Polymer Degradation and Stability 98 (2013) 361–367

Contents lists available at SciVerse ScienceDirect

Polymer Degradation and Stability

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

Effects of mechanical stresses, thickness and atmosphere on aging of polyimide thin films at high temperature

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ARTICLE INFO

Article history:
Received 4 July 2012
Accepted 12 September 2012
Available online 21 September 2012

Keywords:
Polyimide BPDA/PDA
Thermal aging
Thermo-oxidation
Breakdown field
Surface degradation

ABSTRACT

This work deals with the isothermal aging mechanisms and their impact on the behaviour of polyimide thin films, usually used as dielectric material in high temperature electronic applications. The objectives were to achieve a better knowledge of the atmosphere and mechanical stress effects on the degradation mechanisms of deposited thin films during high temperature isothermal aging. Hence, BPDA/PDA aromatic polyimide (PI) thin films deposited on two different substrates (stainless steel and silicon) were aged slightly below their glass transition temperature (0.8 T_g) in air and in nitrogen atmospheres. During the aging, the dielectric strength, morphological characteristics (thickness, surface profile) and chemical variation were monitored for different initial film thicknesses (<10 μm). Results show that films aged under nitrogen and those deposited on silicon substrates aged in air do not show any remarkable degradation during the aging period. In contrast, the films deposited on stainless steel substrates present significant degradation during aging in air and the material lifetime is thickness dependent. In the latter conditions, the measured mean thickness losses for long aging periods are about 0.5 nm/h for all initial thicknesses, indicating that the degradation is not related to the bulk variation of the material but to a surface degradation mechanism. In addition, the breakdown field presents stabilization after an initial aging period, leading us to conclude that the bulk of the material is not affected by the aging. The coupled results indicate that the BPDA/PDA thermal degradation mechanism at temperature below its glass transition one is due to the attack on the outer film layer, related to the presence of oxygen in the atmosphere and strongly dependent on thermo-mechanical substrate properties. Hence, studying of the thermo-oxidative stability of freestanding polyimide films can lead to misestimated reliability.

1. Introduction

Aromatic polyimides (PIs), with stiff molecular backbones containing aromatic rings, offer high glass transition temperatures and high thermal stability. For high temperature electronic applications, some unique properties of PIs like the chemical stability and the excellent mechanical and electrical properties are of great interest [1,2]. Polyimides used at high temperature can be subjected to thermal and thermo-oxidative degradation which will cause the final breakdown of the insulating film under applied voltages. Consequently, it is of major interest to understand and predict the structural changes in those materials when submitted to specific conditions for long periods of time, as well as the effect of these changes on the dielectric properties.

In the aging conditions under concern here, aging-related degradation of high temperature polymers may be a result of complicated interaction of both physical and chemical aging processes, such as physical creep and relaxation during the aging period and the chemical degradation of polymer such as chain scission, hydrolysis, and oxidation induced degradation [3]. It is especially important to consider such chemical and physical aging for aeronautical applications, where hot and oxidative environments are commonly encountered [4].

The effect of long time aging of polyimide at high temperature (>200 °C) and in oxidative environment on the mechanical properties [5], weight loss [6,7], and chemical properties [8,9], has been widely investigated for thick polyimide matrix composites (1 mm thick) used in aerospace applications. It has been found that while thermal degradation occurred throughout the material, the oxidative degradation occurs mainly within a thin surface layer where oxygen diffuses into the material. The developed oxidized surface layer during thermal aging has shown a variation in the mechanical

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0141-3910/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.polymdegradstab.2012.09.005

properties compared to the unoxidised interior material [10]. Also, a lot of papers discussed the effect of thermal aging on the electrical properties of polymer dielectric materials but for thick and free-standing films [11–14]. Consequently, an overall understanding of the mechanisms of oxidative degradation of thin deposited polyimide films (thickness < 20 μm) and their effects on the electrical properties are still lacking. After having investigated the electrical properties of thin unaged polyimide BPDA/PDA (biphenyltetracarboxylic dianhydride acid *p*–phenylene diamine) films in a wide temperature range [15,16], it seems important to study the effect of its aging in various conditions as well, in view of a possible use for high temperature applications and a better comprehension of the occurring degradation mechanisms at temperatures close to the glass transition one. In this work, the effect of isothermal aging at 300 °C in different conditions on the degradation kinetics of BPDA/PDA PI films, was investigated by monitoring electrical, physical and chemical properties. Based on the different obtained results, a degradation mechanism for deposited thin films aging is proposed.

2. Sample preparation and measurements

2.1. Sample preparation

The studied polyimide is a commercial electronic grade of BPDA-PDA with a high decomposition temperature (T_d = 620 °C), a high glass transition temperature (T_g = 360 °C), a low dissipation factor (2×10^{-3} at 1 kHz and 25 °C), a high breakdown field (>2 MV/cm) and a low coefficient of thermal expansion CTE (3–5 ppm/°C). PI films were obtained from a polyamic acid (PAA) precursor dissolved in *N*-methyl-2-pyrrolidone (NMP) solvent. PI coatings were prepared by dispensing successively an adhesion promoter and the PAA solution on cleaned stainless steel (SS) substrates and highly doped n++ (resistivity < 3×10^{-3} Ω cm) cleaned silicon wafers (after dipping in a reduced HF/H_2O solution to remove the native oxide from the silicon surface), followed by a spin-coating with different rotation speeds during 30 s. Various rotation speeds were used in order to obtain different film thicknesses. A soft-bake at 175 °C on a hot plate for 3 min in air was performed. Then, the coatings were cured at 400 °C for 1 h in an oven under N_2 atmosphere in order to drive off the NMP solvent and to complete the imidization reaction [17]. The chemical structure of the PAA and the BPDA-PDA polyimide are presented in Fig. 1.

The final film thicknesses, of 1.5, 3.0, 4.2, 5.7 and 8.0 μm were obtained and measured before the aging using a KLA Tencor profilometer. The obtained structures were tested at the initial time and were placed in an oven at 300 ± 2 °C in ambient air or in a tubular furnace under N_2 flux. After the aging, Metal–Polyimide–Metal and Semiconductor–Polyimide–Metal structures were achieved for electrical characterizations. The top gold electrodes were evaporated with an approximate thickness of 180 nm and they were given their geometrical shape and size by chemical etching through a photo-resist mask owning circular patterns of 0.6 mm in diameter for dielectric breakdown tests.

2.2. Aging conditions

All the measurements presented below were performed on PI films aged at 300 °C in different conditions. The time at the beginning of the aging is noted as t_0. The different aging conditions are summarized in Table 1. At scheduled times, a part of the specimens were removed from the oven and subjected to non-destructive and destructive tests. The thicknesses noted in the text and labels refer to the initial ones measured at t_0.

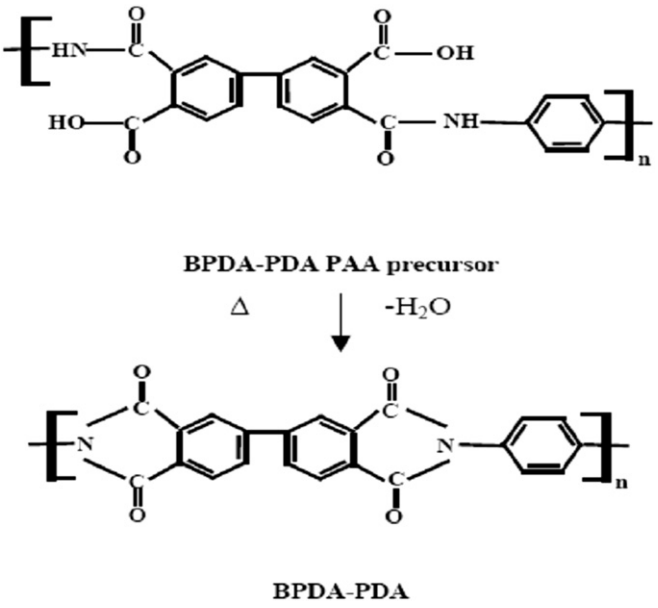

Fig. 1. Polyamic acid and polyimide BPDA-PDA chemical structures.

2.3. Measurements

The film thickness and the surface roughness were controlled using a KLA Tencor profilometer with an accuracy of 1 nm, and an optical phase shifting interferential profilometer Veeco NT 3300 with a depth resolution of 3 nm.

The dielectric breakdown voltage and leakage current measurements were performed under a linearly increasing applied DC voltage at a rise rate of 200 kV cm^{-1} s^{-1} from 0 V up to the breakdown event, using a Keithley SM 2410 source metre (0–1100 V) owning an internal ammeter (1 nA–150 mA) for the thinnest films and a FUG 6500 V DC voltage source for thicker ones. When the breakdown occurs, the voltage source switches into current source supplying a short-circuit current limited to 20 mA. The dielectric breakdown field of PI films was calculated using the following relation:

$$E_{BR} = \frac{V_{BR}}{d} \quad (1)$$

where V_{BR} is the non reversible breakdown voltage and d is the film thickness. For each condition, 20 capacitor structures were tested. The scale parameter α (MV/cm) corresponding to the breakdown field for a probability of failure $F(\alpha) = 63.2\%$ is presented according to the Weibull statistical law [18]. The represented leakage current density was calculated from the measured current during the step voltage rise for the initial 1.5 μm thick film.

Fourier transform infrared spectroscopy (FTIR) was carried out using a Vertex 70 spectrometer used in attenuated total reflexion mode with a 45° incident angle. An average of 20 scans was collected for each spectrum in the 500–4000 cm^{-1} range. All spectra were obtained at a resolution of 2 cm^{-1}. A background was

Table 1
Aging conditions and corresponding studied thickness range.

Condition number	Atmosphere	Substrate	Thickness range
C1	Air	Stainless steel	1.5–8 μm
C2	Air	Silicon	1.5–8 μm
C3	N_2	Stainless steel	1.5 μm