

# A Quantitative Adhesion Test for Thin Polymer Films on Silicon Substrates

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## SYNOPSIS

The standard 90° peel test was modified in order to apply it to testing adhesion of thin polymer films to surfaces of silicon substrates, such as the silicon nitride passivation layer used in our solid-state chemical sensors. The goal of this task was to develop a procedure for testing adhesion of both dry and wet films, which would yield repeatable, quantitative results quickly, and with simple sample preparation. It is important to produce valid comparisons of adhesion both over variations of a given polymer composition, and between films made of dissimilar polymer matrices. The method described herein could be applied to adhesion testing of a wide variety of thin polymer layers to solid surfaces.

## INTRODUCTION

Central to the design of longer-lifetime solid-state chemical sensors is development of thin polymer films (membranes) having good adhesion to the surface of the integrated sensor.<sup>1,2</sup> The leading cause of failure in these microsensors has been electrolyte shunts around the membrane due to poor membrane adhesion.<sup>3,4</sup> Unfortunately, methods for characterizing the adhesion of thin polymer films have been imprecise and irreproducible.

The mechanical adhesion of a material to a substrate is a function of substrate surface morphology, temperature, interfacial electrostatic forces, and interfacial chemical bonding. Exact determination of the adhesive strength of a material to a given substrate is difficult because the material is usually deformed by the test procedure. Often, the best that can be achieved is to quantify the adhesion through a threshold test, or to measure a peel force which includes film thickness and elasticity, as well as adhesion. Common methods for adhesive evaluation of thin films are tape,<sup>5,6</sup> blister,<sup>6-9</sup> scratch/scrape,<sup>5,7</sup> ultrasonic bath,<sup>2,4</sup> and peel<sup>5-8</sup> tests.

The tape test involves cutting the polymer film into a grid pattern with a knife, applying an adhesive

tape over the film, peeling off the tape, and observing the percentage of squares that were removed from the substrate. This is a threshold test since the pulling force of the tape is assumed to be constant [roughly 6 lb/in.<sup>2</sup> for poly(vinyl chloride)]. This most popular test for thin film adhesion has a number of drawbacks. Adhesion of the tape itself varies with film material; some polymers have very poor adhesion to the tape. This variation invalidates comparisons between types of polymers. Adhesion is also a function of several uncontrolled variables: preparation technique, angle of the tape, pulling force, and pulling rate. The tape test cannot be used on wet polymer films (the condition of greatest interest for our work). Finally, results of the tape test are binary for all polymer films except those having adhesion to the substrate which is similar to their adhesion to the tape.

The blister test is implemented by forming a suspended polymer membrane structure and applying an increasing pressure to the membrane backside until peeling from the substrate is initiated. Average work of adhesion can be calculated from spatial deflection, pressure, and area peeled.<sup>9</sup> The blister test yields quantitative results, but depends on operator judgment in determining the area peeled. In addition, it requires rather involved processing to prepare samples for testing (backside masking and micro-machining of the silicon substrate). In sample preparation, membranes are exposed to the wafer etching

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process, which can alter their characteristics before the test begins. Because membranes are deformed in this test, results are subject to membrane elasticity and thickness. Polymers having strong adhesion compared to cohesion cannot be tested with this method because they rupture before peeling begins. More complex structures have been developed to extend the range of measurements.<sup>9</sup>

The scratch/scrape test is performed by contacting the film with a moving stylus and increasing the normal force until the substrate is seen. This test, too, gives quantitative results, but is dependent upon operator judgment. Observed adhesion will be a strong function of other polymer physical properties, and of film thickness. In some cases the stylus crushes the film and the applied force is not correlated to adhesion.<sup>5</sup>

The ultrasonic bath is also a threshold test, since the forces induced on the polymer/substrate interface by ultrasonic stimulation fall within a narrow range. This method inherently convolves effects of soaking with forces to dislodge the polymer film. When the polymers have strong adhesion, the test is very time-consuming, lasting days, during which time the polymer films must be checked at regular

intervals for detachment. Unless its temperature is controlled, the solution is heated over time by the ultrasonic energy, increasing the effect that soaking has on results. In evaluating a variety of polymer materials in ultrasonic-bath accelerated lifetime tests, a correlation between adhesion time and compliance of the polymer film has been observed.<sup>2</sup> The ultrasonic vibrations are more effective at detaching rigid films which are unable to absorb the ultrasonic energy through elastic deformation. Comparisons of dissimilar polymer matrices with this method suffer from a systematic error which favors softer matrices.

Peel tests are used primarily to study adhesion of metal films to various surfaces. A machine similar to the tensilemeters used for finding Young's modulus and other physical properties from stress/strain curves<sup>10</sup> is used to peel the film from the substrate while maintaining a constant pulling rate and angle. Physical attachment to metal film is usually made by soldering a metal strap to it. When the film is not metal, it is often deposited over a bracket at one end, which can be gripped by the test equipment. The pulling force is monitored as the film is peeled. From the pulling force data, and the width of the strip removed, peeling force is calculated. Peel tests produce a more quantitative and reliable measure of interfacial adhesion than any of the tests described above.

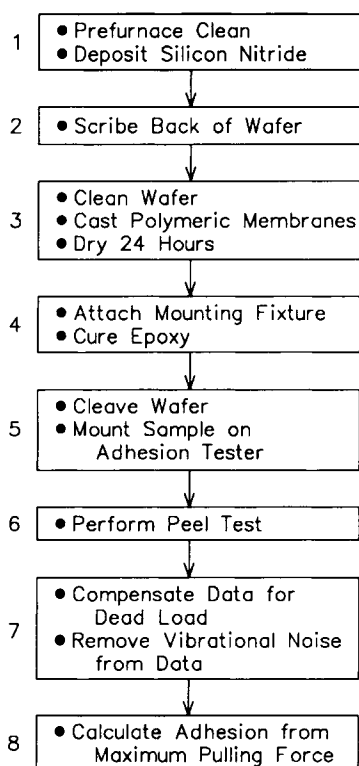
## EXPERIMENTAL

A well-controlled peel test was developed for evaluating the adhesion of thin polymeric membranes to solid surfaces. The test yields repeatable, quantitative results for both dry and wet membrane adhesion. In this example, the solid material is silicon nitride ( $\text{Si}_3\text{N}_4$ ), and four membrane compositions are evaluated:

- Poly(vinyl chloride) (PVC)
- Poly(vinyl chloride) with the hydroxylated copolymer poly(vinyl chloride/vinyl acetate/vinyl alcohol) [(PVC)/(PVC/Ac/Al)]
- Polyurethane (PU) with the hydroxylated copolymer [(PU)/(PVC/Ac/Al)]
- Moisture-curable silicone.

## Sample Preparation

Figure 1 outlines the overall adhesion test; the first five steps in this figure show the process flow for sample preparation. The sample preparation for this test, though straightforward, is important in assur-



**Figure 1** Process flow for membrane adhesion test, including sample preparation (1-5), peel test (6), signal processing (7), and computation (8).

ing reliable data. After a prefurnace clean, 7.62 cm silicon wafers are coated with a 360 nm layer of silicon nitride deposited by chemical vapor deposition. A programmable diamond saw is then used to cut an  $203.2\ \mu\text{m}$  deep by  $76.2\ \mu\text{m}$  wide scribe lane across the center of the  $381\ \mu\text{m}$  thick wafers on the back side. Acetone, isopropyl alcohol, deionized water, and nitrogen are used to clean and dry the wafers, which are then ready to have polymeric membranes cast on the front side.

Membrane casting solutions are mixed by completely dissolving the polymer membrane components in 1.2 mL of anhydrous tetrahydrofuran (THF; water content  $< 0.005\%$ ). Glass rings, 22 mm in diameter, are placed on the front of the silicon wafer, centered over the backside scribe lane. These glass rings are filled with casting solution, and the solvent is allowed to evaporate for 30 min until the membranes are partially cured. The glass rings are then removed, and the membranes are dried for 24 h. The average membrane thickness was determined by a micrometer to be  $101.6\ \mu\text{m}$ .

Mounting brackets are attached with epoxy to the back side of the wafer on either side of the scribe lane. When the epoxy is dry the wafer is ready for adhesion testing. The wafer is scribed down the pre-cut lane and the wafer is cleaved by carefully folding the halves, held together by the membrane, forward, so that the membrane halves are touching.

### Adhesion Testing Apparatus

The cleaved wafer is mounted on an Instron 1131 mechanical tester (see Fig. 2) with one half attached to the load cell (Cardinal Scale SP-50L) the other to a stationary grip. This mounting method leaves the membrane free of deformation from mounting fixtures or grips since the membrane contacts only the substrate. Previously reported polymer peel tests depend on clamping the film.<sup>11</sup> The tester has a traveling crosshead which moves at 1.27 cm/min, inducing a pulling force at both membrane/substrate interfaces. The membrane peels from both surfaces at approximately the same rate, maintaining a constant peel angle of  $90^\circ$ . The load cell converts the pulling force to a corresponding differential voltage.

The load-cell voltage is amplified by a precision instrumentation amplifier and then converted to digital representation at 135 samples/s by a 12-bit A/D converter, which is part of a programmable data acquisition and control adapter card (IBM part# 6451502) in an IBM-XT microcomputer. The microcomputer stores the force data and calculates

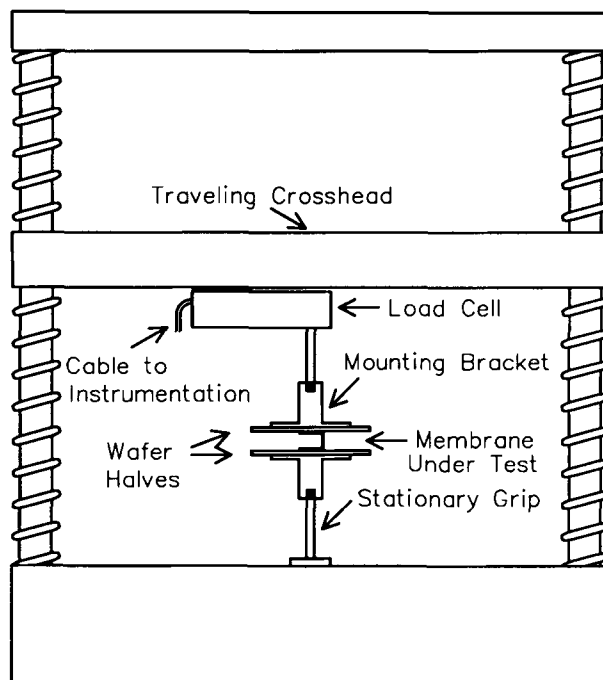


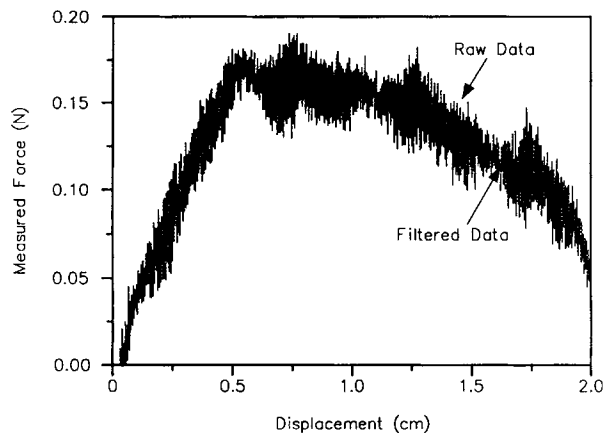
Figure 2 Schematic drawing of adhesion tester.

the crosshead position from the known pulling speed.

### Signal Processing

Processing variations such as imprecise scribing of the wafer, variations in mounting-bracket weight, and differences in the amount of epoxy used on the brackets bias the force data. These effects are compensated by reading a dead-load weight after the membrane is completely peeled, and subtracting it from the force data. For consistency, the membrane weight is always included in the dead load.

Crosshead motion, being driven by mechanical gears and screws, imparts vibrational noise to the load cell. This random (white) noise becomes part of the data stream. We have used both averaging and median filters to remove noise from the signal, with virtually identical results. Since no advantage was seen using the median filter, a computationally simpler averaging algorithm is used. Averages are calculated on samples in a sliding data window. The window is sized large enough so that vibrational noise is removed, but small enough to avoid distorting data by excessive smoothing. Figure 3 shows the raw sampled data compared to the filtered data. The filtered signal follows all of the trends of the raw data, but without the noise. The small fluctuations in the filtered curve are due to mechanical



**Figure 3** Raw and filtered force data versus displacement for a typical polymeric membrane.

imperfections of the interface. Adhesive failures propagate along these imperfections.<sup>8,12</sup>

The processed data is then scanned for the maximum force value, which is taken to represent the adhesion of the material. Use of the maximum value eliminates artifacts related to membrane elasticity, plastic or viscoelastic deformation, or membrane thickness, which shift the force curves and make their shapes peculiar to membranes of different matrices. In our experience, the maximum force the interfacial bond can withstand before yielding is the best representation of the adhesive strength of the membrane material. Since all of our tests are comparative, rather than absolute, and membranes are all of the same size, there is no need to normalize for area.

## RESULTS AND DISCUSSION

The four polymeric membrane compositions were evaluated for adhesion using the procedure described. Table I lists the membrane compositions. Three types of tests were conducted: in case A, the adhesion of membranes having different matrices were compared; in case B, adhesion of a particular matrix was studied over variations in composition; and in case C, membrane adhesion was monitored as a function of adhesion promoter content.

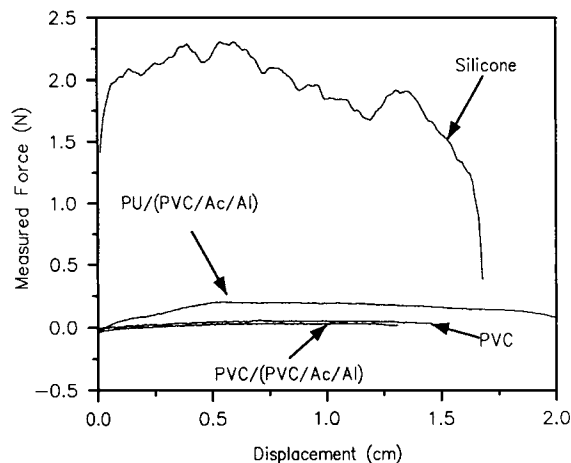
### Case A

Samples for three adhesion test runs were made: (a) a dry adhesion test using three samples of each of the four membrane matrices; (b) a dry adhesion test using three samples each of membranes 1–3 (see Table I), with 10 wt %  $\text{SiCl}_4$  (adhesion promoter) mixed with the casting solution; and (c) a wet adhesion test using samples identical to those in (b). Figure 4 plots typical data for the four membrane types. Peel test data from multiple samples is averaged and summarized in Table II normalized to the value obtained for the dry PVC matrix containing no adhesion promoter. The results show that silicone has better adhesion to the sensor surface than the PU/(PVC/Ac/Al) matrix and that PVC has greater adhesion than the PVC/(PVC/Ac/Al) membrane, which is not brought out by conventional tape testing. For example, tape test results showed that all of the PVC and PVC/(PVC/Ac/Al) films

**Table I** Compositions of the Four Polymer Matrices Evaluated in This Study

Composition of Matrix (wt %) <sup>a</sup>		Composition Notes
1. PVC	33%	PVC poly(vinyl chloride) PVC/Ac/Al 80% vinyl chloride
2. PVC	20%	5% vinyl acetate
PVC/Ac/Al	20%	15% vinyl alcohol
		PU polyurethane
3. PU	26.4%	P-SS polydimethylsiloxane,
PVC/Ac/Al	6.6%	Si-CN silanol terminated
4. P-SS	78%	10–12% (cyano-
Si-CN	21%	propyl)methyl
		88–90% dimethyl-
		siloxane copolymer

<sup>a</sup> The balance of the membrane is DOA (bis(2-ethylhexyl)adipate) plasticizer. (The silicone rubber membrane contains no plasticizer).



**Figure 4** Typical peel-force curves for the four membrane matrices evaluated in this study.

pulled off of the substrate, while none of the PU/(PVC/Ac/Al) or silicone films came off.

Membranes 1–3 peeled from the  $\text{Si}_3\text{N}_4$  surface as expected. The bond strength of membrane 4, silicone rubber, however, is so great that it exhibits cohesive failure before peeling. To increase the cohesive strength of this membrane, a nylon mesh was embedded in the matrix when it was cast. Still, the membrane was pulled apart, while partially losing adhesion to the surface. Although our test is unable to quantify the adhesion of this membrane, it does show that the adhesive strength is greater than the cohesive strength, which is much greater than the adhesive strength of the other membranes.

The test was able to verify that the adhesion of all the membranes is seen to decrease after soaking in room temperature water for 24 h. The quantitative results also show that the adhesion of membranes 1–3 benefit from the addition of the adhesion promoter  $\text{SiCl}_4$  to the membrane matrix. This improvement is thought to derive from formation of a single-bridge link between the polymer and the hydroxyl-bearing surface.<sup>4</sup> (The silicon nitride surface oxidizes, forming approximately 1.5–2 hydroxyl groups per  $\text{nm}^2$ .)

#### Case B

The adhesive effects of the hydroxylated copolymer content (PVC/Ac/Al) in membrane 2 (see Table I) was studied using the modified peel test. A dry adhesion test was run with three samples each of membrane 2 with 5, 20, and 50 wt % hydroxylated copolymer content. The peel test data from the sample is averaged and summarized in Figure 5 for both 1 and 10 wt %  $\text{SiCl}_4$  in the matrix.

The results show that there is a decrease in mem-

**Table II** Peel Test Results for Different Polymer Films on an  $\text{Si}_3\text{N}_4$  Surface

Matrix Type <sup>a</sup>	Normalized Pulling Force		
	Dry		Wet, With $\text{SiCl}_4$
	No $\text{SiCl}_4$	With $\text{SiCl}_4$	
PVC	1.00	1.49	1.01
PVC/(PVC/Ac/Al)	0.54	1.04	1.01
PU/(PVC/Ac/Al)	5.29	54.99	30.84
Silicone	57.87	—	—

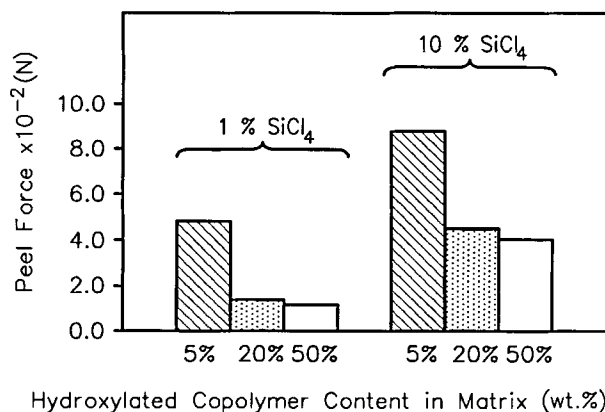
<sup>a</sup> See Table 1 for membrane compositions.

brane 2 adhesion as the copolymer content is increased. The quantitative nature and sensitivity of this adhesion test method make it a useful tool for studying the adhesive contributions of the individual components of a polymer matrix.

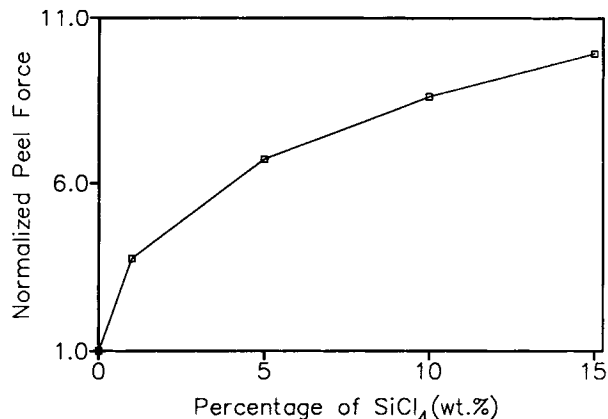
#### Case C

The adhesion test technique was also used to evaluate the effects of adhesion promoter on the adhesion of polymer films. To illustrate this point, a dry adhesion study was run with three samples each of membrane 3 with 0, 1, 5, 10, and 15 wt % of  $\text{SiCl}_4$  added to the matrix. The averaged results are plotted in Figure 6.

The adhesion test was able to show the polymer matrix becoming saturated with  $\text{SiCl}_4$ , at higher concentrations. Since available binding sites at the polymer/substrate interface are becoming full, the increase in membrane adhesion is not as pronounced at higher concentrations of  $\text{SiCl}_4$ .



**Figure 5** Peel test results for a compositional study on the PVC/(PVC/Ac/Al) matrix.



**Figure 6** Peel test results for evaluating the effects of adhesion promoter on the PU/(PVC/Ac/Al) matrix.

## CONCLUSIONS

A quantitative adhesion test useful for both wet and dry testing of thin polymer layers has been developed. This method has general application for polymers on semiconductor substrates, but can also be applied to other polymers on solid substrates. The procedure, a variation of peel testing, was used to compare the adhesion of thin polymeric membranes made of four different matrices. It was shown that this method can be readily used to produce valid comparisons of adhesion for polymers of different compositions, over variations of a given polymer composition, and for a polymer matrix with varying amounts of adhesion promoter. Sample preparation and test execution are straightforward and time-efficient. Results were very repeatable; standard deviation/mean, averaged over all of the samples tested, was 0.11.

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