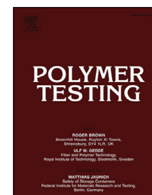
Polymer Testing 64 (2017) 48–54

Contents lists available at ScienceDirect

Polymer Testing

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



Test Method

# Determination of the glass transition temperature in thin polymeric films used for microelectronic packaging by temperature-dependent spectroscopic ellipsometry

Eva Bittrich [a, *], Frank Windrich [b, c], Dominik Martens [a, d], Lars Bittrich [a], Liane Häussler [a], Klaus-Jochen Eichhorn [a]

[a] Leibniz Institut für Polymerforschung Dresden e.V., Dresden, Germany
[b] Center "All Silicon System Integration Dresden", Fraunhofer IZM, Moritzburg, Germany
[c] Organic Chemistry of Polymers, Technische Universität Dresden, Dresden, Germany
[d] New Mexico State University, Las Cruces, NM, USA

A R T I C L E I N F O

*Article history:*
Received 18 April 2017
Received in revised form
5 September 2017
Accepted 19 September 2017
Available online 21 September 2017

*Keywords:*
Glass transition
Polyimide
Thin film
Spectroscopic ellipsometry

A B S T R A C T

We characterized the glass transition temperature $T_g$ of thin polyimide films by temperature-dependent spectroscopic ellipsometry and compared the results to DSC measurements of the bulk polymer. The effect of the curing temperature on $T_g$ and the thermal expansion $\alpha(T)$ was analyzed. An improved ellipsometric data evaluation was used to get most precise and reliable $T_g$ data. $T_g$ increased with increasing curing temperature, while the bulk $T_g$ was considerably lower than the thin film $T_g$. Both observations are attributed to the temperature sensitive release of the imidization by-product 2-hydroxyethyl methacrylate (HEMA) and crosslinker components as well as decomposition products from the material. Variation in the curing temperatures of 230–380 °C led to an increase in the $T_g$ of 34 °C.

© 2017 Elsevier Ltd. All rights reserved.

## 1. Introduction

Thin polymer films are widely used as interlayer dielectric and for microelectronic packaging applications. Here, low processing temperatures become essential in today's 3D integration and advanced packaging technologies due to the complexity of material combinations [1]. New materials with low curing temperatures like BCB or polyimide (PI) materials were developed, and the polymerization (curing) process analyzed [1–3]. For an ester-type photosensitive polyimide, Windrich et al. showed that full imidization can be achieved for a curing temperature of 230 °C after 80 min with previous UV exposure at 200 mJ/cm$^2$ [2]. Additionally, temperature dependent layer thickness and refractive index were modelled from dynamic ellipsometric scans with a heating rate of 5 K/min [3]. The specific changes in the layer parameters were assigned to three sub-processes. The main imidization reaction is assigned to sub-process II from 175 to 260 °C. During the imidization, 2-hydroxyethyl methacrylate (HEMA) crosslinkers are cleaved from the polymer side chains leading to considerable shrinkage of the film. Sub-process III starts at 300 °C and is characterized by further cleavage of HEMA molecules and release of decomposition products (e.g. $CO_2$) of the remaining crosslinker [3]. Between both sub-processes there is a temperature range were the thermal expansion of the film is balanced by slight shrinkage due to outgassing and decomposition of film components, and the film thickness stays constant.

During the polymerization process physical properties of polymer materials, like the glass transition temperature $T_g$, change drastically and can, in principle, be utilized for process control. For example, for BCB it was shown, that its $T_g$ increased with the degree of polymerization/cross-linking, highly dependent on the curing conditions [1]. On the other hand, low molecular weight compounds lead to a depression of $T_g$ [4].

The $T_g$ of bulk polymer materials is commonly characterized by DSC measurements, while for application-oriented thin films the $T_g$ can be determined by ellipsometry [5,6]. Determination of $T_g$ in thin films allows to characterize the polymer material directly on the substrate with respect to certain process conditions. $T_g$ differences between bulk and thin films should be considered. For thin

* Corresponding author.
*E-mail address:* bittrich-eva@ipfdd.de (E. Bittrich).

https://doi.org/10.1016/j.polymertesting.2017.09.030
0142-9418/© 2017 Elsevier Ltd. All rights reserved.

films $T_g$ is derived from the modelled layer thickness (and refractive index) or from the original ellipsometric angles. The abrupt change in the respective parameter at the glass transition is evaluated, which is due to the change of the thermal expansion at $T_g$. Evaluation of $T_g$ can be done either by tangent fitting [7], derivation of the thickness data to directly evaluate the thermal expansion [8], or by using a fit-function for the temperature dependent layer thickness [5,9].

In this work, we investigate the dependency of the $T_g$ of polyimide films on curing temperatures in the range of sub-processes II (imidization) and III (release of small molecule weight compounds). We study films with a high degree of imidization by using curing temperatures ≥230 °C, and focus on the effect of the release of low molecular weight compounds on the thin film properties. Additionally, we compare $T_g$ of the thin films with values obtained for bulk samples.

## 2. Materials and methods

### 2.1. Materials

A photosensitive poly (amic ester) PI precursor was obtained from FUJIFILM Electronic Materials (LTC9300 series). The low-temperature cure PI precursor is modified with an oxime derivate curing catalyst that allows for a reduction of the curing temperature. It consists of a photo-crosslinkable poly (amic methacrylate ester) with 2-hydroxyethyl methacrylate (HEMA) functional groups in the side chain (Fig. 1). The double bonds of the methacrylate can be crosslinked by UV light, initializing a "free-radical" reaction. Additionally, a photo-initiator, external methacrylate based crosslinking additives, stabilizers, adhesion promoter and optical modifiers are used. The details of all the components are not published by the manufacturer. Precursor and additional components are dissolved in a mixture of γ-butyrolactone (GBL) and dimethylsulfoxide (DMSO). Dilution of the PI precursor was done in a mixture of DMSO/GBL (20/80 wt%).

### 2.2. Film preparation

A double side polished, boron-doped 300 mm CZ silicon wafer was spin coated with the diluted PI precursor solution ($\eta_{20}$ = 139 mPas) to get a thickness of 1220 ± 20 nm. The casted film was soft baked in a contact hot plate at 100 °C for 300 s in a CDA atmosphere, and UV exposure (365 nm wavelength) was performed with a 5kW mercury-vapor lamp on a SUSS MA300 Gen2 Mask Aligner. Curing was either done at a Koyo Thermo Systems Co. VF5700B-F vertical furnace under $N_2$ or in the ellipsometry heating cell under Argon. Curing temperatures were 230 °C, 260 °C, 300 °C, 350 °C, and 380 °C. All samples were cured for 3 h, except at 350 °C. This sample was cured for 60 min as given in the data sheet of the manufacturer. Depending on the curing conditions the film shrinks differently due to the release of volatile components and imidization by-products. The homogeneity of the films was investigated by an interferometric sensor using white light (CWL-FT on MicroProf 300, FRT GmbH, Bergisch Gladbach, Germany) before and after curing at 350 °C for 60 min (Fig. 2 a, b). Refractive indices were set to n = 1.73 and n = 1.85, respectively. Mapping was done with a minimum resolution of 0.2 × 2.2 mm. Thicknesses are 1.21 ± 0.01 μm for the film as coated and 0.62 ± 0.01 μm after curing. Please note that the thickness after curing differs from the thickness given in Table 1 (in 3. Results and discussion) due to the pre-set refractive index. The error is given as twice the standard deviation over all data points. AFM measurements (Dimension 3100 Nanoscope IIIa, Veeco, USA) were done on a 10 × 10 μm area of the sample (cured 350 °C, 60 min) after three heating cycles for $T_g$-determination (Fig. 2c). The film was very homogeneous with very low roughness of $R_q$ = 0.5 nm.

### 2.3. Differential scanning calorimetry and thermogravimetric analyses

Differential scanning calorimetry (DSC) measurements were performed on a DSC Q 2000 (TA Instruments, New Castle, DE, USA) under nitrogen atmosphere. The measurements were carried out within the temperature range of −80 °C to 300 °C with 2 $Kmin^{-1}$ heating and cooling rates. The glass transition temperatures $T_g$ were determined from the second heating run to exclude the effects of thermal history. They were calculated according to the half-step method.

Thermogravimetric analyses (TGA) were done using a TGA Q5000 (TA Instruments, New Castle, DE, USA) under nitrogen atmosphere. The measurements were carried out under isothermal conditions with 230, 250, 280 and 350 °C process temperature. The heating rate from 30 °C to the desired isothermal process temperature was 10 $Kmin^{-1}$.

### 2.4. Temperature dependent ellipsometry

Ellipsometric measurements are sensitive to changes in the polarization state of light, reflected from a surface. The ellipsometric parameters tan Ψ (relative amplitude ratio) and Δ (relative phase shift) are derived from the reflected intensities $I_p$ (p-polarized electrical field) and $I_s$ (s-polarized electrical field) [10,11]. These parameters are connected to the Fresnel reflection coefficients, which are complex functions of the angle of incidence $\Phi_0$, the wavelength λ, the optical constants of the substrate ($N_s$), the ambient medium ($n_{amb}$), and the optical constants of surface layers ($n_j$,$k_j$) as well as their layer thicknesses $d_j$. These layer properties can be modelled by an iterative fitting algorithm from the ellipsometric data.

Temperature dependent spectroscopic ellipsometry was done on a rotating compensator ellipsometer at multiple wavelengths (245–1680 nm) in reflection mode (M2000-UI, J.A. Woollam, Co. Inc. USA). The angle of incidence was fixed at 70°. Measurements

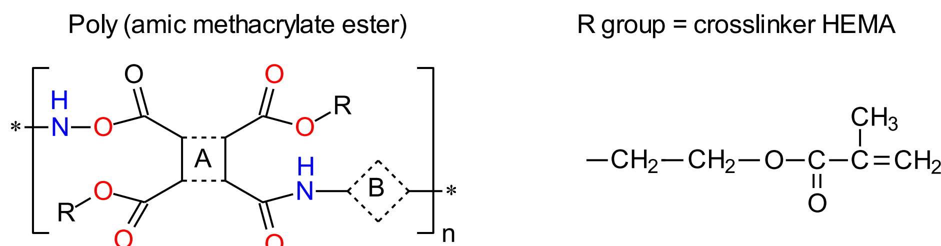



**Fig. 1.** Principal structural formula of the photo-crosslinkable poly (amic methacrylate ester) and the 2-hydroxyethyl methacrylate (HEMA) functional groups. "A" represents the backbone of an aromatic dianhydride and "B" the backbone of an aromatic diamine.

Download English Version:

https://daneshyari.com/en/article/5205207

Download Persian Version:

https://daneshyari.com/article/5205207

Daneshyari.com