Novel Technique for Measuring Through-Plane Modulus in Thin Polymer Films

Kaushal S. Patel, Paul A. Kohl, *Member, IEEE,* and Sue Ann Bidstrup-Allen

***Abstract*— Polymer thin films are widely used as coatings and interlevel dielectrics in microelectronic applications. In multilayer structures, stresses generated in the films due to interaction with adjacent layers and solvent evaporation induced shrinkage, cause the polymer chains to orient in the plane of the film resulting in anisotropic film properties. Characterization of properties in all directions is essential for accurate electrical and mechanical design and modeling.**

A new technique has been developed to measure, *in-situ*, the through-plane (z) stress-strain behavior of thin polymer films. A parallel plate capacitor device and an interdigitated electrode structure were used as sensors to detect changes in dielectric constant and thickness of thin polymer films under compression. Results are reported for 8–14 micrometer thick, Dow Chemical Cyclotene 3022 benzocyclobutene (BCB) films. The dielectric constant was found to change linearly with stress. Using this result, the through-plane stress-strain curve was obtained.

***Index Terms*— Benzocyclobutene, dielectric constant, elastic modulus, interdigitated electrode, parallel plate capacitor, polymer thin film, stress-strain curve, through-plane.**

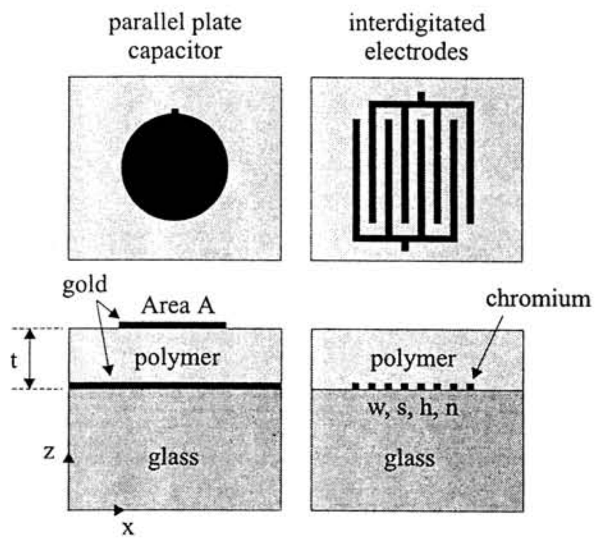

Fig. 1. Parallel plate capacitor and interdigitated electrodes.

I. INTRODUCTION

THIN polymers films (<20 μm) used as inter-level dielectrics and passivation layers are essential components of advanced electronic packages [1], [2]. Polymer films are typically deposited from solution by spin-coating, spraying, or extrusion coating. During processing, stresses are generated in the film as the solvent evaporates and the film collapses in the through-plane (z) direction while being constrained by the substrate in the in-plane (x) direction. Stresses also arise due to mismatches in the coefficient of thermal expansion (CTE) between the film and the substrate [3], [4]. These residual stresses can cause polymer chain orientations [5] which result in different thermo-mechanical properties in the plane and normal to the plane of the film. Since thin film mechanical properties are critical for electrical and mechanical design and modeling, it is desirable to have the properties characterized *in-situ* in order to accurately determine the conditions during use. Some properties, however, are difficult to measure. Measurement of the through-plane elastic modulus (E_z) is limited by the high sensitivity needed to detect z-direction strain in thin films. Some researchers have used indirect, ex-situ techniques like Brillouin scattering [6] and laser induced ultrasonic wave propagation [7] to measure E_z for free standing films. Wu and Questad [8] used an air capacitance gauge to measure strain in thick (> 75 μm), free standing, polyimide films under compression. This paper presents a novel, *in-situ* technique for measuring the through-plane stress-strain behavior, and hence the modulus, of constrained, thin polymer films (< 20 μm) for small strains. The results reported in this paper are the first measurements for Dow Chemical Cyclotene 3022–57 benzocyclobutene (BCB) films on a substrate. An "effective" modulus ($E_{z,\text{eff}}$), defined as the stiffness of the film while it is constrained on the substrate and determined here as slope of the stress-strain curve, was calculated and compared with reported modulus measurements.

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II. BACKGROUND

This technique involves the use of two devices, shown in Fig. 1, as capacitive sensors to detect changes in dielectric constant and thickness of a polymer film under normal, compressive stress. The capacitance between unequal parallel plates, represented by (1), depends upon the dielectric permittivity of the polymer ϵ', the area of the smaller plate A and the thickness of the film t

$$C = \frac{\epsilon' \epsilon_0 A}{t} + C_f. \tag{1}$$

C_f is the fringing field correction [9] and ϵ_0 is the permittivity of vacuum equal to 8.854×10^{-12} F/m. When a through-plane stress is applied to the film, both the thickness and dielectric permittivity of the polymer change thereby changing the capacitance. In order to calculate the thickness change, the dependence of dielectric permittivity on applied stress must first be determined. This was done using the interdigitated electrodes (IDE). The capacitance of these electrodes is a function of the geometry parameters such as the width of the electrode fingers (w), spacing between the fingers (s), height of the metal (h), the number of fingers (n) and the dielectric permittivity of the substrate (ϵ'_{sub}) and the polymer (ϵ'). The capacitance is independent of film thickness for thickness-to-electrode spacing ratios greater than two because the electric field does not fringe through the air and is contained mostly within the polymer and the substrate. This was confirmed by the authors through finite element modeling of the electrodes. Since the geometry of the electrode and permittivity of the substrate do not change significantly on application of a through-plane stress, change in capacitance of the electrode is primarily because of changes in dielectric permittivity of the polymer. The permittivity-stress relationship was obtained by finite element modeling and used to calculate the thickness change and hence, the stress-strain curve for the film.

The stress-strain behavior measured using this technique represents the through-plane deformation of the film for small strains, under a normal applied stress, while it is constrained on the substrate. The nature of this curve is a consequence of the state of initial stress in the film and the no-slip adhesion constraint at the interface with the substrate. Thus, in order to determine E_z, the stress in the film must be modeled with the appropriate boundary and initial conditions. As a preliminary estimate, however, the slope of the stress-strain plot or the "effective" modulus can be used.

III. Experimental Method

The structures shown in Fig. 1 were fabricated with BCB as the dielectric and soda-lime or low expansion borosilicate glass as the substrate. The substrates were rectangular with dimensions 40 × 30 × 1.5 mm. The capacitor structures were fabricated by spin-coating the polymer onto a sputtered layer of gold on glass. The spin speed was adjusted to obtain films between 8 and 14 μm thick. A 0.5 weight% solution of 3-aminopropyltriethoxysilane (3-APS) was used as the adhesion promoter between the gold and the polymer. The films were cured in a tube furnace under nitrogen for one hour at 250 °C. The top layer of gold, about 3000 Å thick, and a thin chromium adhesion layer were then sputtered onto the polymer and patterned using photolithography to form 10 mm diameter circular capacitors. The interdigitated electrodes were patterned from chromium coated glass plates and coated with the polymer film. The electrodes were composed of 200 lines each with 3 μm linewidth and 3 μm spacing. The fabricated electrode and capacitor structures on glass were mounted in a polycarbonate sample holder and mechanically loaded to failure by a screw driven Instron 5567 testing machine with a polycarbonate piston.

Capacitance and conductance of the devices were measured using a Hewlett Packard 4263A LCR meter at a frequency of 10 kHz and an input level of 1 V. The reported values are the average of 128 consecutive measurements.

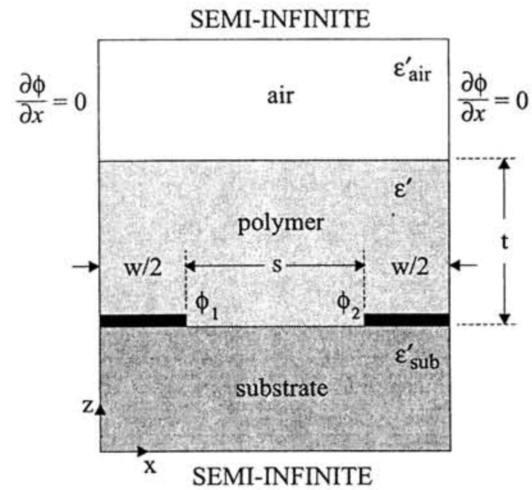

Fig. 2. Finite element modeling of interdigitated electrodes.

The capacitance of the parallel plate capacitor device was corrected for fringing fields as per ASTM standard D150–92 [9] and modeled using (1). The IDE structures were modeled using Maxwell EM 2D, a commercially available electromagnetic modeling program from Ansoft Corporation, Pittsburgh, Pennsylvania. The two-dimensional (2-D), electrostatic model for a segment of the structure is shown in Fig. 2. The model represents the halves of two electrodes coated with a polymer film and is symmetrical about the plane passing through the center of each electrode. ϕ_1 and ϕ_2 are the potentials of each electrode and ϕ represents the electric field potential. The finite element mesh was dynamically generated by the software using Delaunay triangulation. The convergence criteria was 0.01% error in the total energy of the model.

IV. Results and Discussion

The change in dielectric permittivity of a 14-μm thick BCB film under compression, measured using the interdigitated electrodes, is plotted in Fig. 3. The permittivity increases linearly (R^2 greater than 0.975) for compressive stresses greater than 2.5 MPa, with a slope of 0.5148 ± 0.0615 GPa^{-1} averaged over two samples. The data shown in Fig. 3 was obtained from one of the samples over multiple loading-unloading cycles. The absolute value of capacitance and hence permittivity differed between experiments but were within the measurement accuracy of the LCR meter (±0.03 pF for 100 pF at 10 kHz). This, however, did not affect the gradient since the same offset was incurred during each measurement in an experiment. The capacitance increase detected by the electrodes was not very large and could have been attributed to several factors. Contributions due to changes in electrode geometry, such as deformation in the metal lines, were modeled and shown to be insignificant. Also, the high modulus of the glass substrate (72 GPa for soda-lime glass) discounted any deformation-induced changes in dielectric constant of the substrate. Hence, the increase in capacitance was only due to an increase in dielectric permittivity of the polymer. Below

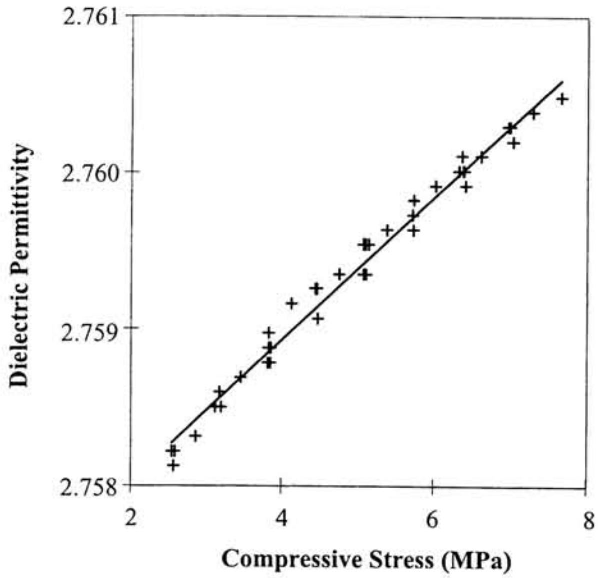

Fig. 3. Change in dielectric permittivity of Cyclotene 3022-57 thin film under compression.

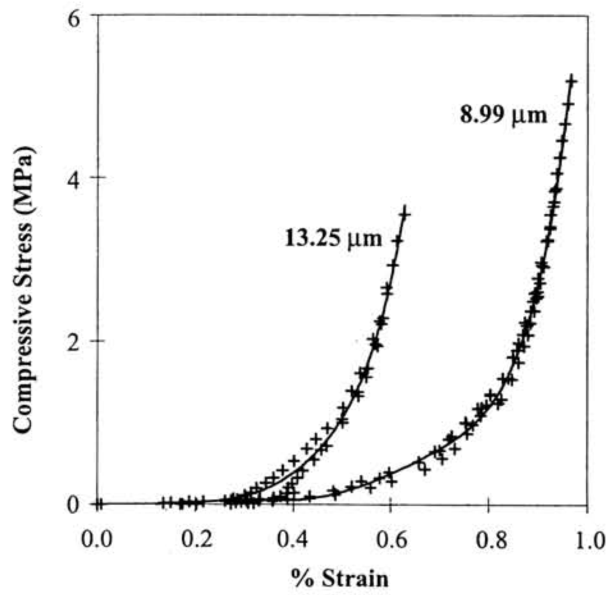

Fig. 4. Compressive stress-strain curve for constrained Cyclotene 3022-57 thin film.

2.5 MPa, the permittivity change was not linear but dependent on the initial state of stress in the polymer.

The increase in dielectric permittivity can be explained in terms of free volume reduction in the polymer film. Xie *et al.* [10] used positron annihilation lifetime spectroscopy to measure changes in the volume and number density of microvoids in amorphous polycarbonate due to thermal expansion and applied stress. Under uniaxial compression, they observed that the void volume fraction decrease was linear with stress for small strains. Such a reduction in free volume would cause the charge density in the polymer to increase, thus increasing the dielectric permittivity.

The through-plane, compressive stress-strain curve measured using parallel plate capacitors and interdigitated electrodes for two constrained films, 8.99 and 13.25 μm thick, is shown in Fig. 4. The linear relationship for dielectric permittivity versus stress was used to decuple the thickness and permittivity contributions to the change in capacitance of the parallel plates. The shape of these curves depends upon the residual stress in the film. Above 3 MPa, the curves are linear with a slope 4.0 GPa ($R^2 = 0.99$) for the 8.99 μm film and 4.5 GPa ($R^2 = 0.97$) for the 13.25 μm film. This is referred to as the effective modulus $E_{z,\text{eff}}$ of the film. The significance of this modulus is evident from the following explanation. Recall, residual stresses are generated in the plane of the film due to CTE mismatches with the substrate. Since the CTE of BCB (52 ppm/°C) is higher than the CTE of glass (9.4 ppm/°C of soda-lime, 3.7 ppm/°C for low expansion borosilicate), at room temperature the polymer film experiences biaxial tension because the substrate constrains the film. This causes the substrate to bow slightly with the polymer film on the concave side [11]. As a through-plane compressive stress is applied to the sample, the bow of the substrate is straightened out. This causes a significant increase in the in-plane tensile stress resulting in a large compressive deformation in the through-plane direction. Compressive strain is also a direct consequence of the applied stress. This is the low stiffness region in Fig. 4.

After the bow is mitigated, through-plane strain occurs because of the applied stress. The deformations are small, but independent of the initial state of stress in the film. Hence, the effective modulus is calculated in this high stiffness region.

The elastic modulus of BCB is not well characterized. A value of 2.0 GPa was reported for uniaxial, in-plane, tensile modulus of free standing BCB film in a non peer-reviewed publication [12]. A recently published book gives the value of the modulus of BCB as 2.9 GPa [1]. Measurements of planar, biaxial modulus made using a wafer curvature technique by Hodge [13] reports 4.290 ± 1.469 GPa for 15-μm thick films which yields 2.83 GPa for in-plane modulus. The in-plane Poisson's ratio for BCB is 0.34.

The $E_{z,\text{eff}}$ measured by this technique can be related to the through-plane modulus E_z by conducting a simplified stress analysis of the system. First, all the Poisson's ratios are assumed to be the same and equal to 0.34. The film is constrained by the substrate and the stress is assumed to be axisymmetric in the plane of the film. Using the generalized Hooke's law, a relationship between the through-plane stress, through-plane strain, and the in-plane strain is obtained by substitution for in-plane stress from expressions for in-plane and through-plane strains. Next, the in-plane strain is expressed in terms of the volumetric strain (compression in volume) and through-plane strain in the film. $E_{z,\text{eff}}$ and E_z can then be related by

$$\frac{1}{E_z} = \left(\frac{1}{1+\nu}\right)\left[\frac{1}{E_{z,\text{eff}}} + \left(\frac{\nu}{1-2\nu}\right)\frac{1}{K_z}\right] \tag{2}$$

where K_z is the volumetric strain per unit through-plane stress and can be determined from the dielectric permittivity data using the Classius–Mossotti equation. E_z calculated using this relationship is 3.0 ± 0.2 GPa and 3.2 ± 0.2 GPa for 8.99 and 13.25 μm thick films, respectively [14].

Since BCB is an electrically isotropic, glassy polymer, it follows that it is likely to be mechanically isotropic. Hence, assuming the Poisson's ratios to be equal is reasonable. The match between the calculated through-plane modulus and the reported in-plane modulus further validates this assumption.

To accurately determine E_z, the stress in the film must be modeled by finite element methods with consideration for edge effects and the no-slip adhesion constraint on the film at the interface with the substrate.

V. Conclusion

Thin polymer dielectrics in microelectronic applications are known to possess direction-dependent thermo-mechanical properties. This anisotropy is caused by residual stresses created in the polymer because of solvent evaporation induced shrinkage and CTE mismatches with the substrate. Since these properties are critical in electrical and mechanical design, *in-situ* characterization of directional properties is required to duplicate the conditions the film experiences during use. A novel, *in-situ* technique was presented for estimating the through-plane modulus of thin polymer films. The technique utilizes a parallel plate capacitor and an interdigitated electrode as capacitive sensors to detect changes in dielectric permittivity and thickness of the polymer film on application of a through-plane compressive stress. Results were reported for 8–14 μm thick BCB films. The material property response at low applied stress was found to depend upon the residual stress in the polymer. At higher stresses, the thickness and the permittivity changed linearly with stress. An effective modulus of the film was determined as 4.0 GPa for a 8.99 μm film and 4.5 GPa for a 13.25 μm thick film and was found to compare well with reported modulus values.

Acknowledgment

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