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3.B Dynamically Loaded Scratch Tester for Thin-Film Adhesion Measurements

The American Society for Testing and Materials (ASTM) defines adhesion as the state in which two surfaces are held together by interfacial forces, which may consist of valence forces or mechanical forces or both.[1] Mittal[2] describes the sum of all interfacial intermolecular reactions as "basic adhesion." He uses the term "practical adhesion" to represent the forces needed to disrupt the adherate-adherend system, either at the interface of the two, or in the interfacial region. The interfacial region (interphase) can be either a contamination layer on the substrate (oxides, oils, etc.) or it can be formed by the diffusion of the adhering materials.

The "practical adhesion" of dielectric thin-film antireflecting (AR) and highly reflecting (HR) coatings to optical glass and crystalline substrates is of considerable importance to LLE. Optics in OMEGA are periodically cleaned with a methanol-tissue wipe to remove dust. This type of routine maintenance can be performed on hard, well adhered coatings with no deleterious effects. More important, the laser-damage resistance of well adhered, hard dielectric films is thought to be superior to that of more weakly adhered films,[3] although experiments performed to demonstrate this correlation have not been conclusive.[4,5]

Because of our long-term interest in laser-damage-resistant coatings (refer to previous articles in LLE Review **7**, p. 2; **14**, p. 36; **20**, p. 175), we have sought to develop a reliable diagnostic for measuring relative adhesive strength in our thin-film coating facility. The standard, military cellophane-tape pull test,[6] and tests such as the plug pull test, topple test, and peel test,[7] yield only vague, qualitative pass/fail data, or simply do not work for hard dielectrics deposited with modern techniques.

At LLE we have improved the scratch test, originally developed by Heavens[8] and theoretically enhanced by Benjamin and Weaver.[9] Our objective is to develop a rapid and reliable method for measuring the relative adhesive strength of samples within a given coating-substrate system as a function of any of the following parameters: substrate surface polishing, substrate cleaning, coating deposition method, substrate temperature during deposition, and post-deposition baking.

Our approach, which we refer to as dynamically loaded scratch testing,[10] minimizes the damaged regions of a coated part, yields real-time information in certain circumstances, and provides for the possibility of a limited amount of spatially resolved information. Specifically, by making in-house modifications to a commercial unit, we have developed a scratch tester that continuously increases the load applied using a spherical diamond stylus to a coated part in motion. The critical load for coating delamination is detected with an acoustic emission sensor (real-time) adjacent to the stylus, or with Nomarski microscopy. Adhesion information can be obtained with one scratch with a linear extent less than 2 mm. In this initial work we have addressed two problems:

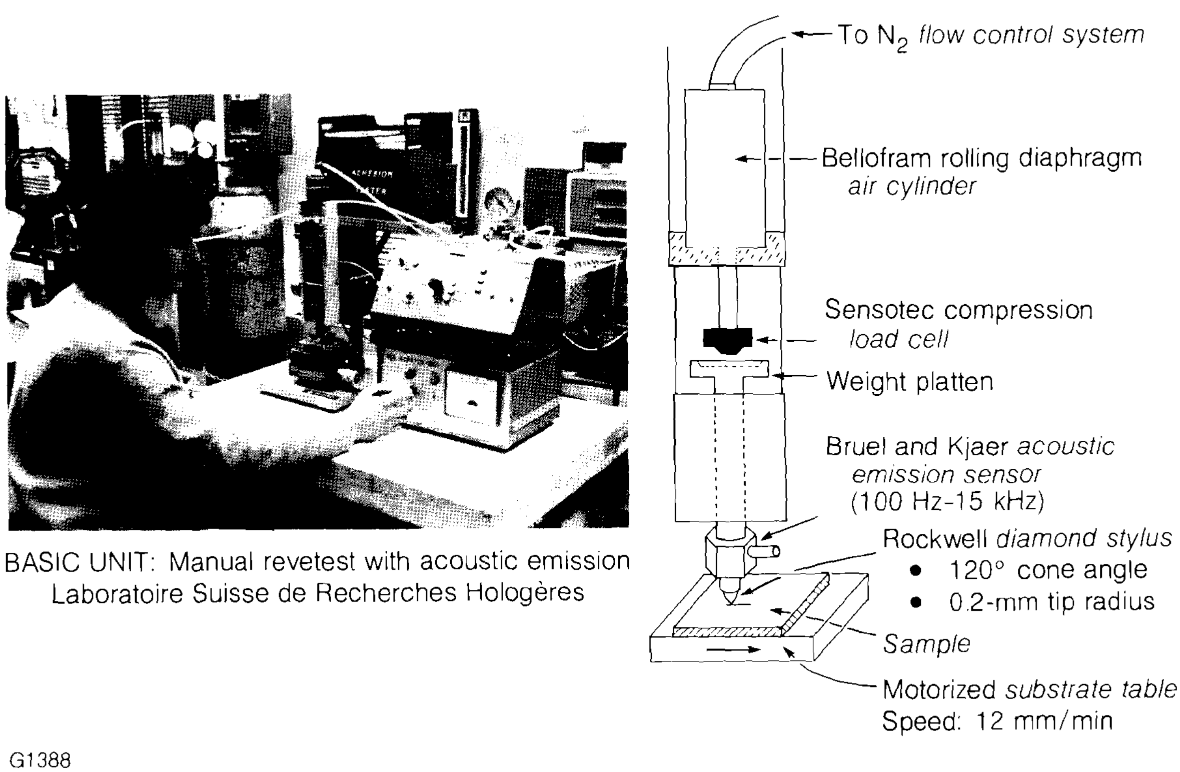


Fig. 22.26
Dynamically loaded scratch tester with acoustic emission. Our modifications to the commercial unit include the addition of a flowing gas load system and load sensor. The modified apparatus linearly increases load during the scratching process.

(1) How useful is the acoustic emission feature as a sensor of adhesive failure for optical coatings?

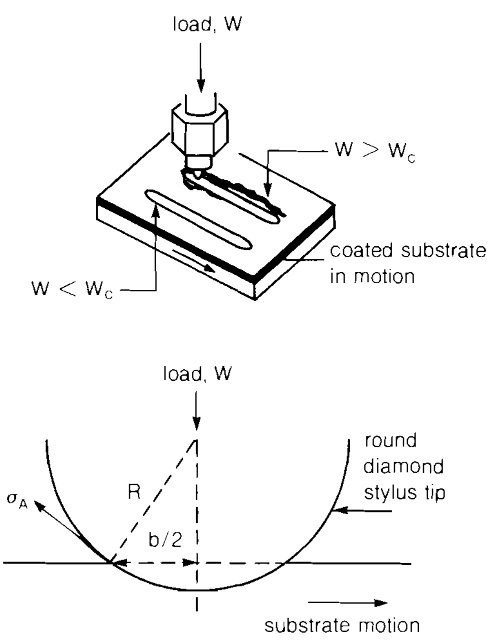
(2) Which optical coating-substrate systems exhibit adhesive failure within the loading range of the tester?

The dynamically loaded scratch tester is shown in the photograph at the left-hand side of Fig. 22.26. Details of the apparatus are given in the schematic diagram on the right-hand side of Fig. 22.26. Major modifications to the commercial unit[11] include the compression-loading capability consisting of an N_2 gas flow and control system, rolling diaphragm air cylinder, and compression load cell. With this apparatus and a dual pen chart recorder we can monitor the acoustic emission signal (y-axis) as a function of increasing load (x-axis).

In principle, at low loads W, deformation to the coating surface may occur with no adhesive failure. In Fig. 22.27 we illustrate how, when the applied load reaches some critical value W_c, the coating peels away from the substrate. It is the acoustic emission accompanying the coating-substrate separation process that we attempt to measure.

The equation accompanying Fig. 22.27 gives an expression for the actual adhesion strength of the coating, and the strength is proportional to the hardness H of the substrate divided by the stylus-tip radius R. It can alternately be expressed in terms of the indented track width b if

Fig. 22.27
Critical load and adhesion strength. The critical load W_c for coating removal can be related to the adhesion strength of the thin film with knowledge of substrate hardness and, under certain conditions, of plastic deformation.



$$\sigma_A \cong \frac{1}{\pi^{1/2} R} (W_c H)^{1/2} \text{ or } \frac{2\,W_c}{\pi R b}^{*}$$

WHERE . . .

σ_A = adhesion strength (kgf/mm^2)

R = radius of stylus point (mm)

W_c = detected critical load (kgf)

b = width of track caused by W_c (mm)

H = hardness of substrate (kgf/mm^2)

ASSUMING . . .

- $R \gg b$
- Substrate deformation is plastic.

*From ref. 9

G1389

hardness is unknown, provided that b≪R. Several articles in the literature[12,13] dispute the validity of Benjamin and Weaver's interpretation of the scratch test when it is used to compare different hard-coating-substrate systems. For our present work we seek values of critical load only within a given system and not among different systems.

We performed an initial experiment in conjunction with A. J. Perry (Balzers, AG) to verify the accuracy of our modified apparatus. He and others have used the standard commercial unit to evaluate nonoptical coating-substrate systems with considerable success.[13,14] Figure 22.28 shows his results (left side) versus ours (right side) for chemical-vapor-deposited (CVD) TiN on stainless steel, on samples he provided. The increasing fixed load and dynamically loaded results give the same value of critical load within 7%. The utility of acoustic emission sensing is also apparent for this nonoptical coating system. In fact, using acoustic emission, it is possible to locate regions of the coating that fail at loads significantly below W_c (refer to region a) in both the plot and the micrograph of Fig. 22.26 at a load of W = 1.2 kg. Perry interprets this as conclusive evidence for localized regions of poor adhesion.[13]

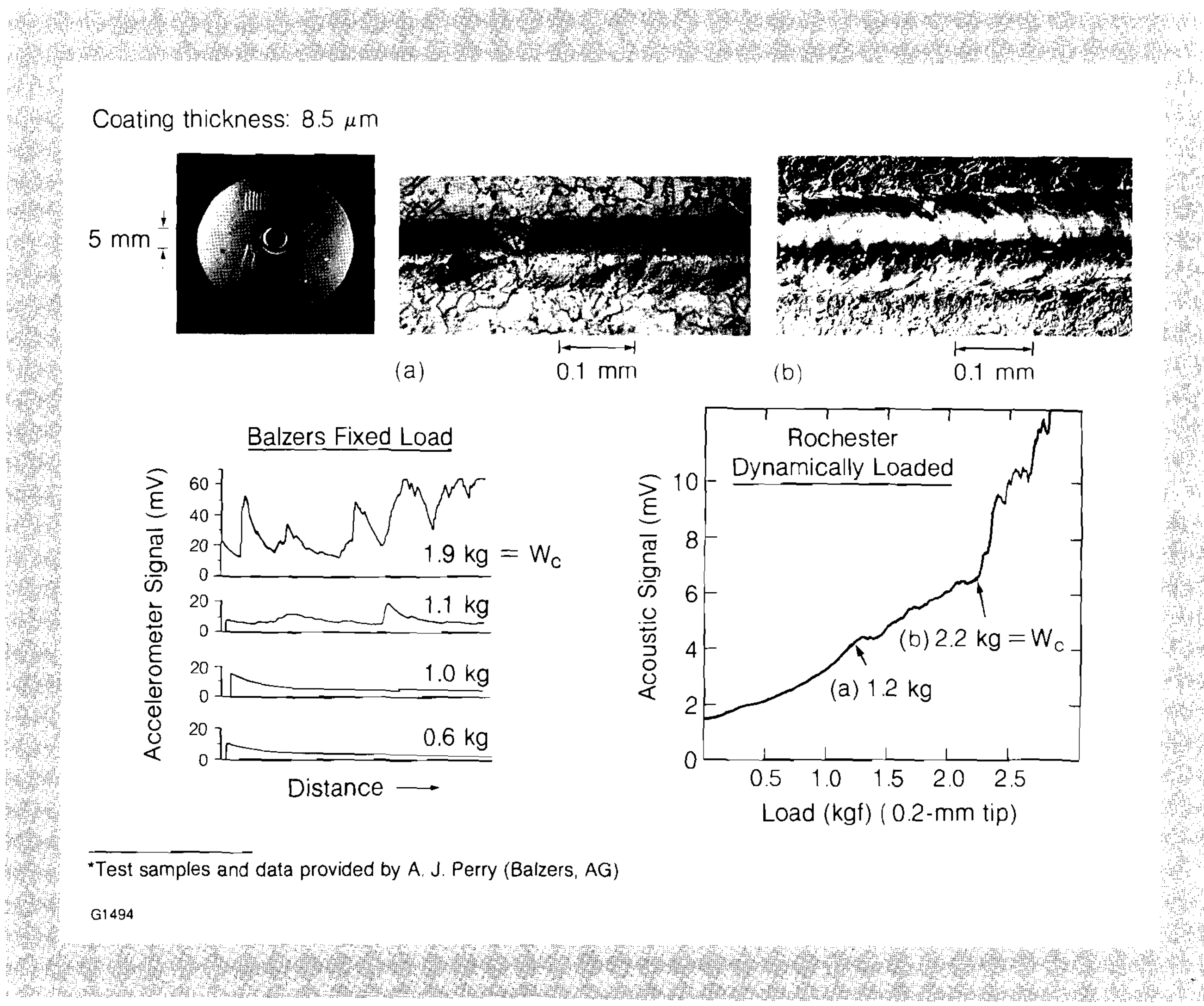


Fig. 22.28
Comparison of conventional and dynamically loaded scratch tests for CVD TiN on stainless steel. Measured critical loads are in excellent agreement using acoustic emission sensing for this nonoptical system. The advantage of using the dynamically loaded apparatus lies in the operator's ability to obtain W_c from a single scratch.

Our attempts to extend the utility of dynamically loaded scratch testing to systems with optical applications are summarized in Table 22.I. We have examined glass, single crystal and polycrystalline substrates, and many different coating materials using three deposition methods. Results have been mixed. In several instances we have detected substrate fracture prior to coating removal, as determined after careful examination with Nomarski microscopy. This observation is noted in Table 22.I and illustrated in Fig. 22.29 for CdS on borosilicate (BSC) glass. The acoustic signal in this case is derived from the fracture of the glass surface at loads near 2.7 kg, and not from the removal of the coating which occurs above 3.5 kg.

Substrate*	Coating	(Method)	Physical Thickness (μm)	Observations w/ 0.2-mm Tip
• Stainless Steel	TiN	(CVD)	8.5	useful results w/ acoustic signal
• Irtran II ZnS (PC)	Ta_2O_5	(E-gun)	1.0	useful results w/o acoustic signal
• BSC Glass	CdS	(E-gun)	0.08	substrate fracture before coating removal
	HfO_2	(E-gun)	1.0	useful results w/o acoustic signal
• Irtran I MgF_2 (PC)	Nd_2O_3	(thermal)	0.3	substrate fracture . . . .
	SiO_2	(etch, sputter)	0.75	substrate fracture . . . .
	Ta_2O_5	(E-gun)	1.0	useful results w/o acoustic signal
	ZnS/ThF	(thermal)	multilayer stack	useful results w/o acoustic signal
• Fused Silica	Ta_2O_5	(E-gun)	10.0	substrate fracture before coating removal
• Ge (SC)	Al_2O_3	(E-gun)	1.0	useful results w/o acoustic signal
• Si (SC)	SiO	(thermal)	0.37	useful results w/o acoustic signal; cleaning experiment
	Nd_2O_3	(thermal)	0.3	substrate fracture . . . .
	SiO_2	(sputtered)	0.75	useful results w/ acoustic signal; cleaning experiment
	TiO_2	(E-gun)	0.75	useful results w/o acoustic signal
	Ta_2O_5	(E-gun)	1.0	useful results w/o acoustic signal; cleaning experiment
	Al_2O_3	(E-gun)	1.0	useful results w/o acoustic signal; cleaning experiment

* PC = polycrystalline, SC = single crystal

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Table 22. I
Extension of adhesion measurements to systems with optical applications.

Other systems we sampled have given useful results when examined with Nomarski microscopy, but usually without any real-time acoustic signal. Three substrate cleaning experiments will be reviewed here.

Substrate Cleaning Experiment 1

We examined the effect of three standard cleaning processes upon the adhesion of metal oxides to the (111) surface of electronic-grade

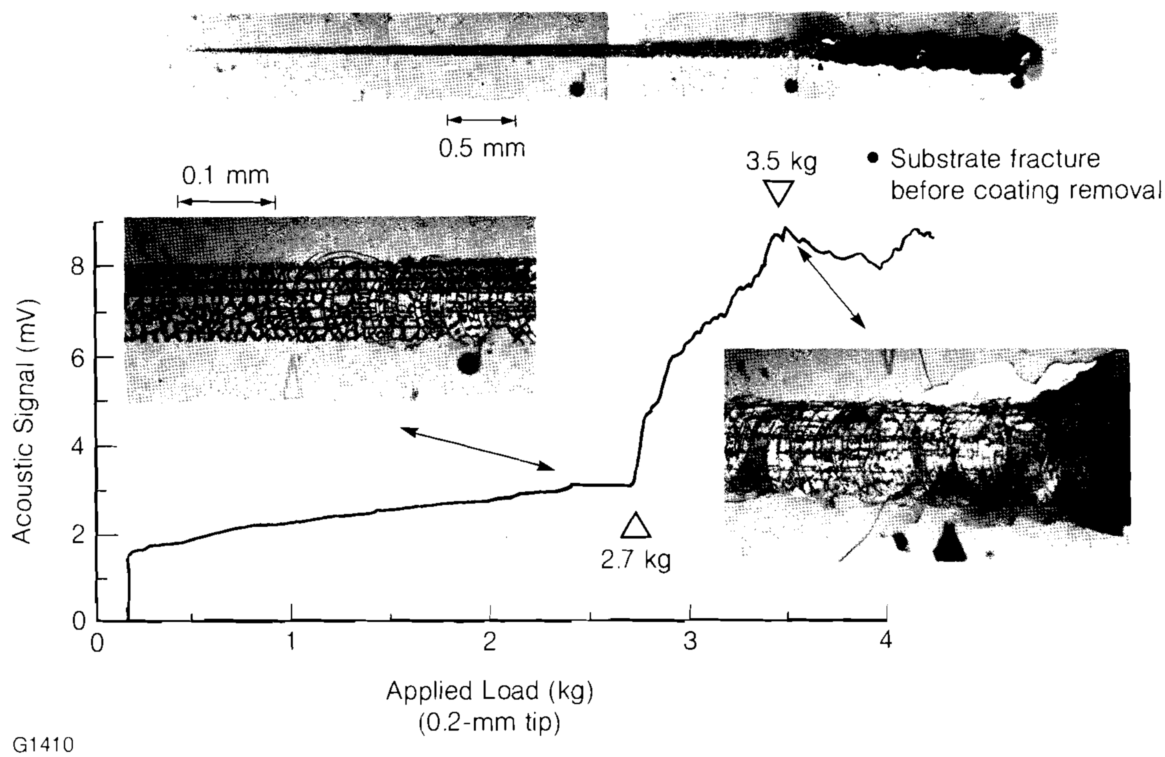


Fig. 22.29
Results for 800-Å-thick CdS film on borosilicate (BSC) glass. The substrate fractured at a load of 2.7 kg prior to the occurrence of coating removal at 3.5 kg. The acoustic emission corresponds to the initiation of substrate fracture. This sequence of events invalidates the test for coating adhesion.

silicon. Twelve samples 25 mm × 25 mm × 1.5-mm thick were cut from three wafers. Cleaning was performed using one of the following:

(a) HPLC alcohol wipe

(b) Aqueous/Ultrasonic/UV(185 nm)-Ozone[15]

(c) Liquinox/DI water/Freon T-DFC

SiO was deposited using resistance evaporation at 2×10^{-5} Torr to a physical thickness of 0.37 μm on parts cleaned in each of the above ways. Ta_2O_5 was deposited using E-gun evaporation at 4×10^{-5} Torr to a physical thickness of 1.0 μm on a second set of parts. Adhesion test results are tabulated in Fig. 22.30 for both evaporations; examples of scratches are also shown in Fig. 22.30. Cleaning method (b) produced such superior results that the substrate fractured before the coating was removed. The possibility that the UV ozone treatment creates a reactive surface that enhances adhesion is suggested by the observation that a post-UV ozone treatment alcohol wipe prior to coating did not lower W_c, whereas the alcohol wipe by itself did not exhibit particularly good results. No useful acoustic signals were detected for this experiment.

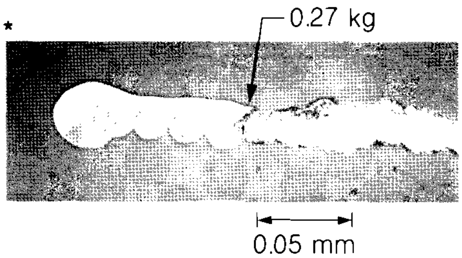
SiO on Si (resistance evaporation)
(physical thickness, 0.37 μm)

	Process	W_c, kg
(a)	Alcohol*	<0.27
(b)	UV/ozone	>0.99
(c)	Liquinox	failed tape test

Ta_2O_5 on Si (E-gun)
(physical thickness, 1.0 μm)

	Process	W_c, kg
(a)	Alcohol	<0.70
(b)	UV/ozone†	$>0.95 \pm 0.05$
(c)	UV/ozone + Alcohol	>0.95

*



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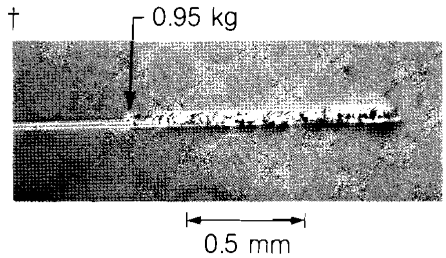

Substrate Fracture

No Useful Acoustic Signal

G1498

Fig. 22.30
Cleaning experiment 1. A UV-ozone cleaning performed on Si prior to coating deposition greatly improves the adhesion of two separate metal oxides. No useful acoustic signals were measured for this experiment.

Substrate Cleaning Experiment 2

In this experiment a set of silicon samples was sputter coated using argon and an SiO_2 target with and without a cleaning etch. Coatings were deposited to a physical thickness of 0.75 μm. Additional experimental parameters are given in Fig. 22.31, which also shows the photomicrographs. Excellent acoustic signals were obtained with good reproducibility. The data clearly demonstrate a factor of 5 improvement in adhesion with sputter etching prior to deposition.

Substrate Cleaning Experiment 3

The versatility of the dynamically loaded scratch tester was demonstrated by evaluating a system consisting of silver, deposited with E-beam evaporation to a physical thickness of 0.10 μm, on a polyethylene film base 0.15-mm thick (see Fig. 22.32). We measured a twentyfold improvement in adhesion when the substrate was cleaned with a butane-methylene-chloride process. Previous attempts to select an optimum cleaning process for improved adhesion met with no success because all films failed the cellophane-tape pull test.

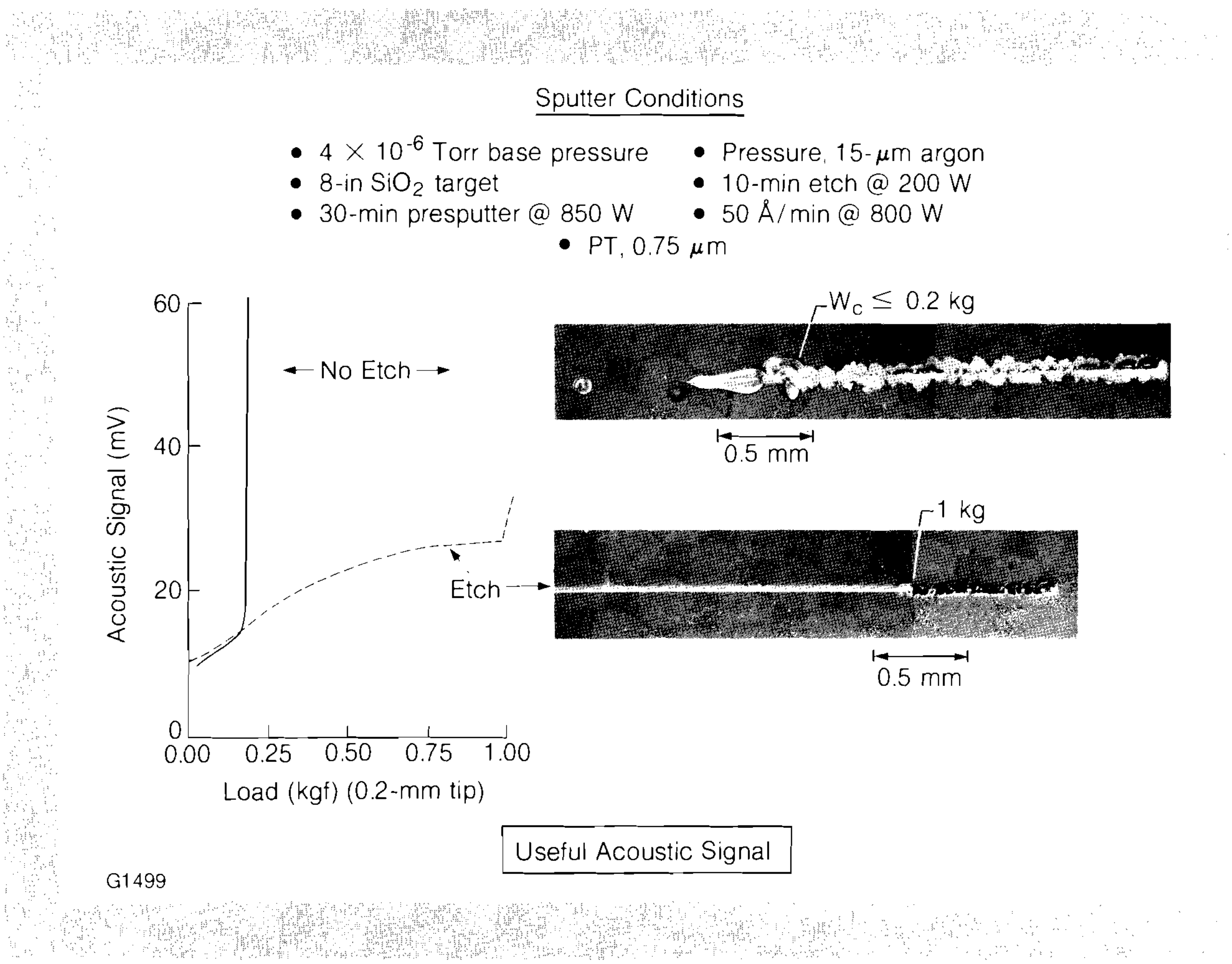

Fig. 22.31
Cleaning experiment 2. Sputter etching of Si prior to sputter coating improves the adhesion of SiO_2 film by more than a factor of 5. Excellent acoustic signals gave real-time information during this experiment.

Our preliminary survey has shown that the dynamically loaded scratch tester gives relative adhesive strength information for some interesting optical thin-film-substrate systems. Substrate fracture prior to adhesive failure limits the utility of the present device for many other systems of interest, and acoustic emission has been shown to be useful in but a few situations. Future work must attempt to understand the reasons for the limitations imposed upon this apparatus and, if possible, modify the stylus geometry to reduce substrate fracture and enhance acoustic emission signals. The apparatus as presently constructed will enable us to continue our work to relate coating adhesion to processing variables in thin-film coating technology.

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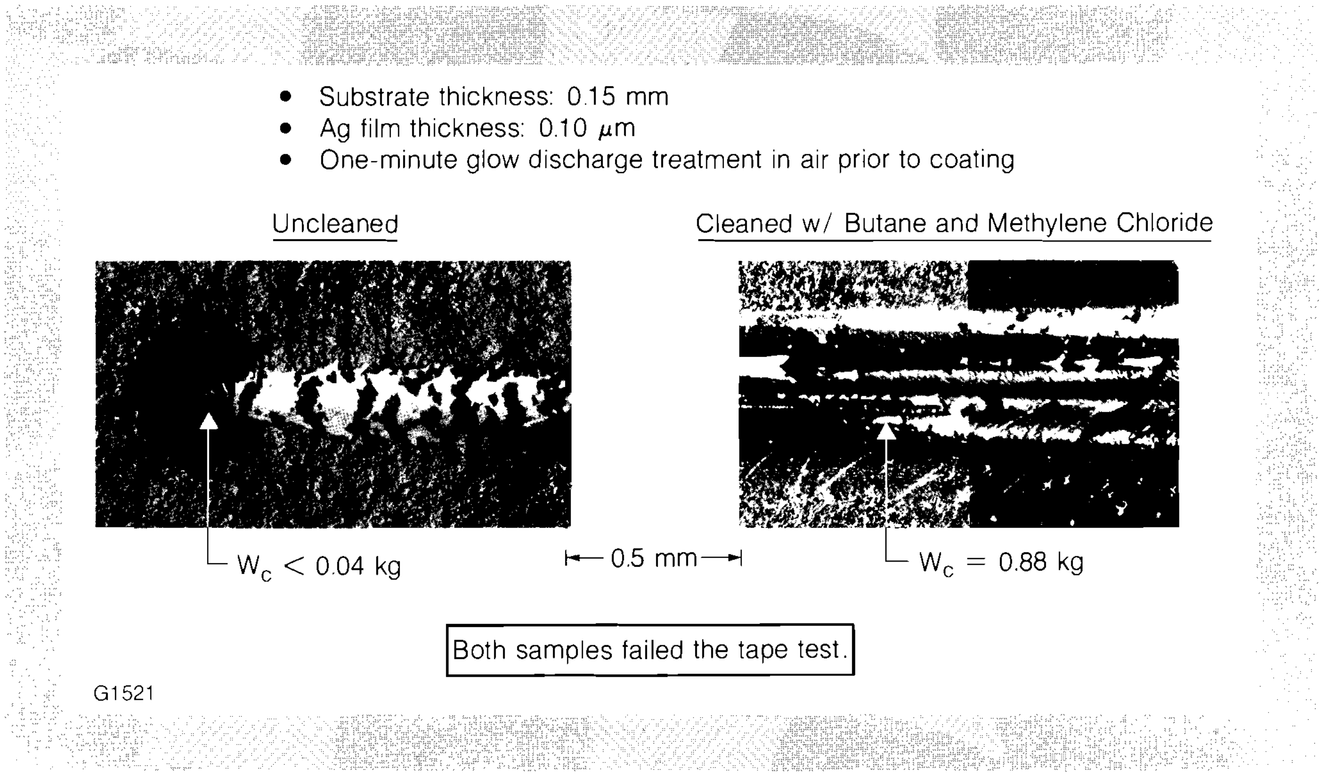

Fig. 22.32
Cleaning experiment 3. We succeeded in differentiating between poor and good adhesion in a system of E-gun-deposited silver on polyethylene film base. This is significant because both samples failed the cellophane-tape pull test, which provided no useful information.

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