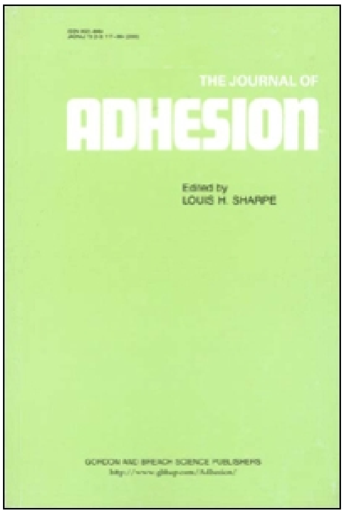
This article was downloaded by:
On: *22 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



The Journal of Adhesion

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

A Blister Test for Adhesion of Polymer Films to SiO_2

J. A. Hinkley[a][b]

[a] Electron Devices Division, National Bureau of Standards, Washington, DC, U.S.A. [b] Naval Research Laboratory, Washington, DC, U.S.A.

To cite this Article Hinkley, J. A.(1983) 'A Blister Test for Adhesion of Polymer Films to SiO_2', The Journal of Adhesion, 16: 2, 115 — 125

To link to this Article: DOI: 10.1080/00218468308074909

URL: http://dx.doi.org/10.1080/00218468308074909

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

J. Adhesion, 1983, Vol. 16, pp. 115–126
0021-8464/83/1602-0115 $18.50/0

Printed in the United Kingdom

A Blister Test for Adhesion of Polymer Films to SiO_2†

J. A. HINKLEY‡

Electron Devices Division, National Bureau of Standards, Washington, DC 20234, U.S.A

(*Received May 9, 1983; in final form June 27, 1983*)

Films of polystyrene or polymethyl methacrylate were cast on oxidized silicon substrates, then detached by the application of gas or water pressure from the back side of the film through a hole in the substrate. Critical detachment pressures showed good repeatability and could be used to calculate the work of adhesion. For polystyrene on a hydrophilic silica in the presence of water, the apparent work of adhesion is 78 mJ/m^2. Other polymer/substrate combinations gave meaningful variations in detachment pressure.

INTRODUCTION

The adhesion of films and coatings is of great practical interest, and a variety of tests to measure adhesion have been developed.[1] The "blister test" of Dannenberg[2] has not been widely used even though it offers several favorable features. First, nothing needs to be attached to the top surface of the film, so potentially detrimental effects due to diffusion of an adhesive into the film under test are avoided. Second, an engineering analysis of the measurement conditions is available,[3] a feature which stands in contrast to the semiquantitative nature of scratch and peel tests. Finally, the test may be conducted with or without a wetting liquid at the interface. This is a great advantage where the purpose of the film is to protect the substrate from attack, as is the case for photolithographic resists and most paints.

---

† Contribution of the National Bureau of Standards. Not subject to copyright.

‡ Current address: Naval Research Laboratory, Code 6120, Washington, DC 20375, U.S.A.

In the past, the blister test has been applied to elastomers[4] and to rigid bulk adhesives[5]; this work explores some aspects of polymer/surface interactions in the adhesion of thin films.

EXPERIMENTAL

The substrates for all tests were 38-mm diameter silicon wafers of the type used for integrated circuit fabrication. Wafers were heated in a controlled and purified atmosphere of wet oxygen to grow an oxide layer about 80-nm thick. Thus, the adherend was initially pure glassy SiO_2 free from contaminants. Prior to use, wafers were stored in laboratory laminar-flow hoods for up to two days. Polymer adsorption studies conducted during this same period showed that longer storage led to erratic results; the nature of the change in the surface during storage was not investigated, but reproducible results could be obtained by using freshly prepared wafers.

Water for the contact-angle measurement was deposited from a microsyringe steadied by a clamp arrangement, so that a small drop could be deposited quickly. The droplet was photographed within two seconds, and angles were measured on the print. Untreated, the oxide surface exhibited a water contact angle of 60°. Some wafers were given a subsequent surface treatment either by boiling them in a 1N H_2SO_4 solution to give a hydrophilic surface or by flooding them with hexamethyl disilazane (HMDS) and spinning them dry just before coating with polymer to give a surface with exposed methyl groups.[6]

The polymer was applied as a 20% solution in xylene, and the wafer was spun at 4000 rpm for about 15 s to produce a uniform polymer coating. Each coated wafer was then baked at 120°C for 15 min to completely remove the xylene. Film thicknesses, determined with a surface profilometer, were about 10 μm.

A 5-mm diameter hole was then etched through to the film from the back of the wafer using a 2:3 volume mixture of 48 wt % HF and concentrated (70 wt %) HNO_3. The area around the hole was protected with wax, and fresh etchant was continuously applied in a fine stream. After a clean hole had been produced the specimen was rinsed with distilled water and allowed to dry at room temperature.

The test procedure consisted of mounting the wafer in the jig shown in Figure 1 and slowly raising the N_2 pressure using a pressure regulator. The pressure was read from a gauge. When the critical pressure was reached, the blister suddenly grew to about 2-cm diameter and split

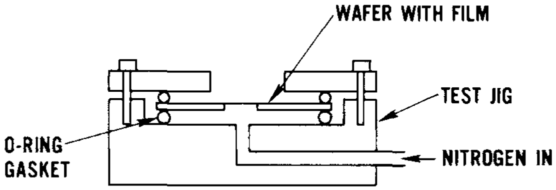


FIGURE 1 Cross section of assembled test jig for adhesion measurement.

open. Failure appeared to occur at the polymer/SiO_2 interface. This was based on the observation that the oxide in the debonded area showed a water contact angle similar to the angle measured before coating with polymer, indicating that no polymer remained on this surface. The critical pressures reported are averages of at least two trials; in nearly all cases, agreement among trials was within 10%.

In a few tests, the deflection of the blister was followed with a microscope. After pressure was applied, the microscope was refocused on the top surface of the film. The translation of the microscope required to keep the blister in focus could be read from a micrometer dial. These readings were corrected for movement of the substrate due to compression of the jig upper O-ring; the correction as a function of N_2 pressure was determined using an unetched wafer with no hole in place of the test specimen.

RESULTS

Specimen Geometry

Previous applications of the blister geometry[4] have assumed that the adhesive was rigid and underwent only small deflections. In the present case, however, the film is so thin that it offers negligible resistance to bending, and the deflections, shown in Figure 2, are very large compared to the film thickness.

The initially flat blister is stretched to a near spherical cap as shown by the profile in Figure 3. An analysis of this situation using membrane theory may be found in the Appendix in which the profile is assumed to be spherical.

Under a pressure p, the strain energy in a spherical cap is

$$U = \frac{\pi}{4} a^2 p \cdot h$$

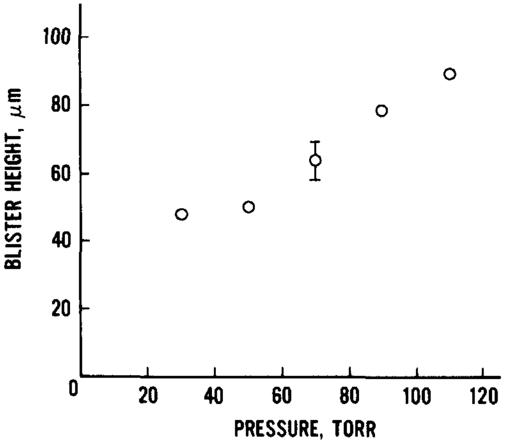


FIGURE 2 Deflection at center of blister vs. inflating pressure.

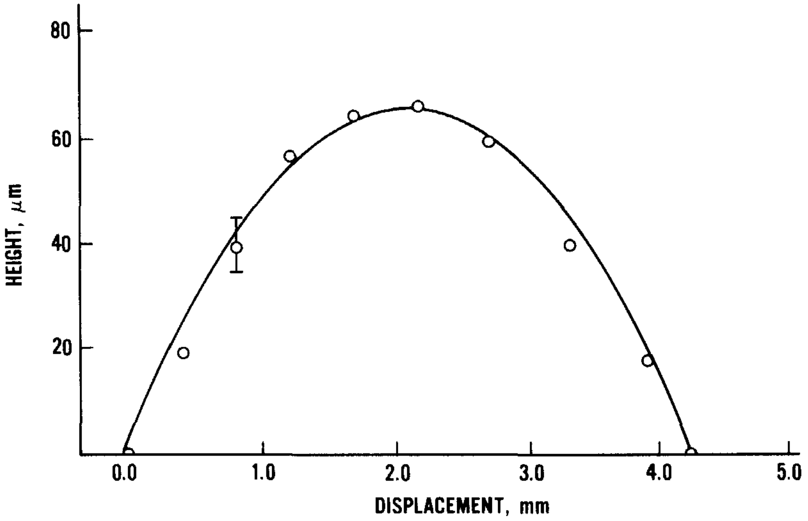


FIGURE 3 Blister profile at 80 Torr pressure. Line: spherical cap model; points: experimental.

where h is the blister height and $2a$ is its width. Equating the potential strain energy decrement to the energy to create new surface when the blister diameter increases gives the equation for the surface energy:

$$\gamma = \frac{p_c h_c}{4}, \qquad (1)$$

where h_c is the blister height at the critical pressure for blister growth p_c.

Once the critical pressure for the initial blister width is reached, the blister will continue to grow unless the pressure is reduced. In practice, the blister grows to the edges of the specimen almost instantaneously, providing a convenient and easily detected end point for the measurement.

Effect of Wetting Liquid

Table I compares adhesion values for polystyrene blisters pressurized with dry nitrogen and with water. In the former case, the substrate always cracked before adhesive failure could be observed. Thus, p_c could not be determined, but the pressure at which the wafer burst gave a lower bound for the adhesive strength, indicated by "$>$" in the table. The presence of water lowers the bond strength dramatically on hydrophilic wafers.

TABLE I

Critical Pressures for Film Detachment (Polystyrene/Silica)

Substrate	p_c, Torr N_2	 H_2O
hydrophilic	>200	47
hydrophobic	>180	>170

According to Gent and Schultz,[7] the work of detachment W is decreased in the presence of a wetting liquid by an amount $\Delta\gamma$ given by

$$\Delta\gamma = W - W_l = \gamma_l (\cos\theta_a + \cos\theta_s). \qquad (2)$$

In this equation, γ_l is the surface tension of the wetting liquid, θ_a is

TABLE II

Water Contact Angles and Calculated Interfacial Energies (Polystyrene/Silica)

Substrate	θ_s	$\cos\theta_s$	θ_a	$\cos\theta_a$	$\Delta\gamma$, mJ/m^2†
hydrophilic	2°	1.0	85	0.09	80
hydrophobic	60°	0.48	85	0.09	42

† 1 mJ/m^2 = 1 erg/cm^2 = 1 dyne/cm
s = substrate (silica)
a = adhesive (polystyrene)

the contact angle on the adhering polymer film, and θ_s is its contact angle on the substrate. Calculated values of $\Delta\gamma$ for the hydrophilic and hydrophobic surfaces are shown in Table II. Using the measured p_c for the hydrophilic substrate in the presence of water, Eq. (1) yields $\gamma = 78$ mJ/m^2. The dry work of adhesion is this value plus the decrease in the work of detachment caused by the liquid or $78 + 80 = 158$ mJ/m^2. This is in the range accessible to experiment, yet as shown in Table 1 detachment did not occur.

The situation is therefore not as simple as Eq. (2) would suggest. It would be interesting to try various wetting liquids in combination with Eq. (2) to see whether a consistent value of γ (dry) could be derived. A possible explanation for the failure of Eq. (2) is that the geometry of the crack tip itself may be different under wet conditions, or at large stresses. It is recognized, too, that fracture is usually rate-dependent, and the theory is based solely on equilibrium considerations. It is known[8,9] that water affects the reversibility of polymer adsorption on glass from solution; in the absence of water, desorption is so slow that it cannot be observed. If a similar condition holds at the solid/solid interface, detachment under wet conditions may be essentially reversible; whereas under dry conditions, equilibrium may not be attained during the experiment, so that the thermodynamic theory may not apply.

Effect of Specific Polymer/Surface Interactions

Table 3 shows the results of a separate experiment designed to determine the effects of different surface treatments on adhesion. Notice that relative comparisons within a column in Table III are valid, since the values apply to identical films. Direct comparison with the results of the last section should not be attempted, however, since the film thicknesses were different and the previously measured blister heights do not apply (see Eq. (1)). These measurements were made immediately after the holes

TABLE III

Critical Pressures (Torr) for Film Detachment Under Wet Conditions

Substrate	polystyrene	poly (methylmethacrylate)
hydrophilic	26	>200
HMDS-treated	46	100

were etched through the wafers so there was water present at the crack. As a result, all the values in Table III correspond to wet conditions.

The data in the first column show clearly the expected improvement in adhesion of polystyrene when the "adhesion promotor" HMDS is used. This may be understood as follows: the reversible work of detachment is

$$W_l = \gamma_{al} + \gamma_{sl} - \gamma_{as}$$

where the γ's are interfacial energies and the subscripts refer to adhesive, liquid, and substrate, respectively. For the HMDS-treated surface

$$W'_l = \gamma_{al} + \gamma'_{sl} - \gamma'_{as},$$

where the primes refer to the values affected by the presence of HMDS. The difference between the untreated and the treated surface work of detachment is

$$W_l - W'_l = \gamma_{sl} - \gamma'_{sl} - (\gamma_{as} - \gamma'_{as}). \tag{3}$$

In the case of the low-polarity polymer, polystyrene, it is reasonable to assume that the polymer and substrate interact primarily through dispersion forces and to substitute Fowkes' expression for the interfacial energies[10]

$$\gamma_{as} = \gamma_a + \gamma_s - 2(\gamma_a^d \gamma_s^d)^{1/2}. \tag{4}$$

Here γ_{as} is the interfacial energy, γ_a and γ_s are surface energies, and the γ^d's are the contributions to the respective surface energies due to London dispersion forces. With a further substitution of Young's equation

$$\gamma_s - \gamma_{sl} = \gamma_l \cos\theta, \tag{5}$$

Eq. (3) becomes

$$W_l - W_l' = 2[(\gamma_a^d \gamma_s^d)^{1/2} - (\gamma_a^{d'} \gamma_s^{d'})^{1/2}] - \gamma_l(\cos\theta_{sl} - \cos\theta_{sl}') \qquad (6)$$

where again γ_l is the surface tension of a wetting liquid and the θ's are contact angles. The first term is the result of film-substrate interactions, while the second results from liquid-substrate interactions. Although the surface energy dispersion components were not determined directly, they can be estimated from the work of Yanazawa *et al.*[11] Using values listed in Table IV, the first term in Eq. (6) is positive and of magnitude 20 mJ/m^2. The second term is of the order of 72 mJ/m^2 leading to the prediction that the work of detachment should be about 50 mJ/m^2 lower on the hydrophilic surface, in agreement with what was observed.

The data for PMMA on silica in Table III show the reverse trend. In other words, the "adhesion promotor" HMDS *worsens* adhesion as compared to the hydrophilic untreated surface. Consideration of Eq. (3) leads to the conclusion that the difference in dry adhesion between the two different surface treatments must override the difference in substrate wettability. This is a striking example of how a high surface energy substrate and specific interactions (in this case, presumably hydrogen bonding between surface silanols and ester groups in the polymer) can promote good adhesion. Thus, we have a quantitative basis for the observations of Gipstein and co-workers,[12] who found that polar photoresist compositions could offer better adhesion than nonpolar compositions on hydrophilic substrates.

TABLE IV

Contact Angles and Dispersion Energies of Substrates and Adhesives

Surface	$\theta(H_2O)$ (this work)	γ^d, mJ/m^2 [Ref. 11]
hydrophilic	0	41
hydrophobic	60	
HMDS		22
PS	85	44
PMMA	75	

CONCLUSION

The blister test has been shown to have good reproducibility and the ability to distinguish quantitatively the interfacial adhesive strengths of glassy polymer films. The values obtained correctly reflect changes in the polymer, substrate, and displacing fluid.

Because the surface chemistry of silica is known and can be varied, the test is suitable for basic investigations of polymer/surface interactions. Variations in measured energies of detachment are close to the theoretical values, suggesting that viscoelastic energy dissipation, which is usually the major contributor to the adhesive strength of rubbery polymers,[13] is relatively unimportant for these glassy films.

Future work using the blister test technique might focus on the quantitative effect of film thickness and different wetting liquids. It should not be difficult to extend the technique to other polymers, such as resists for the newer, more sophisticated etching technniques or for dry processing.

Acknowledgements

This work was performed while the author held a National Research Council Postdoctoral Associateship. Thanks are due to Dr. Donald Novotny for helpful guidance and to William Cullins for suggestions on design of test fixtures.

APPENDIX

The membrane strain along ε_ψ a tangent in the plane of Figure A1 is given by[14]

$$\varepsilon_\psi = \frac{1}{E}[N_\psi - \nu N_\theta]$$

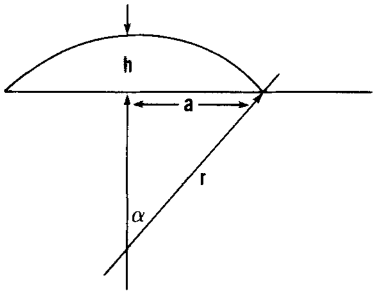


FIGURE A1 Description of parameters.

where N_ψ and N_θ are the meridional and circumferential stresses, ν is Poisson's ratio, and E is Young's modulus. If the bubble is spherical

$$N_\psi = N_\theta = \frac{pr}{2t}$$

p being the normal pressure, r the radius and t the thickness of the bubble.

When a diameter of the originally flat plate is stretched to a circular arc (Figure A1), the strain is

$$\varepsilon_\psi = \frac{r\alpha}{a} - 1$$

where

$$\alpha = \sin^{-1}\frac{a}{r} = \frac{a}{r} + \frac{1}{6}\left(\frac{a}{r}\right)^3 + \ldots$$

so that

$$r^3 = \frac{a^2 Et}{3p(1-\nu)}.$$

From geometry, $r = (a^2 + h^2)/2h$; thus

$$p = \frac{8h^3 Et}{3a^4(1-\nu)}.$$

The maximum strain used in the present paper was $h \cong 0.1$ mm, $a = 2$ mm, giving $\varepsilon \leqslant 2 \times 10^{-4}$.

References

1. ASTM *The Adhesion of Thin Films*, K. L. Mittal, Electrocomponent Science and Technology **3**, 21 (1976).
2. H. Dannenberg, *J. Appl. Polym. Sci.* **5**, 125 (1961).
3. G. P. Anderson, S. J. Bennett and K. L. DeVries, *Analysis & Testing of Adhesive Bonds* (Academic Press, New York, 1977), p. 58.
4. M. L. Williams, *J. of Appl. Polym. Sci.* **13**, 29 (1969).
5. R. R. Despain *et al.*, *J. Dental Research* **52**, 517 (1973).

6. A. C. Zettlemoyer and H. H. Hsing, *J. Coll. Interface Sci.* **55**, 637 (1976).
7. A. N. Gent and J. Schultz, *J. Adhesion* **3**, 281 (1972).
8. R. Perkel and R. Ullman, *J. Polym. Sci.* **54**, 127 (1961).
9. R. R. Stromberg and W. H. Grant, *J. Res. NBS* **67A** (6), 601 (1963).
10. F. M. Fowkes, *Ind. Eng. Chem.* **56**, 40 (1964).
11. H. Yanazawa, T. Matsuzawa and N. Hashimoto, Proc. Kodak Microelectronics Seminar, 1977. Publication G-48 available from Eastman Kodak Co., Rochester, NY 14650. Also, N. Hashimoto *et al.*, *Electrochemical Society 145th Meeting Extended Abstracts* **145** (1974).
12. E. Gipstein, W. Moreau and O. Need, *J. Electrochem. Socy* **123** (7), 1105 (1976).
13. A. Ahagon and A. N. Gent, *J. Polym. Sci., Polym. Physics* **13**, 1285 (1975).
14. S. Timoshenko and S. Woinowsky-Krieger, *Theory of Plates and Shells*, 2nd ed. (McGraw-Hill, New York, 1959).