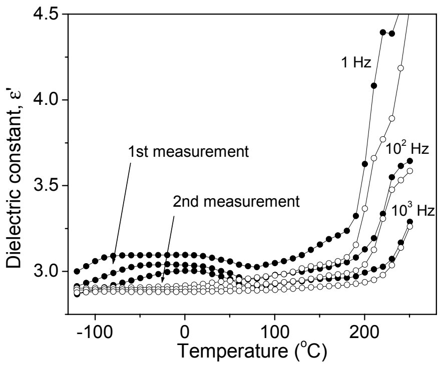


Fig. 1. Dielectric constant vs temperature and frequency for polyimide **PIb**.

In the first measurement, in the negative temperature region a relaxation peak appears on *ε''* corresponding to *γ* local relaxation, and a step increase of *ε'* is observed. On further increasing the temperature, starting around 50ºC, *ε'* decreases with increasing temperature. In the same temperature region there are some irregular variations of *ε''* as a function of temperature.

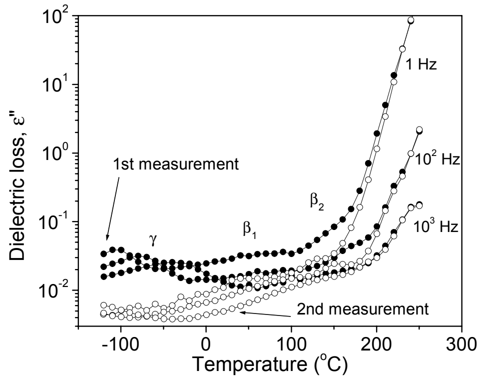


Fig. 2. Dielectric loss vs temperature and frequency for sample **PIb**.

This variations may be due to the removal of polar molecules (like water), especially since on the second heating *γ* relaxation is reduced and *ε'* is increasing continuously with temperature. In this temperature region the shape of dielectric loss indicate the presence of other two sub-glass relaxation processes (β_1 and β_2). At even higher temperatures, around 150-200ºC, *ε'* and *ε''* increase abruptly, especially at low frequencies, due the accumulation of charges at electrode-sample interface [7]. For this process, in electric modulus representation appears a conductivity relaxation, (σ process in figure 3) due to the decay of the applied electric field [8]. The appearance of *σ* relaxation marks the temperature at which the dielectric properties are altered and the values are: **PIa**: 210ºC, **PIb**: 210ºC, **PIc**: 145ºC, **PId**: 205ºC, at 1 Hz. For the polyimides **PIe** and **PIf**, *σ* relaxation temperature is higher than 250ºC.

In second heating cycle *γ* relaxation intensity is reduced, and β_1 and β_2 processes are better evidenced. For *γ* relaxation some studies found correlation between water content and the intensity of this transition, while other studies evidenced that *γ* relaxation encompasses both the coupled water molecules and limited motions such as phenyl ring oscillations [9,10]. For our polymers the temperature of *γ* relaxation is lower for the polymers with dimethyl-substituted diamine segment and the same dianhydride unit. The β_1 relaxation was associated with motions in the diamine part of repeating unit, while the β_2 relaxation was caused by motions of the dianhydride segment [11,12].

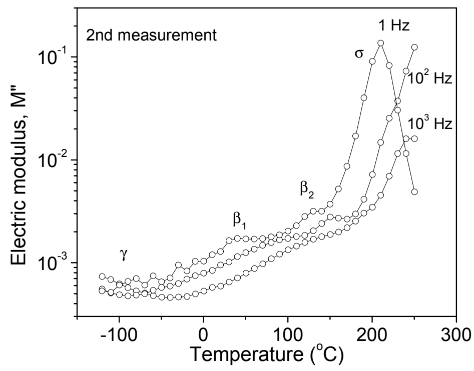


Fig. 3. Electric modulus M'' vs temperature and frequency for polyimide **PIb**.

For polymers having methyl substituents on diamine segment the temperature of β_1 relaxation is higher than for their analogues.

3.3. Frequency and Temperature Dependence of AC Conductivity

For conductivity data analysis, the AC conductivity was calculated from the imaginary part of complex permittivity using the relation $\sigma_{ac} = \sigma' = \varepsilon_0\, \omega\, \varepsilon''$ [13], where ε_0 is the permittivity of free space and ω is the angular frequency. Figure 4 presents the variation of AC conductivity with frequency for temperatures in 0 - 240ºC range for polymer **PIc**. Up to a certain temperature, the AC conductivity increases linearly with increasing frequency in a double logarithmic scale for all the samples, not only for the one shown in figure 4. On increasing temperature, starting from a certain value (e.g., 180ºC for **PIc** sample) the AC conductivity is nearly independent of frequency in the low frequency region.

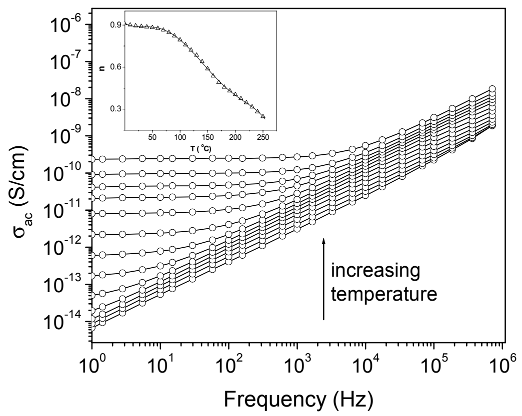


Fig. 4. AC conductivity vs. frequency for polyimide **PIc** in 0 – 240ºC temperature range at 20ºC intervals and temperature dependence of frequency exponent, *n*.

In this region the conductivity is DC in nature: the decrease in polymer viscosity with increasing temperature permits the long range charge transport trough the media.

AC conductivity increases with increasing frequency for all the samples, characteristic to hopping type conduction [14]. AC conductivity patterns showing a frequency independent plateau in low frequency region and a dispersion at the higher frequency can be described by Jonscher's universal power law [15], $\sigma(\omega) = \sigma_{dc} + A\omega^n$, where σ_{dc} is the DC conductivity, A is the pre-exponential factor and n is the fractional exponent ($0 < n < 1$). The value of n is used to understand the conduction or relaxation mechanism in insulating materials [16].

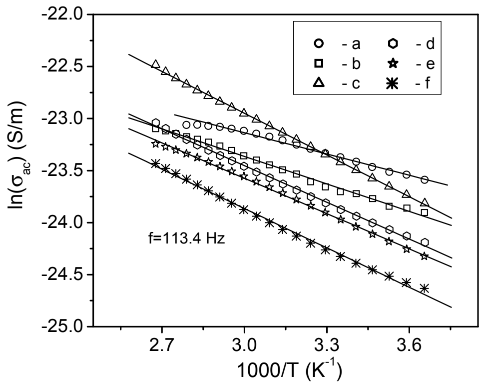


Fig. 5. ln(σ) vs 1000/T for f=113.4 Hz.

The exponent n was calculated from the frequency dependent conductivity and is represented in the diagram inside of figure 4 for sample **PIc.** Values close to unity are measured when the process involved is dipolar and the values in the range 0.5–0.9 are normally associated with the higher losses due to charge carrier transport [14]. The exponent n decreases with increasing temperature and is generally contained within the limits $0.5 < n < 1$. This characterizes the electronic conduction via hopping process [17]. The frequency exponent, n, decreases with increasing temperature for all the polyimide films. The same behaviour was reported for other polyimides [18, 19].

Figure 5 presents the variation of logarithmic AC conductivity ln(σ_{ac}) at 113.4 Hz with inverse absolute temperature. The activation energy for AC conductivity was calculated from the slope of the graph using the equation 5:

$$\sigma_{ac} = \sigma_0 \exp\left(\frac{Ea}{kT}\right) \qquad (5)$$

where σ_0 is the pre-exponential factor, Ea is activation energy for AC conductivity, k is Boltzmann constant.

The values of activation energy for AC conductivity at 113.4 Hz are: sample **PIa** - 0.06 eV, **PIb** – 0.08 eV, **PIc** – 0.11 eV, **PId** – 0.1 eV, **PIe** – 0.1 eV, **PIf** – 0.11 eV. The low activation energy (<1 eV) indicates the predominance of electronic conduction [19]. The AC conduction in polyimide films is due to electronic hopping.

4. CONCLUSIONS

The polyimide films exhibited low dielectric constant values, being in the range of 2.88 - 3.48 at 1 Hz at room temperature; the lowest values was shown by those polymers containing hexafluoroisopropylidene units in their chemical structure, being 2.88 – 2.91.Three dipolar relaxation processes which depend on polyimide structure and conformation were observed.

The AC conductivity data show the polymers have an electronic conduction via hopping process, as judged by the low values, under 1 eV, of the activation energy of conductivity. The analysis of the dielectric results in terms of electric modulus and AC conductivity showed that the maximum temperature at which these materials can be used as dielectrics is in the range of 145 ºC–250ºC. In addition, the polymers **PIe** and **PIf** presented lower values for dielectric constant. All these characteristics associated with high thermal stability make the present polymers potential candidates for applications as high performance dielectrics.

Acknoledgement–The financial support provided by CNCSIS-UEFISCDI through the Project PN II-RU, code TE_221, no. 31/2010 is acknowledged with great pleasure.

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