RESIDUAL STRESS IN THIN-FILM PARYLENE-C

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ABSTRACT

This paper reports the influence of thermal annealing on the residual stress in parylene-c thin-films on silicon. Although recently others have used the diaphragm bulge testing method to measure the residual stress in parylene, this is the first extensive study of residual stress in parylene using the load-deflection method and rotating tip strain gages. This paper supports the hypothesis that stress is relaxed in parylene-c films at elevated temperatures (>100 °C) and that thermal stress accounts for 90% of the residual stress in films that have undergone annealing at these elevated temperatures. It was found that this held true up to 180 °C which is above the glass transition temperature of the material.

INTRODUCTION

Parylene has shown promise as a MEMS material because it is bio-compatible and can be conformally deposited at room temperature. It has been used to create microfluidic devices such as check valves, nozzles, and electrophoresis chips.[1-3] However, if the residual stress of the parylene is outside the parameters of the device design, the device could fail. Therefore, it is important to properly understand the role of temperature history in the residual stress of parylene. Earlier work lays a foundation for this study.

Dabral *et al.* [4] studied the stress in thermally annealed parylene films using the radius of curvature method. They found that higher annealing temperatures resulted in higher residual stresses in their samples. They also found that controlled cooling would result in lower stress than quenched samples. In their study they use the stress equation, Eq. 1, to calculate the thermal coefficient of expansion (TCE, α) of parylene-c.

Sim *et al.* [5] used the idea that the stress in the film is relaxed at the elevated temperature to correlate their simulation results. They used the stress equation and published values of the TCE for parylene-c and silicon to calculate what the thermal stress would be. In this study, we also accept the TCE provided by the dimer manufacturer and use the stress equation to calculate the stress due to thermal expansion.

$$\sigma_{th} = \frac{E}{1-\nu}(\alpha_{Si} - \alpha_{Pa-C})\Delta T \tag{1}$$

This paper presents experimental results from stress measurements of parylene-c films annealed at different temperatures and correlates them with the thermal stress in the film. The measurements are made using two different methods, rotation tip strain gages and load-deflection membranes.

STRUCTURES AND EXPERIMENTAL SETUP

Rotation Tips

Rotation tips convert strain into a rotation whose angle is directly proportional to the strain of the material [6]. This is a particularly useful gage because it can simultaneously measure compressive and tensile stress and does not require an array of structures to perform the measurement. Fig. 3 illustrates the rotation tip structure. The strain in the film can be calculated with Eq. 2.

$$\varepsilon = \frac{\tan(\alpha) * \mathrm{O}}{\mathrm{LA} + \mathrm{LB} + \mathrm{W}} \tag{2}$$

The rotation tips were fabricated using the process illustrated in Fig. 1. First, 2 µm polysilicon was

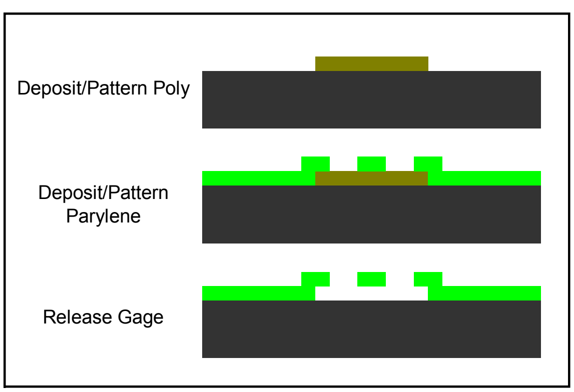

Fig. 1: Fabrication for the rotation tip

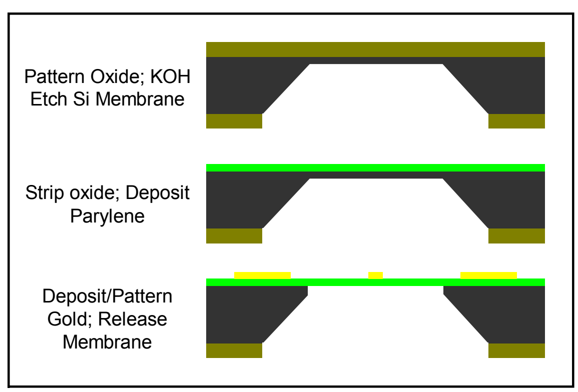

Fig. 2: Fabrication for the membrane

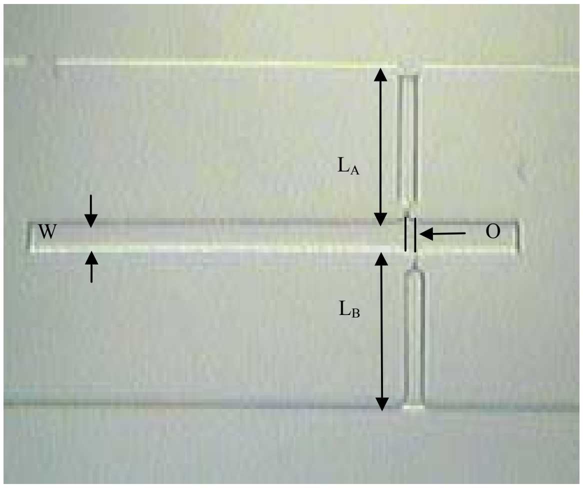

Fig. 3: Rotation Tip

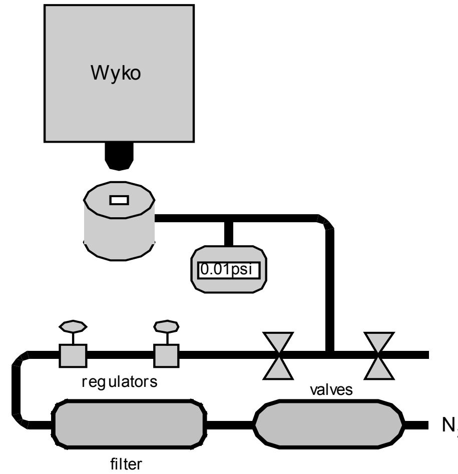

Fig. 4:Testing Setup

deposited on the oxide surface and it was patterned using DRIE. Then, 0.5 µm parylene was deposited on top of the polysilicon and patterned using O_2 plasma. At this point, the wafer was diced into individual samples and annealed at various temperatures. Finally, the rotation tip was released using BrF_3 etching.

The rotation tips are a direct measurement of the strain in the material. Therefore, the tips were recorded using a CCD camera and optical microscope. The rotation angles were then measured from the pictures.

Load-Deflection Membranes

In the bulge test, a load is applied to a membrane as pressure and the deflection is then measured [7]. For a rectangular membrane, Eqn. 3 relates the load and deflection where P is the pressure, h is the deflection, σ is the stress in the film and E is the Young's modulus. The dimensions of the membrane are 2a and 2b (a<b) with thickness t. The coefficients are functions n = a/b and ν, the poisson ratio. This provides a means for measuring both the stress and the modulus simultaneously[7].

$$P = \frac{C_1(n)\sigma th}{a^2} + \frac{C_2(n,\nu)Eth^3}{a^4} \qquad (3)$$

The membranes used in the load-deflection test were approximately 1.5x2.7 mm^2 with a thickness of 3 µm. Fig. 2 illustrates the fabrication of the load-deflection membrane. First, a suitable silicon membrane was produced. The desired membrane pattern was etched into the oxide mask on the backside of the wafer. Then, KOH etching was used to produce silicon membranes with a thickness of ~20 µm. Second, the remaining oxide on the front side was removed using BHF and the wafer was placed in the parylene deposition chamber. Approximately 3µm of parylene-c were deposited. Third, 10nm Cr/10nm Au was evaporated on the wafer and patterned to provide reference points for interferometric measurement. On the center of the membrane, a single 20x20 µm^2 square was patterned. The wafer was diced into individual samples at this point and annealed at various temperatures. Finally, BrF3 etching from the backside released the parylene-c membrane from the silicon membrane. Fig. 5 shows a finished membrane.

The load-deflection measurements were made using a simple set of pressure regulators and needle valves for pressure regulation in the low pressure region (< 1 psi) and a Wyko NT2000 interferometer for measuring the deflection. The setup is illustrated in Fig. 4. The pressure regulators regulated between 0.5 - 30 psi and the needle valves functioned as pressure dividers reducing the effective pressure into repeatable 0.01 psi increments. The pressure was measured with an Omega PCL100-30 pressure calibrator with 0.001 psi resolution.

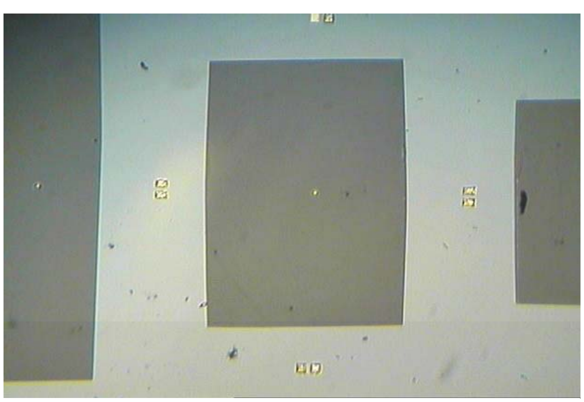

Fig. 5: Parylene-c membrane

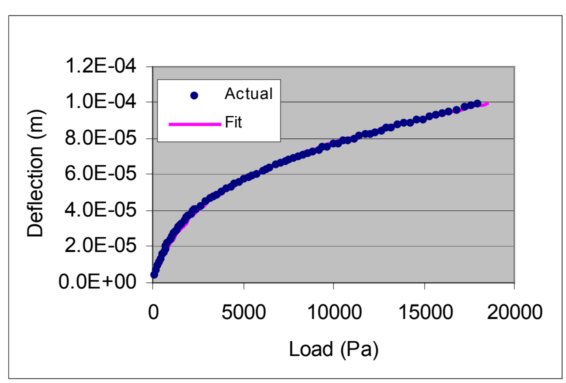

Fig. 6: Load-Deflection Measurement

The Wyko interferometer measures 3D surface profiles with an accuracy of 0.05 µm. However, the measurement of thin films introduces small offsets in the measurement. Therefore, small gold reference points were introduced to allow the Wyko to record accurate measurements of the deflection of the membrane. The resulting data was then fit to Eq. 3 to calculate the stress and modulus of the material. Fig. 6 shows an example of the load-deflection data acquired by this method.

In fitting the data to Eqn. 3, a poisson's ratio of 0.4 was used. While the ratio used has a significant effect on the young's modulus determined, it has a no effect on the residual stress determined.

RESULTS & DISCUSSION

Rotation Tips

The rotation tips were annealed for 30 minutes at intervals from 100 °C to 200 °C. Table 1 summarizes the results. The calculated strain is obtained using Eq. 2. The theoretical strain is the strain based solely on thermal stress. This produced a curve that had the same slope as the calculated values but had an offset. In Dabral's paper, they found that the material would maintain a 10 MPa compressive stress at the elevated temperature. Therefore, an intrinsic stress of –10MPa was added to the theoretical strain formula. Eq. 4 was used to calculate the theoretical strain.

$$\varepsilon = \frac{\sigma_{th}}{E} = \frac{(\alpha_{Si} - \alpha_{Pa-C})\Delta T}{1-\nu} + \frac{\sigma_{offset}}{E} \qquad (4)$$

Table 1: Stress in rotation tips annealed 30 mins

Annealing Temperature	Rotation Angle	Calculated Strain (%)	Theoretical Strain (%)
100	1.44	0.17	0.22
120	2.80	0.33	0.34
140	3.35	0.39	0.46
160	4.10	0.48	0.57
180	5.62	0.66	0.69
200	6.21	0.73	0.81

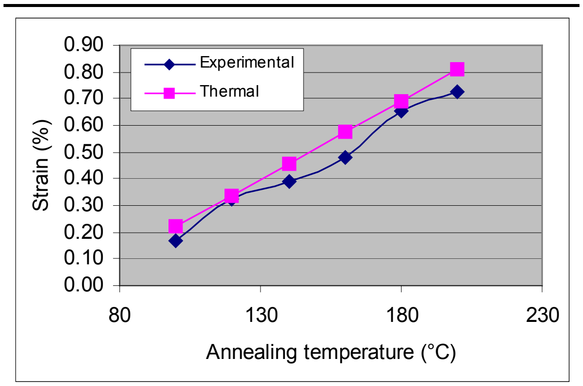

Fig. 7: Stress in rotation tips annealed 30 mins

The TCE for Si is 2.6×10^{-6} and the TCE for parylene-c is 3.5×10^{-5}. While the published value for parylene-c is 3.5×10^{-5} [8], the TCE was also estimated at 3.8×10^{-5} by heating a rotation tip to 140 °C and measuring the rotation angle. A poisson's ratio of 0.4 for parylene-c was assumed in all calculations in this paper.

Fig. 7 compares the strain in the rotation tips with theoretical strain due to thermal mismatch. The experimental results match the theoretical predictions. However, this method does not directly measure stress and requires accepted values for the Young's modulus and poisson's ratio for the material. Therefore, the load-deflection method was pursued.

Load-Deflection Membranes

There are two cases when annealing parylene-c. The fixed case is where the film is bound to a substrate and stresses develop along the substrate film interface during thermal processing. The free case is where the film is bound to a substrate at the boundaries, but is free from the substrate everywhere else. Typical parylene structures have a combination of these two boundary conditions.

Table 2: Stress in Free Membranes annealed 60 mins

Annealing Temperature	Stress (MPa)	Modulus (GPa)	Thermal Stress (MPa)	Stress Ratio
100	21.3	4.82	22.6	1.06
120	28.4	4.90	28.3	1.00
140	34.7	5.29	34.0	0.98
160	42.1	4.87	39.6	0.94
180	50.6	4.10	45.3	0.89

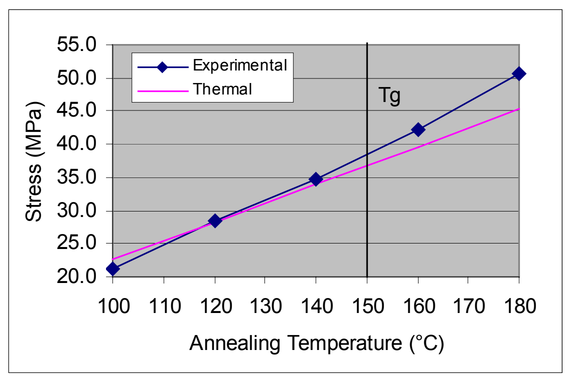

Fig. 8: Stress in free membranes annealed 60 mins

To study the free case, the parylene-c membranes described earlier were released prior to annealing. Then the load-deflection curve was measured and the stress and modulus were calculated. The results are summarized in Table 2. The measured stress was then compared with the stress due to thermal mismatch. The average observed modulus was used to calculate the theoretical stress due to thermal mismatch.

Fig. 8 illustrates the fact that more than 80% of the stress in the free case can be accounted for by thermal mismatch even at temperatures above the glass transition temperature (T_g=150 °C) of the polymer. It is also important to note that at the high stress levels observed at 180 °C the film is dangerously close to the yield strength of parylene-c (55 MPa)[8]. In fact, the membrane burst during testing.

To study the fixed case membranes were annealed for 60 mins prior to BrF_3 release. The results are summarized in Table 3.

Fig. 9 illustrates the fact that there is a very good match between the observed stress and the theoretical thermal mismatch at 140 °C and above. The 100 °C and 120 °C nodes clearly do not fit the theory well. One possibility for this is that the samples may not have been annealed long enough. At lower temperatures the relaxation process should take a correspondingly longer time.

Table 3: Stress in fixed membranes annealed 60 mins

Annealing Temperature	Stress (MPa)	Modulus (GPa)	Thermal Stress (MPa)	Stress Ratio
100	37.8	5.50	24.6	0.65
120	47.6	5.11	30.7	0.65
140	33.8	4.77	36.9	1.09
160	38.1	5.53	43.0	1.13
180	44.4	5.13	49.2	1.11

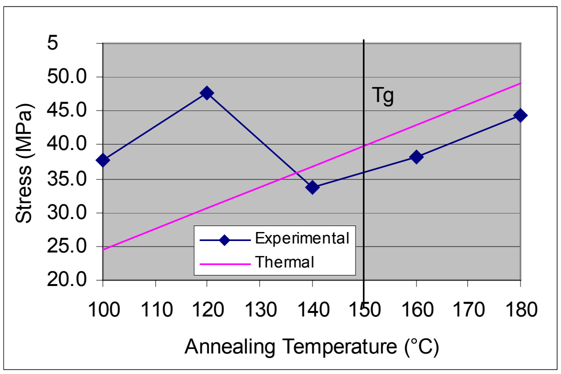

Fig. 9:Stress in fixed membranes annealed 60 mins

Therefore, fixed membranes were annealed for 360 mins to investigate this possibility. The results are summarized in Table 4. Unfortunately, the results for 100°C and 120°C were inconsistent. It is clear that the fixed case is more complicated than the free case and below 140°C the difference in boundary conditions seems to have a significant effect. At 140°C,. the data matches the other results surprisingly well. However, at 160°C and 180°C the results do not match as closely. The extended exposure to temperatures above the glass temperature could have a significant effect. It is also not recommended to expose parylene-c to an air atmosphere at these temperatures because oxygen attacks the polymer causing it to dissociate slowly. The 180°C membrane also burst during testing in this case due to the high residual stress in the film.

Table 4: Stress in fixed membranes annealed 360 mins

Annealing Temperature	Stress (MPa)	Modulus (GPa)	Thermal Stress (MPa)	Stress Ratio
140	33.9	4.65	31.6	0.93
160	52.0	4.34	36.9	0.71
180	48.1	4.41	42.2	0.88

CONCLUSION

The observed residual stresses are within 15% of the calculated thermal stress. From this data we can conclude that the stress in thin-film parylene-c is primarily due to stress relaxation at the annealing temperature and mismatch between the thermal coefficients of expansion of parylene-c and the substrate. This is particularly true near the glass transition temperature.

Since most structures built from parylene can be described in terms of fixed films and free standing membranes, the results here are particularly applicable to parylene devices. The most common form of thermal processing that parylene-c experiences is the baking of photoresist during lithography. This typically involves exposure to 90-120 °C for 10-30 mins. This may happen multiple times during the fabrication of the device. Annealing at 140 °C can bring the residual stress in the device to a known and repeatable value (34 MPa). It is also important to not expose the device to very high temperatures (>160 °C) for extended periods of time. If the device is designed with this in mind, the performance and yield of the device could be significantly improved.

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