PERGAMON

Journal of the Mechanics and Physics of Solids
51 (2003) 1395–1412

JOURNAL OF THE
MECHANICS AND
PHYSICS OF SOLIDS

www.elsevier.com/locate/jmps

Glass-modified stress waves for adhesion measurement of ultra thin films for device applications

Vijay Gupta[a,*], Vassili Kireev[a], Jun Tian[a], Hiroshi Yoshida[b], Haruo Akahoshi[b]

[a] *Department of Mechanical and Aerospace Engineering, 38-137E, Engg IV Bldg, University of California, Los Angeles, CA 90095-1597, USA*

[b] *Applied Electrochemistry Group, Department of Electronic Materials and Devices Research, Hitachi Research Laboratory, Hitachi Ltd., Japan*

Received 13 September 2002; received in revised form 13 February 2003; accepted 31 March 2003

Abstract

Laser-generated stress wave profiles with rarefaction shocks (almost zero post-peak decay times) have been uncovered in different types of glasses and presented in this communication. The rise time of the pulses was found to increase with their amplitude, with values reaching as high as 50 ns. This is in contrast to measurements in other brittle crystalline solids where pulses with rise times of 1–2 ns and post-peak decay times of 16–20 ns were recorded. The formation of rarefaction shock is attributed to the increased compressibility of glasses with increasing pressures. This was demonstrated using a one-dimensional nonlinear elastic wave propagation model in which the wave speed was taken as a function of particle velocity. The technological importance of these pulses in measuring the tensile strength of very thin film interfaces is demonstrated by using a previously developed laser spallation experiment in which a laser-generated compressive stress pulse in the substrate reflects into a tensile wave from the free surface of the film and pries off its interface at a threshold amplitude. Because of the rarefaction shock, glass-modified waves allow generation of substantially higher interfacial tensile stress amplitudes compared with those with finite post-peak decay profiles. Thus, for the first time, tensile strengths of very strong and ultra thin film interfaces can be measured. Results presented here indicate that interfaces of 185-nm-thick films, and with strengths as high as 2.7 GPa, can be measured. Thus, an important advance has been made that should allow

*Corresponding author. Tel.: +31–08250223; fax: +31-02062302.
E-mail address: vgupta@ucla.edu (V. Gupta).

0022-5096/03/$ - see front matter © 2003 Elsevier Science Ltd. All rights reserved.
doi:10.1016/S0022-5096(03)00057-7

material optimization of ultra thin layer systems that may form the basis of future MEMS-based microelectronic, mechanical and clinical devices.

© 2003 Elsevier Science Ltd. All rights reserved.

Keywords: Laser-generated stress waves; Interface strength; Rarefaction shock; Nonlinear elastic; Thin films; Spallation; Interferometery; Adhesion; Multilayers

1. Introduction

Films and coatings have widespread use in different industries. Examples include, thermal barrier coatings for engines; tribological coatings in cutting tools, seals, and joints; polymeric layers in paint assemblies; fiber coatings in composites; electrical, magnetic and optical multilayers in electronic devices; metal and ceramic films in MEMS-based mechanical and clinical devices, among others. Adhesion of films is a prerequisite to carryout their intended functions. Thus, the central goal in all these applications is to avoid film delamination and coating failures by *maximizing* adhesion, and to predict long-term reliability of the coated components. These issues are usually addressed by seeking a fundamental understanding of the adhesion between different layers as a function of process (film deposition and surface variables) and service (moisture and temperature) variables. This is accomplished using adhesion metrology tools, which can be broadly classified into two categories.

The first and the more widely used are techniques that measure the fracture energy of the interface, inclusive of the plastic deformation that occurs inside the deformable separating parts. Because the plastic work depends on many extrinsic factors, (e.g., coating/substrate geometry: number and thickness of each layer; loading-type: strain rate, temperature, and ratio of the far-field mode I to mode II stress ratio) such measurements can be only used for design if failure during service and fabrication occurs under identical local stress conditions. Most of the interface characterization test methods, including the direct pull test, scratch test, indentation test, four point bend test, blister test, and the double cantilever beam test, fall in this latter category. Reader is referred to Mittal (1987) for an extensive review of these and other techniques.

The second set includes techniques that measure the intrinsic strength and toughness of the interface which depend upon the atomic structure and chemistry of the interfacial region. The intrinsic toughness can also be regarded as the area under the fundamental interface stress-atomic separation curve, the peak of which is the intrinsic strength of the interface. Thus, intrinsic strength and intrinsic toughness can be regarded as fundamental parameters characterizing interface decohesion on the atomic scale. Here, all defects introduced during sample manufacturing are considered as part of the intrinsic interfacial structure. Several techniques to measure the intrinsic toughness exist (e.g., see Pronin and Gupta, 1998; Gupta and Pronin, 1995a, b), but direct measurement of the intrinsic strength is only possible using a laser spallation experiment developed by Gupta and coworkers (Gupta et al., 1992; Yuan and Gupta, 1993a, b; Yuan et al., 1993, Yuan and Gupta, 1995; Yuan et al., 1995). In the laser spallation experiment, a laser-generated compressive stress pulse in the substrate reflects into

Boeing Ex. 1019, p. 2 of 22
Boeing v. Regents Univ. Cal.

a tensile wave from the film's free surface and pries off its interface at a threshold amplitude.

2. Specific aims

The aim of this paper is to present hitherto unreported observations of stress wave profiles with rarefaction shocks in glasses, and to demonstrate their application in measuring the tensile strengths of ultra-thin-layer interfaces by adopting the basic laser spallation methodology. Substantial enhancement in the interfacial tensile stress using such waves is also shown, which allows separation of very strong interfaces. Interface systems chosen to demonstrate the above concepts have significance in device fabrication. These are also the systems in which substrate failures were observed when tested using the basic spallation methodology without the use of glass-modified waves.

An experimental effort to measure adhesion of ultra-thin layers is rather timely as films with thickness below 5000 Å are now the focus of research in the microelectronics industry for developing ultrahigh density devices using nanotechnology. Also, adhesion at similar length scales will become important in the material optimization of MEMS-based mechanical and clinical devices when they are mass-produced.

A brief description of the basic laser spallation methodology and its limitations are discussed first for a more efficient presentation of the new technology.

3. The basic laser spallation experiment

In the basic laser spallation experiment (Fig. 1, without the glass substrate), a 3-nanoseconds (ns) long Nd:YAG laser pulse is made to impinge over a 3 mm-dia area on a 0.5 μm thick aluminum film that is sandwiched between the back surface of a substrate disc (12–25 mm diameter and 1-mm thick) and a 10–20 μm thick layer of SiO2. The melting-induced expansion of aluminum under confinement generates a compressive stress pulse (with 1 ns rise time) directed towards the test coating, which is deposited on the substrate's front surface. The compression stress pulse reflects into a tensile wave from the coating's free surface and leads to its spallation (complete removal) at a sufficiently high amplitude. The interface tensile stress is obtained by measuring the transient displacement history of the coating's free surface (induced during pulse reflection) by using an optical interferometer (Pronin and Gupta, 1993), a schematic of which is shown towards the right in Fig. 1. For a coating of density ρ and thickness h, the interface stress σ is calculated from the measured transient velocity $v(t)$ as

$$\sigma(h,t) = \frac{1}{2}\rho c\left[v\left(t+\frac{h}{c}\right) - v\left(t-\frac{h}{c}\right)\right], \tag{1}$$

where c is the longitudinal stress wave velocity in the film.

Interface strengths in a variety of systems, including those between metal, ceramic, and polymeric coatings and engineering substrates, have been measured. It has been

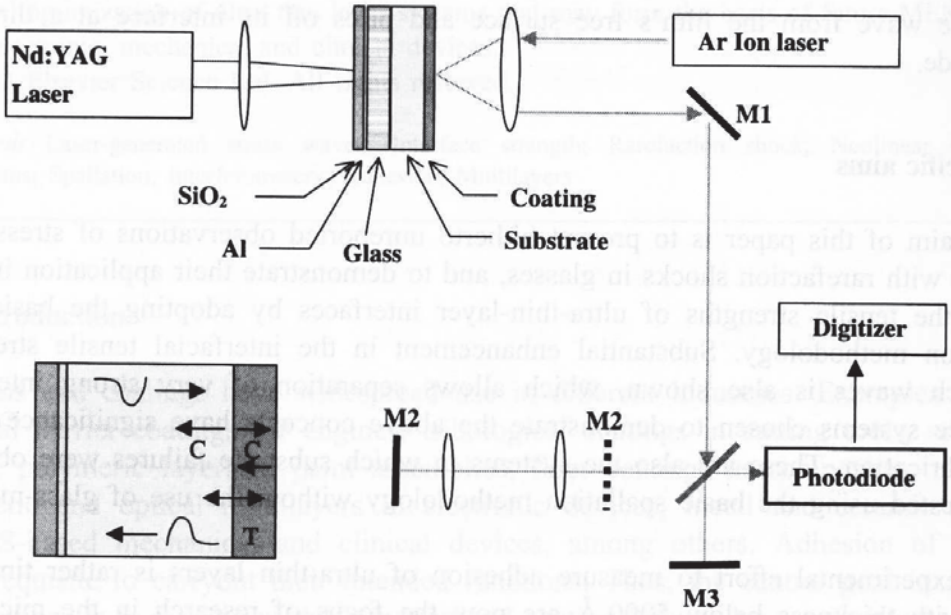


Fig. 1. A schematic of the laser spallation setup along with that of an interferometer used to record the free surface velocities of the film.

amply shown (Yuan et al., 1995; Yuan and Gupta, 1995) that the laser spallation experiment allows a correlation between the interface tensile strength and the interface microstructure. This allows optimization of the coating deposition processes and a more robust prediction of service reliability. For reasons discussed next, the technique is generally limited to testing films with thickness greater than 1 μm.

Laser-generated stress wave profiles measured in a bare Si wafer are reproduced in Fig. 2. The rise and post-peak decay time do not change significantly with increasing stress pulse amplitudes obtained at increasing laser fluences. A typical stress pulse profile has a rise-time of 1–2 ns, and a gradual post-peak decay of about 16–20 ns. If the film is very thin compared to the length of the stress wave, then the tail end of the initial compression pulse is still at the interface while its front end has returned as a tensile wave after reflecting from the film's free surface. Because of destructive interference, the peak interfacial tensile stress is always less than the amplitude of the initial compression wave. The amplitude of the peak interface tensile stress decreases non-linearly with the film thickness, the rise-time and post-peak decay time of the stress pulse, and as expected, becomes zero in the limiting case of zero film thickness. Thus, for thin layers, the peak interfacial tensile stress can be much lower than the peak tensile stress inside the substrate. For intrinsically strong interfaces, such a condition usually leads to failure within the substrate before the desired interface can be separated. This is demonstrated through results presented in Table 1, which summarizes interface tensile strength measurements using the basic laser spallation technique for a Cu/TaN bilayer system sputter-deposited on a Si wafer at the Hitachi Laboratory. Failure was observed inside the Si for the first three samples because of insufficient film thickness. Note the consistency in the peak tensile stress inside the Si for these samples, indicating a tensile

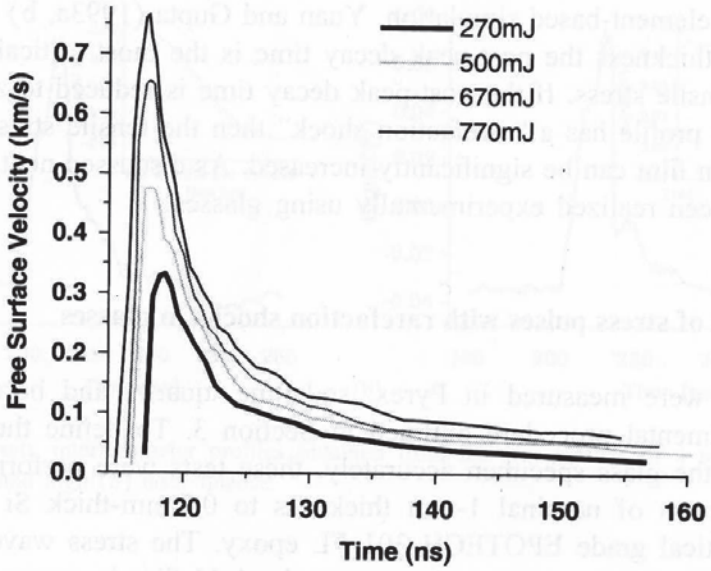


Fig. 2. Measured stress pulse profiles in Si at increasing laser fluence.

Table 1
Effect of film thickness on the failure mode in the laser spallation experiment

Configuration	Peak interface tensile stress (MPa)	Peak tensile stress in the substrate (MPa)	Failure locus
Cu[100 nm]/TaN[20 nm]/Si	38 ± 4	5100	Si failure
Cu[500 nm]/TaN[20 nm]/Si	260 ± 18	4900	Si failure
Cu[1 μm]/TaN[20 nm]/Si	280 ± 29	5200	Si failure
Cu[5 μm]/TaN[20 nm]/Si	1380 ± 110	4700	Interface failure
Cu[10 μm]/TaN[20 nm]/Si	1370 ± 140	4200	Interface failure

strength of Si of about 5 GPa. For these samples the Si/TaN interface tensile stress is rather low, and below its interfacial strength. As the film thickness was increased, the failure locus changed from the substrate to the interface. Consistently the peak tensile stress inside Si was lower than its strength measured in previous samples. The interface strength was found to be the same for the last two samples, indicating that if the interface chemistry is the same for films of varying thicknesses then the experiment measures the same fundamental strength. Thus, the interface strength can be measured in ultra thin film samples by simply increasing the film thickness or adding another layer on top to provide enough "room" for the reflecting compression pulse. This was demonstrated by Kitty van Dijk, et al. (1998). However, because of issues related to possible film structure and chemistry changes due to increased film thickness in several systems, the preferred way is always to test films in their initial low thickness state or in the same form as to be used in actual service devices. Accordingly, the focus of research leading to this paper was to devise strategies to allow successful spallation of ultra thin films and consequently measure their adhesion.

Boeing Ex. 1019, p. 5 of 22
Boeing v. Regents Univ. Cal.

Using a finite element-based simulation, Yuan and Gupta (1993a, b) showed that for a given coating thickness the post-peak decay time is the most critical in maximizing the interfacial tensile stress. If the post-peak decay time is reduced to zero, or in other words, the wave profile has a "rarefaction shock" then the tensile stress applied at the interface of a thin film can be significantly increased. As discussed next, this theoretical possibility has been realized experimentally using glasses.

4. Observations of stress pulses with rarefaction shocks in glasses

Stress waves were measured in Pyrex, sodalime, quartz, and borosilicate glasses using the experimental procedure outlined in Section 3. To define the entering stress wave profile in the glass specimen accurately, these tests were performed by bonding the glass specimens of nominal 1-mm thickness to 0.7 mm-thick Si wafers using a 0.5 μm-thick optical grade EPOTECH 301 FL epoxy. The stress wave was generated inside the Si by exfoliating a waterglass-constrained Al film in a manner discussed in Section 3. For interferometeric measurements, a 400 Å layer of Al was deposited on the free surface of the glass.

Fig. 3(a) shows an interferogram recorded from the free surface of the soda lime glass, and the corresponding stress wave profile (Fig. 3b) derived from it using the standard interferometery procedures. The increase in the fringe frequency at time corresponding to the peak of the pulse is evident. In this region, the fastest fringe was in the vicinity of the resolution limit of 0.2 ns of our setup. Thus, the drop in the stress is likely to be a "true" rarefaction shock. This was investigated further by recording pulse profiles using the *linear* velocity interferometer, in which the delay leg of the interferometer is adjusted to capture the entire velocity within a single fringe. In such a case, the shape of the velocity profile, which is proportional to the stress profile is recorded accurately but the proportionality constant remains largely undefined (Pronin and Gupta, 1998). Figs. 4a and b show the recorded pulses at low and high amplitudes, with the insets showing resolved post-peak profiles. The post-peak decay time of the

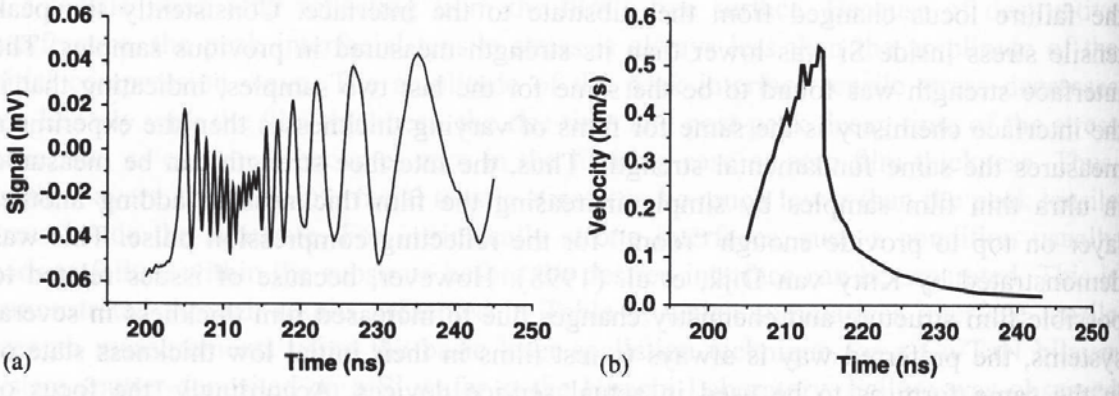


Fig. 3. (a) Interferometer signal observed from the free surface of a soda lime glass. (b) The stress wave profile derived from (a) using the standard interferometeric procedures.

Boeing Ex. 1019, p. 6 of 22
Boeing v. Regents Univ. Cal.

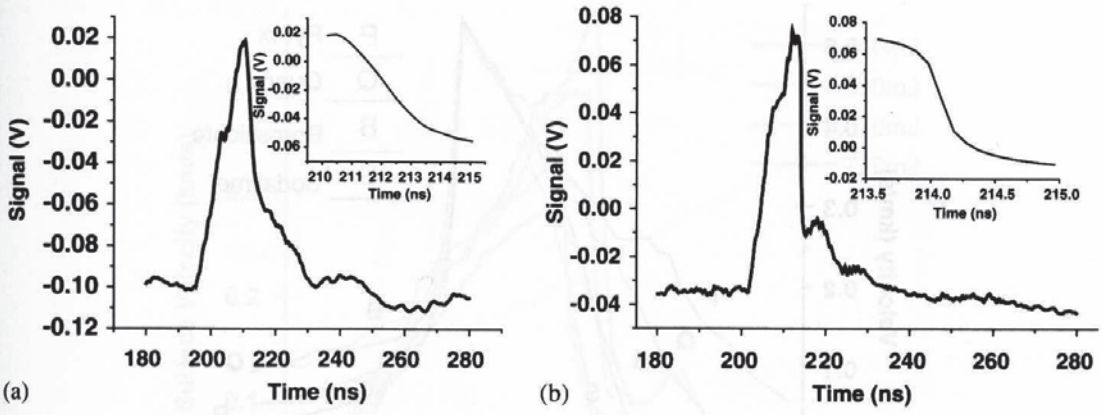


Fig. 4. Linear velocity interferometer profiles obtained from the free surface of a soda lime glass disc. Profiles at low (a) and high (b) laser fluence.

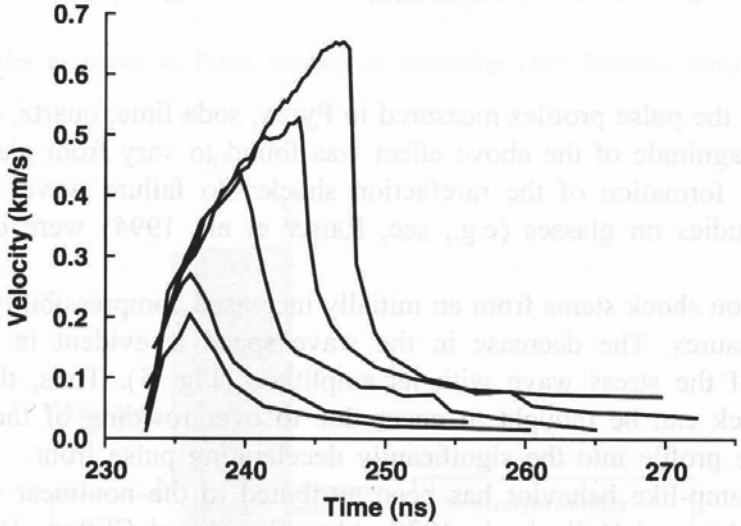


Fig. 5. Stress wave profiles in a soda lime glass under increasing laser fluence.

profile shown in Fig. 4b is within the resolution limit of our interferometer of 0.2 ns. This confirms the formation of the rarefaction shock.

The above effect was found to be a function of the stress pulse amplitude. Fig. 5 shows a series of stress pulse profiles with increasing laser fluence, measured in a soda lime glass. At low stress amplitudes, the profiles are similar to that in Si and other materials, having a finite rise-time and gradual post-peak decay. However, as the stress pulse amplitude exceeds a certain threshold, the rise-time of the stress wave gets longer but the post-peak stress profile starts to decay rather quickly. Ultimately a profile is attained with the post-peak stress dropping instantaneously (the drop time is within the resolution limit of our instrumentation), much like a "rarefaction shock." The modification in the stress wave profile due to glass compared with that due to Si can be appreciated by viewing Fig 8a.

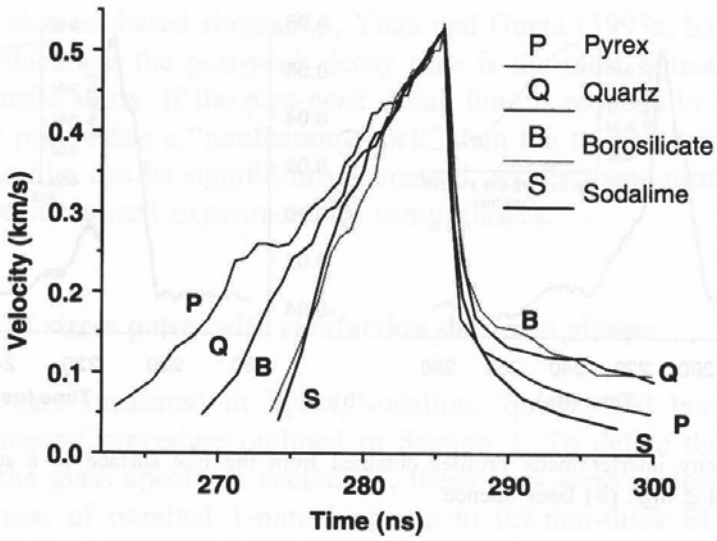


Fig. 6. Measured stress wave profiles in different types of glasses.

Fig. 6 shows the pulse profiles measured in Pyrex, soda lime, quartz, and borosilicate glasses. The magnitude of the above effect was found to vary from glass to glass, but all showed the formation of the rarefaction shock. No failure waves as observed in plate-impact studies on glasses (e.g., see, Raiser et al., 1994) were observed in our experiments.

The rarefaction shock stems from an initially increased compressibility of glass under increasing pressures. The decrease in the wave speed is evident in the increase in the rise-time of the stress wave with its amplitude (Fig. 5). Thus, the formation of rarefaction shock can be thought to occur due to overcrowding of the faster moving post-peak wave profile into the significantly decelerating pulse front.

The initial ramp-like behavior has been attributed to the nonlinear elastic response in glasses (Barker and Hollenbach, 1970; Abou-Sayed and Clifton, 1976). Details of such observations for our study using x-rays will be presented later (Kireev and Gupta, 2003).

It is not possible to make *direct* observations of rarefaction shocks in glasses through plate impact-based setups as the pulse lengths in such experiments is larger than the specimen thickness (e.g., see, Clifton et al., 1998). As suggested above, this effect develops due to finite propagation distance of the pulse into the material. This became possible in our work because of the short length ($\sim$0.1 mm) of the stress wave compared with the specimen thickness ($\sim$1 mm).

The above mechanism was quantified using a simple one-dimensional non-linear wave propagation model in which the wave speed was taken to be a function of particle velocity. The calculations are demonstrated for Pyrex for which the experimentally measured free surface velocity profiles at increasing amplitudes are shown in Fig. 7. To separate the effects of substrate and laser-material interaction, the data in Fig. 7 was generated using the setup shown in Fig. 8 in which a 1-mm-thick Pyrex sample was anodically bonded to a 0.7-mm-thick Si wafer. The stress pulse was generated on the

Boeing Ex. 1019, p. 8 of 22
Boeing v. Regents Univ. Cal.

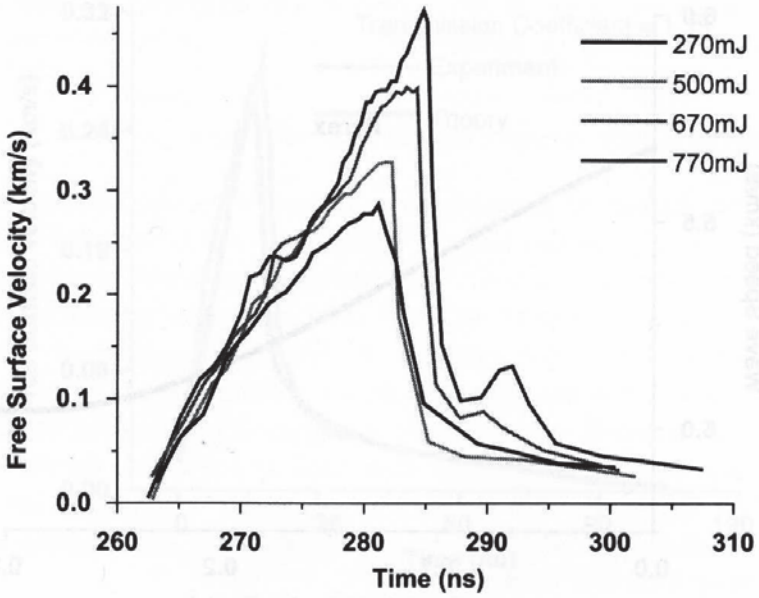


Fig. 7. Pulse profiles measured in Pyrex samples at increasing laser fluences, using the setup shown in Fig. 8.

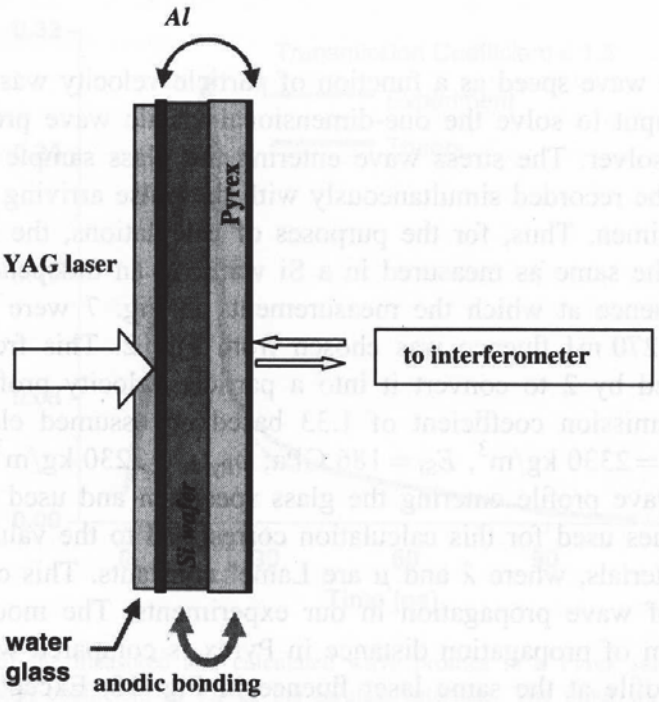


Fig. 8. A schematic of the setup used for validating the one-dimensional elastic nonlinear wave propagation model in Pyrex.

backside of the Si wafer in the standard manner by exfoliating a waterglass-constrained Al film, using a YAG laser pulse. This setup allowed studying the development of rarefaction shocks due to material non-linearity alone. Using the experimentally-observed

Boeing Ex. 1019, p. 9 of 22
Boeing v. Regents Univ. Cal.

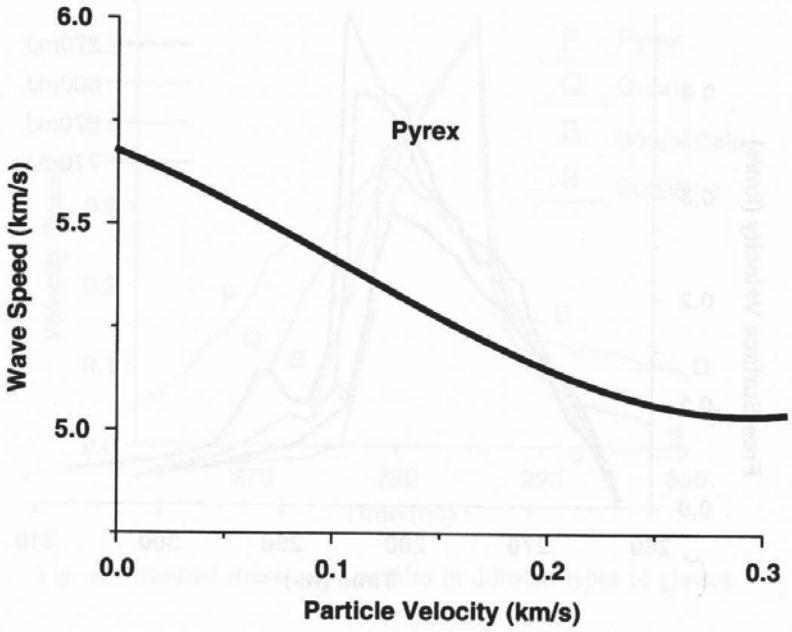


Fig. 9. The wave speed as a function of particle velocity (pressure) for Pyrex as determined after analyzing the experimentally recorded profiles in Fig. 7.

data in Fig. 7, the wave speed as a function of particle velocity was obtained (Fig. 9), and used as an input to solve the one-dimensional elastic wave propagation equation using a standard solver. The stress wave entering the glass sample at the Si/glass interface could not be recorded simultaneously with the pulse arriving at the free surface of the Pyrex specimen. Thus, for the purposes of calculations, the input wave profile was taken to be the same as measured in a Si wafer in an independent experiment at the same laser fluence at which the measurements in Fig. 7 were made. The profile corresponding to 270 mJ fluence was chosen from Fig. 2. This free surface velocity profile was divided by 2 to convert it into a particle velocity profile, and then multiplied by a transmission coefficient of 1.33 based on assumed elastic constants for Pyrex and Si ($\rho_{Si} = 2330$ kg/m^3, $E_{Si} = 186$ GPa; $\rho_{Pyrex} = 2230$ kg/m^3, $E_{Pyrex} = 51$ GPa) to arrive at the wave profile entering the glass specimen and used as an input in the simulation. E values used for this calculation correspond to the values of $(\lambda + 2\mu)$ for the respective materials, where λ and μ are Lame' constants. This choice is consistent with the nature of wave propagation in our experiments. The modified wave profile calculated at 1 mm of propagation distance in Pyrex is compared with the experimentally measured profile at the same laser fluence in Fig. 10. Except for the amplitude information, the model is able to predict the formation of the rarefaction shock and increase in the pulse rise-time quite well. This is not surprising since the wave speed vs. the particle velocity profile, which is the key input to the program, was obtained using the same experiments in which the to-be-predicted wave profiles were measured. The amplitude discrepancy is due to the effects arising from permanent densification, and partly because the transmission coefficient at the Si/Pyrex interface is not exactly known. Fig. 11 shows that for an exact matching of the experimental and calculated

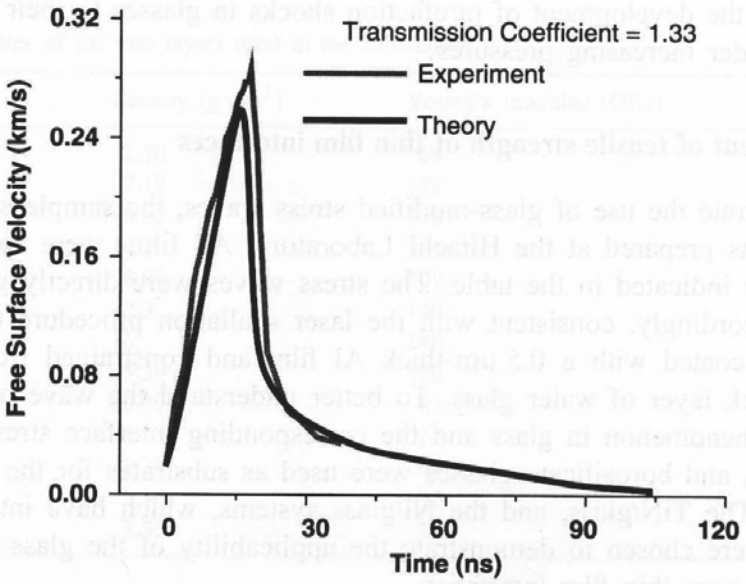


Fig. 10. Comparison of the measured and calculated wave profiles in a Pyrex sample, corresponding to an estimated transmission coefficient of 1.33 at the Si/glass interface. The input wave profile in Si in the simulation was proportional to the profile for 270 mJ in Fig. 2.

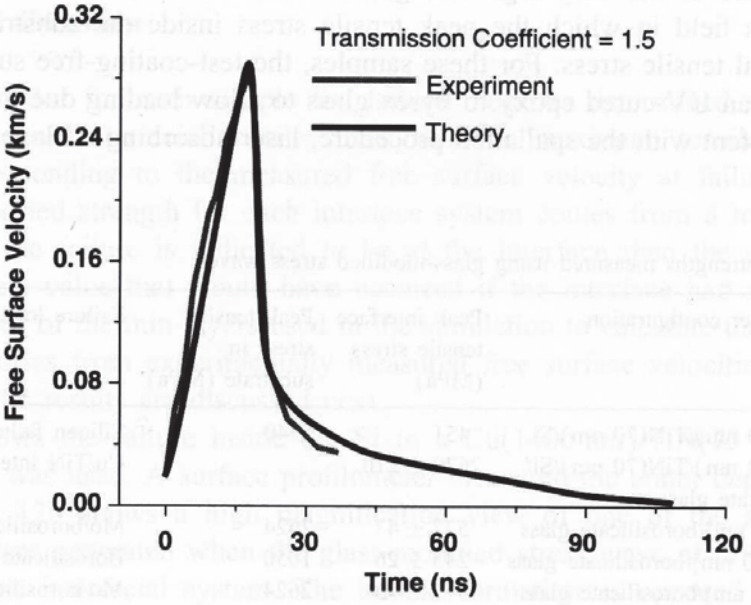


Fig. 11. Comparison of the measured and calculated wave profiles in a Pyrex sample, corresponding to an estimated transmission coefficient of 1.5 at the Si/glass interface. The input wave profile in Si in the simulation was proportional to the profile for 270 mJ in Fig. 2.

profiles, a transmission coefficient of 1.5 would be required. Follow-up experiments are planned in which simultaneous recording of particle velocities at the embedded Si/Pyrex interface, and free surface of Pyrex will be accomplished by taking advantage of the transparency of the glass specimen. In any case, the simple model presented

here confirms the development of rarefaction shocks in glasses to their increased compressibility under increasing pressures.

5. Measurement of tensile strength of thin film interfaces

To demonstrate the use of glass-modified stress waves, the sample sets summarized in Table 2 was prepared at the Hitachi Laboratory. All films were sputter deposited, with thickness indicated in the table. The stress waves were directly generated inside the glass. Accordingly, consistent with the laser spallation procedure the free surface of glass was coated with a 0.5 μm-thick Al film and constrained from top using a 40–50 μm-thick layer of water glass. To better understand the wave modification and propagation phenomenon in glass and the corresponding interface stress development, Pyrex, Quartz, and borosilicate glasses were used as substrates for the Mo/glass interface system. The TiN/glass, and the Ni/glass systems, which have interest in display technology, were chosen to demonstrate the applicability of the glass-modified waves in decohering very thin film interfaces.

In addition to the glass substrates, a Cu(1400 nm)/TiN(70 nm) bilayer system deposited on a Si wafer was considered. Previously, when the stress pulse was directly generated inside the Si wafer, failure within Si was observed. This, as discussed above, resulted because of the very high strength of the interfaces, and due to the inhomogeneous stress field in which the peak tensile stress inside the substrate exceeds the peak interfacial tensile stress. For these samples, the test-coating-free surface of Si was bonded using an UV-cured epoxy to Pyrex glass to allow loading due to glass-modified waves. Consistent with the spallation procedure, laser-absorbing Al layer was deposited

Table 2
Interface tensile strengths measured using glass-modified stress waves

Sample no.	Multilayer configuration	Peak interface tensile stress (MPa)	Peak tensile stress in substrate (MPa)	Failure locus
1	Cu(1400 nm)/TiN(70 nm)/Si	451	5340	Silicon failure
2	Cu(1400 nm)/TiN(70 nm)/Si/ borosilicate glass	2620 ± 210		Cu/TiN interface
3	Mo[400 nm]/borosilicate glass	577 ± 47	2624	Mo/borosilicate glass interface
4	Mo[1000 nm]/borosilicate glass	245 ± 26	1050	Borosilicate glass failure
5	Mo[400 nm]/borosilicate glass	577 ± 33	2624	Mo/borosilicate glass interface
6	Mo[400 nm]/Pyrex	135 ± 11	1125	Mo/Pyrex interface
7	Mo[400 nm]/quartz	99 ± 8	1110	Mo/quartz interface
8	Mo[1000 nm]/borosilicate glass	223 ± 24	980	Borosilicate glass failure
9	Mo[1000 nm]/Pyrex	53 ± 6	470	Borosilicate glass failure
10	Mo[1000 nm]/quartz	48 ± 4	460	Borosilicate glass failure
11	TiN [320 nm]/borosilicate glass	164 ± 11		TiN/borosilicate glass interface
12	Ni [350 nm]/borosilicate glass	102 ± 13		Ni/borosilicate glass interface
13	Cr[400 nm]/borosilicate glass	197 ± 16	2100	Cr/borosilicate glass interface
14	Mo[1000 nm]/Cr[400 nm]/ borosilicate glass	210 ± 19	980	Cr/borosilicate glass interface

Table 3
The elastic properties of the thin layers used in the calculation

Material	Density (g/cm^3)	Young's modulus (GPa)	Poisson's ratio
Al	2.70	69	0.34
Cr	7.19	279	0.21
Cu	8.93	130	0.343
Mo	10.2	324	0.36
Ni	8.90	207	0.33
Si	2.3	130	0.3
TaN	16	180	0.3
TiN	5.39	400	0.2
Ag	10.49	83	0.37
Borosilicate glass	2.5	77	0.22
Pyrex	2.23	64	0.2
Quartz	2.58	92	0.25
Soda lime glass	2.53	77.4	0.22

on the backside of the glass substrate and constrained by a 40–50 mm-thick layer of waterglass from the top.

6. Results and discussion

Table 2 provides for each sample the failure mode as determined via optical microscopy, the peak interfacial tensile stress, and the maximum tensile stress in the substrate corresponding to the measured free surface velocity at failure. The variation in the reported strength for each interface system comes from 8 to 10 successful spallations. If the failure is indicated to be at the interface then the substrate stress is the theoretical value that would have occurred if the interface had not failed. The elastic properties of the thin layers used in the simulation to calculate the interface tensile stress histories from experimentally measured free surface velocities are given in Table 3. Specific results are discussed next.

Fig. 12a shows the failure inside the Si in a Cu(1400 nm)/TiN(70 nm)/Si system when no glass was used. A surface profilometer measured the crater depth to be about 40 μm. Figure 12b shows a high magnification view of one of the several coating bubbles that were generated when the glass-modified stress wave of critical amplitude loaded the same interfacial system. The bubble formation as opposed to a complete separation (spall) of the bilayer is due to the ductility of the Cu. The arrow shows the failure to be at the Cu/TiN interface with no fracture inside the Si. An interface tensile strength value of 2.62 GPa was calculated. This is a rather high value, which was not possible to attain using the basic spallation setup. This is quantitatively shown in Figs. 13(a) and (b). Fig. 13(a) shows the measured free surface velocity profiles in the borosilicate glass and Si substrates corresponding to the failures shown in Fig. 12. The interface tensile stress history corresponding to each profile is shown in Fig. 13(b). The dramatic increase in the interface tensile stress due to the glass-modified wave is evident.

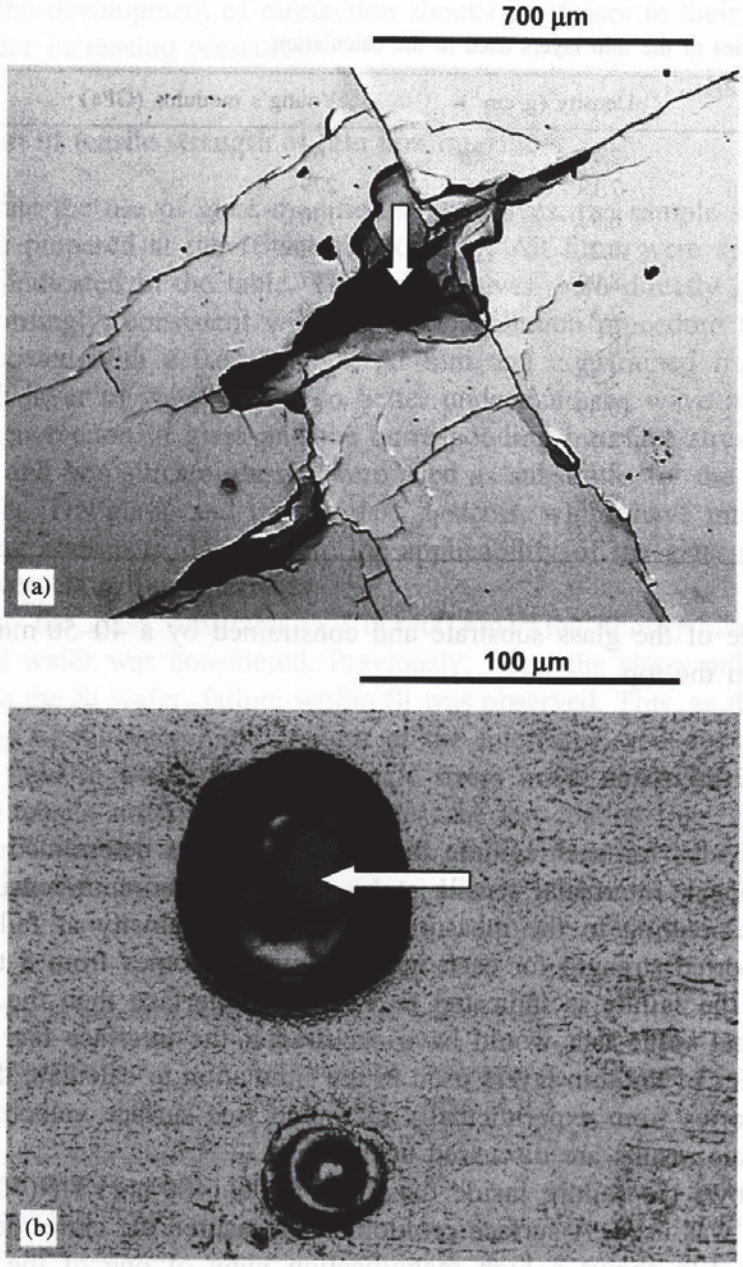


Fig. 12. Failure in a Cu(1400 nm)/TiN(70 nm)/Si system. (a) With no glass attached to the Si, the failure occurred cohesively inside the Si. (b) With glass-modified wave, failure was observed at the interface as shown by the arrow. The failure was determined to be specifically at the Cu/TiN interface.

6.1. Samples 3–10

Failure in sample 3 was at the Mo/borosilicate-glass interface. Optical micrograph of the spalled crater in Fig. 14a shows the interface separation to have occurred from a collection of radially outward propagating central interfacial flaws similar to those observed in a SiC/Si interface (Gupta et al., 1992). As shown in a high magnification view in Fig. 14b, the propagating crack tip appears to kink in and out of the interface

Boeing Ex. 1019, p. 14 of 22
Boeing v. Regents Univ. Cal.

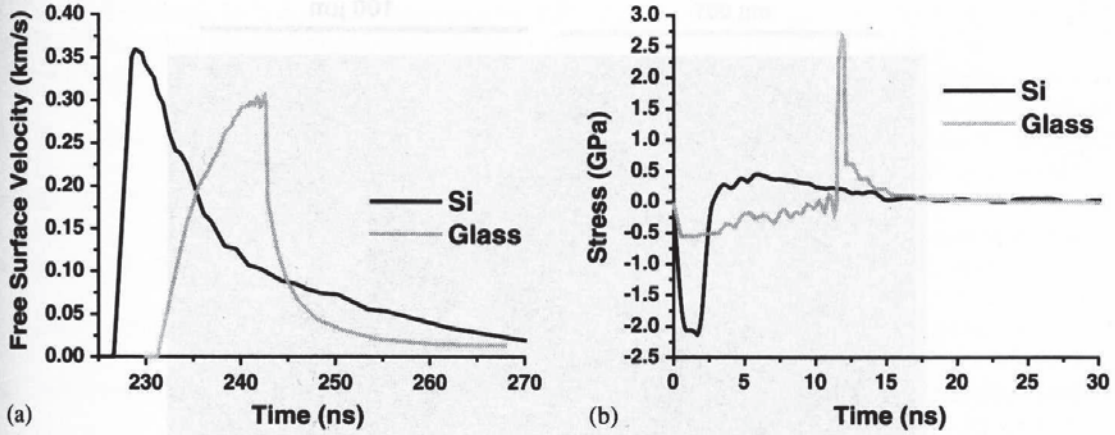


Fig. 13. Free surface velocity profiles (a) and stress history at the Cu/TiN interface with and without the borosilicate-glass-modified waves (b).

causing shallow glass failure. The quantification of the complicated interaction of the stress wave with the film's free surface and crack flanks to result in time-varying mode I to mode II crack-tip stress intensity factors ratio to cause such a failure mode is outside the scope of the present paper.

Rather interestingly, despite larger Mo film thickness compared with the sample 3, the failure in the Sample 4 was dominantly in the borosilicate glass with no interface failure (Fig. 15). Because of the high residual stresses in the Mo film, the near surface region of the glass was found populated with linear cracks as shown by an arrow in Fig. 15. Because of the Poisson's effect, the transverse tensile stress generated parallel to the interface caused premature propagation of such cracks causing cohesive failure inside the glass substrate. Fig. 15 also shows such premature substrate cracks starting from pre-existing cracks. This is consistent with the very low value of tensile strength in glass of 1050 MPa compared with 2624 MPa for Sample 3. Consistently, the Mo/glass interface stress when premature failure in glass occurred in the Sample 4 was only 245 MPa, which is lower than the Mo/borosilicate-glass interface strength of 577 MPa determined from Sample 3.

In samples, 5–7, all failures were at the Mo/borosilicate-glass interface, with the interface strength varying depending upon the type of glass used. As before, when the Mo film thickness was increased to 1000 nm, one would have expected a clean interfacial failure. However, as in Sample 4, all failures were predominantly in the glass for samples bearing a 1000 nm-thick Mo film. When viewing the maximum tensile stress amplitude inside glass for samples 8–10, one must conclude that pre-existing cracks in glass on account of high residual stresses inside the Mo film led to premature failure before the desired interface could be loaded to failure.

In contrast to the Mo/glass case, failure in the TiN/Glass, and the Ni/Glass, interface systems was at the interface. The fracture surface showing the glass surface was featureless. Specific interface strength values are indicated in Table 2. Successful measurements demonstrate the ability of the new technology to decohere very thin film interfaces.

Boeing Ex. 1019, p. 15 of 22
Boeing v. Regents Univ. Cal.

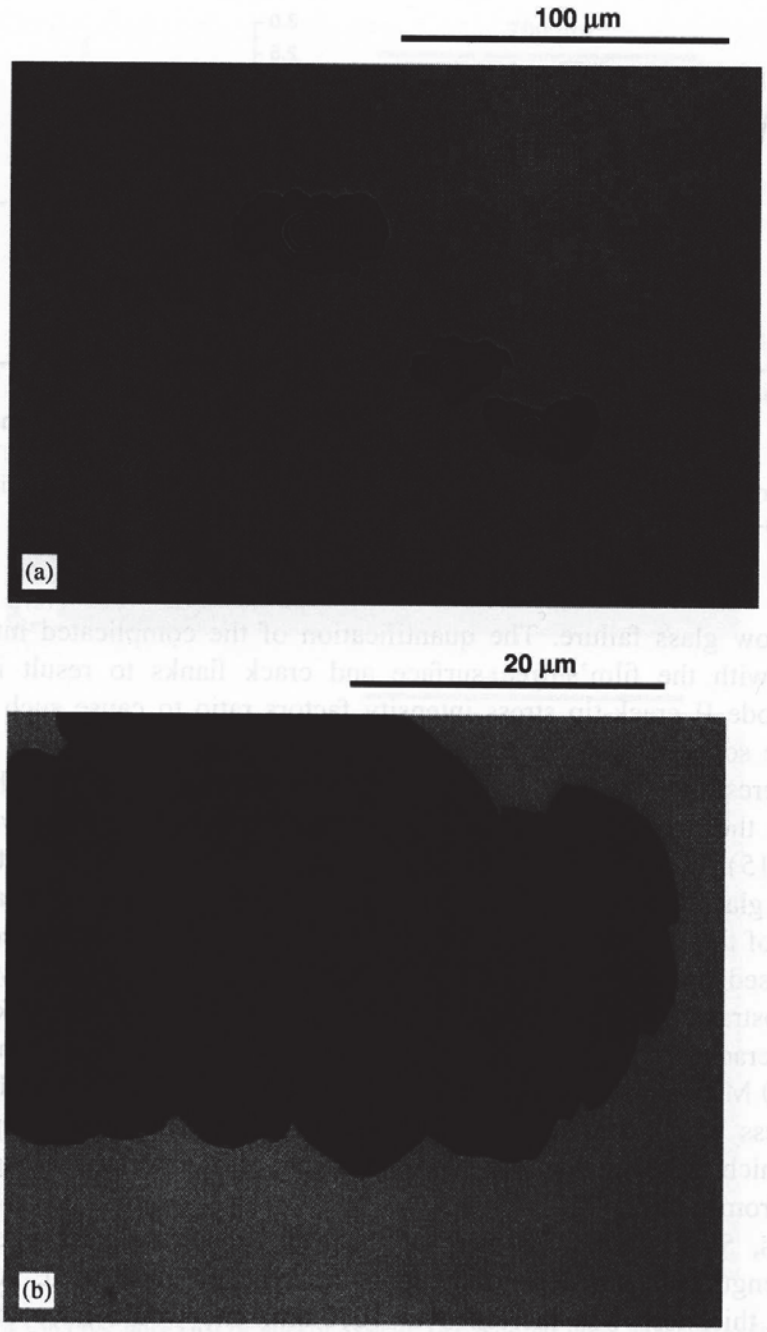


Fig. 14. Failure in Sample 3 at the Mo/borosilicate-glass interface. (a) Low magnification view of the failed interface showing the glass surface. (b) High magnification view of the failed substrate surface showing shallow failure caused in glass by kinking in and out of the interface crack. The Mo film thickness for this sample was 400 nm.

In samples 13 and 14, the failure was observed to be at the Cr/borosilicate-glass interface, with the interface strength values consistent with each other. As expected, for Sample 14, it took a much lower initial stress wave amplitude (reflected in much lower substrate stress) for interface decohesion on account of 1000 nm-thick Mo overlayer.

Boeing Ex. 1019, p. 16 of 22
Boeing v. Regents Univ. Cal.

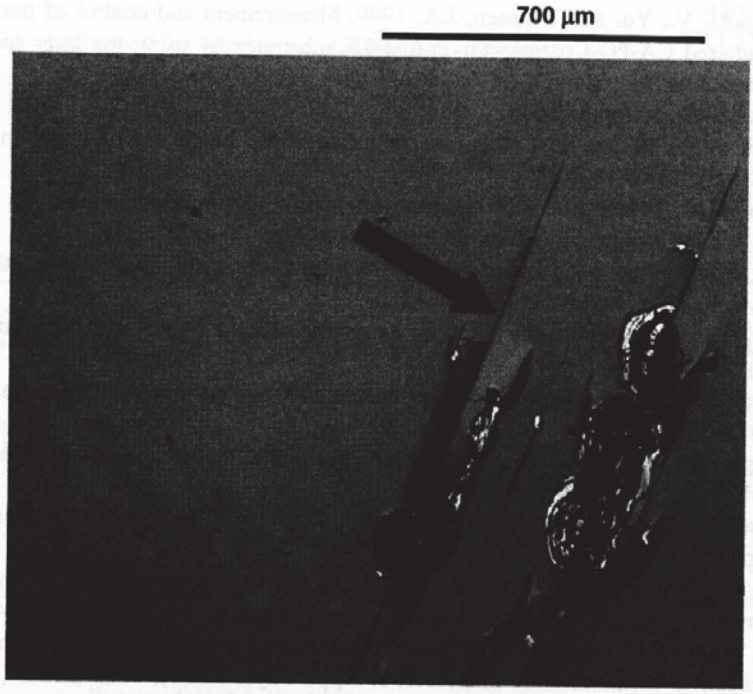


Fig. 15. Optical micrograph showing cohesive failure inside borosilicate-glass in sample 4. Mo thickness was 1000 nm.

7. Conclusions

Observations of stress wave profiles with rarefaction shocks in glasses were presented. The post-peak decay of stress wave was found to be a function of the wave amplitude. Interfaces of films with varying material composition and thickness well below 1 μm were loaded with glass-modified waves using the basic laser spallation test assembly. Results indicate that interfaces with strengths as high as 2.7 GPa, and adhesion of films with thickness as low as 185 nm could be measured. Failure in all interface systems presented here was inside the substrate when tested in the basic laser spallation methodology without the use of glass-modified waves. Thus, an important advance has been made that should allow material optimization of ultrathin layer systems that may form basis of future MEMS-based microelectronic, mechanical and clinical devices.

References

Abou-Sayed, A.S., Clifton, R.J., 1976. Pressure shear waves in fused silica. J. Appl. Phys. 47 (5), 1762–1770.

Barker, L.M., Hollenbach, R.E., 1970. Shock-wave studies of PMMA, fused silica, and sapphire. J. Appl. Phys. 41 (10), 4208–4226.

Clifton, R.J., Mello, M., Brar, N.S., 1998. Effect of shear on failure waves in soda lime glass. Shock Compression of Condensed Matter—1997. The American Institute of Physics, New York, pp. 521–524.

Kitty van Dijk, Gupta, V., Yu, A.K., Jansen, J.A. 1998. Measurement and control of interface strength of rf "magnetron sputtered CA-PO-Coatings on Ti-6Al-4V substrates by using the laser spallation technique." J. Biomed. Mater. Res. 41, 624–632.

Kireev and Gupta (2003), in preparation.

Gupta, V., Pronin, A.N., 1995a. New technique to measure the toughness of thin-film interfaces. J. Am. Ceram. Soc. 78 (5), 1397–1400.

Gupta, V., Pronin, A.N., 1995b. Effect of substrate orientation and deposition mode on the tensile strength and toughness of Nb/sapphire interfaces. J. Am. Ceram. Soc. 80 (12), 3172–3180.

Gupta, V., Argon, A.S., Cornie, J.A., Parks, D.M., 1992. Measurement of interface strength by laser spallation technique. J. Mech. Phys. Solids 40 (1), 141–180.

Mittal, K., 1987. Selected bibliography on adhesion measurement of films and coatings. J. Adhes. Sci. Technol. 1 (3), 247–259.

Pronin, A.N., Gupta, V., 1993. Interferometry on diffuse surfaces in high-velocity measurements. Rev. Sci. Instrum. 64 (8), 2233–2236.

Pronin, A.N., Gupta, V., 1998. Measurement of thin film interface toughness by using laser-generated stress pulses. J. Mech. Phys. Solids 46 (3), 389–410.

Raiser, G.F., Wise, J.L., Clifton, R.J., Grady, D.E., Cox, D.E., 1994. Plate impact response of ceramics and glasses. J. Appl. Phys. 75 (8), 3862–3869.

Yuan, J., Gupta, V., 1993a. Measurement of interface strength by the modified laser spallation experiment. Part I: experimental technique and modeling the spallation process. J. Appl. Phys. 74 (4), 2388–2404.

Yuan, J., Gupta, V., 1993b. Measurement of interface strength by the modified laser spallation experiment. Part II: application to metal–ceramic interfaces. J. Appl. Phys. 74 (4), 2388–2404.

Yuan, J., Gupta, V., 1995. The effect of microstructures and chemistry on tensile strength of Nb/sapphire interfaces, with and without the interlayers of Cr and Sb. Acta Metall. Mater. 43 (2), 781–794.

Yuan, J., Gupta, V., Pronin, A.N., 1993. Measurement of interface strength by the modified laser spallation experiment. Part III: experimental optimization of the stress pulse. J. Appl. Phys. 74 (4), 2405–2410.

Yuan, J., Gupta, V., Kim, M., 1995. Structure and chemistry of Nb/sapphire interfaces, with and without interlayers of Sb and Cr. Acta Metall. Mater. 43 (2), 769–779.

Boeing Ex. 1019, p. 18 of 22
Boeing v. Regents Univ. Cal.

JOURNAL OF THE MECHANICS AND PHYSICS OF SOLIDS

EDITORS

L. B. FREUND
Brown University
Division of Engineering

J. R. WILLIS
Centre for Mathematical Sciences
Department of Applied Mathematics
and Theoretical Physics





PERGAMON

Boeing Ex. 1019, p. 19 of 22
Boeing v. Regents Univ. Cal.

AIMS AND SCOPE

Journal of the Mechanics and Physics of Solids. The Journal publishes papers reporting original research on the mechanics of solids. Emphasis is placed on the development of fundamental concepts of mechanics and novel applications of these concepts based on theoretical, experimental or computational approaches, drawing upon the various branches of engineering science and the allied areas within applied mathematics, materials science, structural engineering, applied physics and geophysics. The main purpose of the Journal is to foster scientific understanding of the processes of deformation and mechanical failure of all solid materials, both technological and natural, and the connections between these processes and their underlying physical mechanisms. In this sense, the content of the Journal should reflect the curent state of the discipline in analysis, experimental observation and numerical simulation. In the interest of achieving this goal, authors are encouraged to consider the significance of their contributions for the field of mechanics and the implications of their results, in addition to describing the details of their work.

© 2003 Elsevier Science Ltd. All rights reserved.

This journal and the individual contributions contained in it are protected under copyright by Elsevier Science Ltd, and the following terms and conditions apply to their use:

Photocopying

Single photocopies of single articles may be made for personal use as allowed by national copyright laws. Permission of the publisher and payment of a fee is required for all other photocopying, including multiple or systematic copying, copying for advertising or promotional purposes, resale, and all forms of document delivery. Special rates are available for educational institutions that wish to make photocopies for non-profit educational classroom use.

Permissions may be sought directly from Elsevier Science Global Rights Department, PO Box 800, Oxford OX5 1DX, UK; phone: (+44) 1865 843830, fax: (+44) 1865 853333, e-mail: permissions@elsevier.co.uk. You may also contact Global Rights directly through Elsevier's homepage (http://www.elsevier.com), by selecting 'Obtaining Permissions'.

In the USA, users may clear permissions and make payments through the Copyright Clearance Center, Inc., 222 Rosewood Drive, Danvers, MA 01923, USA; phone: (978) 7508400, fax: (+1) (978) 7504744, and in the UK through the Copyright Licensing Agency Rapid Clearance Service (CLARCS), 90 Tottenham Court Road, London W1P 0LP, UK; phone: (+44) 171 631 5555; fax: (+44) 171 631 5500. Other countries may have a local reprographic rights agency for payments.

Derivative Works

Subscribers may reproduce tables of contents or prepare lists of articles including abstracts for internal circulation within their institutions.

Permission of the publisher is required for all other derivative works, including compilations and translations.

Electronic storage or Usage

Permission of the publisher is required to store or use electronically any material contained in this journal, including any article or part of an article.

Except as outlined above, no part of this publication may be reproduced, stored in a retrieval system or transmitted in any form or by any means, electronic, mechanical, photocopying, recording or otherwise, without prior written permission of the publisher.

Address permissions requests to: Elsevier Science Global Rights Department, at the mail, fax and e-mail addresses noted above.

Notice

No responsibility is assumed by the publisher for any injury and/or damage to persons or property as a matter of products liability, negligence or otherwise, or from any use or operation of any methods, products, instructions or ideas contained in the material herein. Because of rapid advances in the medical sciences, in particular, independent verification of diagnoses and drug dosages should be made.

Although all advertising material is expected to conform to ethical (medical) standards, inclusion in this publication does not constitute a guarantee or endorsement of the quality or value of such product or of the claims made of it by its manufacturer.

♾™ The paper used in this publication meets the requirements of ANSI/NISO Z39.48-1992 (Permanence of Paper)

JOURNAL OF THE MECHANICS AND PHYSICS OF SOLIDS

Editors

L. B. FREUND
Division of Engineering, Brown University,
Providence, RI 02912, USA
Fax: +1 401 863 1157
E-mail: jmps@engin.brown.edu

J. R. WILLIS
Department of Applied Mathematical and Theoretical Physics,
Centre for Mathematical Sciences, Wilberforce Road, Cambridge CB3 0WA, UK
Fax: +44 (0) 1223 65900
E-mail: J.R.Willis@damtp.cam.ac.uk

Editorial Advisers

R. HILL (Editor-in-Chief 1952–68)
Cambridge, UK

M. C. BOYCE
Department of Mechanical Engineering
Massachusetts Institute of Technology
Cambridge, USA

R. J. CLIFTON
Division of Engineering
Brown University
Providence, USA

H. HORII
Department of Civil Engineering
University of Tokyo
Tokyo, Japan

R. D. JAMES
Department of Aerospace Engineering and Mechanics
University of Minnesota
Minneapolis, USA

J. R. RICE
Division of Applied Science
Harvard University
Cambridge, USA

N. A. FLECK
Department of Engineering
University of Cambridge
Cambridge, UK

J. W. HUTCHINSON
Division of Applied Science
Harvard University
Cambridge, USA

M. ORTIZ
Graduate Aeronautical Labs
California Institute of Technology
Pasadena
USA

P. SUQUET
Laboratoire de Mecanique et d'Acoustique
CNRS
Marseille, France

E. VAN DER GIESSEN
Department of Applied Physics
University of Groningen
Groningen
The Netherlands

Publishing office: The Boulevard, Langford Lane, Kidlington, Oxford OX5 1GB, UK (Oxford 843000)

Advertising information. Advertising orders and enquiries can be sent to: **USA, Canada and South America:** Mr Tino de Carlo, The Advertising Department, Elsevier Science Inc., 655 Avenue of the Americas, New York, NY 10010-5107, USA; phone: (+1) (212) 633 3815; fax: (+1) (212) 633 3820; e-mail: t.decarlo@elsevier.com. **Japan:** The Advertising Department, Elsevier Science K.K., 9-15 Higashi-Azabu 1-chome, Minato-ku, Tokyo 106-0044, Japan; phone: (+81) (3) 5561 5033; fax: (+81) (3) 5561 5047. **Europe and ROW:** Rachel Leveson-Gower, The Advertising Department, Elsevier Science Ltd, The Boulevard, Langford Lane, Kidlington, Oxford OX5 1GB, UK; phone: (+44) (1865) 843565; fax: (+44) (1865) 843976; e-mail: r.leveson-gower@elsevier.co.uk

Published monthly. One volume per annum.

Publication information: Journal of the Mechanics and Physics of Solids (ISSN 0022-5096). For 2003, volume 51 is scheduled for publication. Subscription prices are available upon request from the Publisher or from the Regional Sales Office nearest you or from this journal's website (http://www.elsevier.com/locate/jmps). Further information is available on this journal and other Elsevier Science products through Elsevier's website: (http://www.elsevier.com). Subscriptions are accepted on a prepaid basis only and are entered on a calendar year basis. Issues are sent by standard mail (surface within Europe, air delivery outside Europe). Priority rates are available upon request. Claims for missing issues should be made within six months of the date of dispatch.

Annual Institutional Subscription Rates 2003*: Europe, The CIS and Japan* €2845. *All other countries US$*3183. *Associated Personal Subscription Rates are available on request for those whose institutions are library subscribers. Euro prices exclude VAT. Non-VAT registered customers in the European Community will be charged the appropriate VAT in addition to the price listed. Prices include postage and insurance and are subject to change without notice.*

Author enquiries: Authors can keep a track on the progress of their accepted article, and set up email alerts informing them of changes to their manuscript's status, by using the "Track a Paper" feature of Elsevier's Author Gateway (http://authors.elsevier.com).
For specific enquiries on the preparation of electronic artwork, consult http://authors.elsevier.com
Contact details for questions arising after acceptance of an article, especially those relating to proofs, are provided when an article is accepted for publication.

Orders, claims, and product enquiries: please contact the Customer Support Department at the Regional Sales Office nearest you:

New York: Elsevier Science, P.O. Box 945, New York, NY 10159-0945, USA; phone: (+1) (212) 633 3730 [toll free number for North American customers: 1-888-4ES-INFO (437-4636)]; fax: (+1) (212) 633 3680; e-mail: usinfo-f@elsevier.com

Amsterdam: Elsevier Science, P.O. Box 211, 1000 AE Amsterdam, The Netherlands; phone: (+31) 20 4853757; fax: (+31) 20 4853432; e-mail: nlinfo-f@elsevier.nl

Tokyo: Elsevier Science K.K., 9-15 Higashi-Azabu 1-chome, Minato-ku, Tokyo 106, Japan; phone: (+81) (3) 5561 5033; fax: (+81) (3) 5561 5047; e-mail: info@elsevier.co.jp

Singapore: Elsevier Science, No. 1 Temasek Avenue, #17-01 Millenia Tower, Singapore 039192; phone: (+65) 434 3727; fax: (+65) 337 2230; e-mail: asiainfo@elsevier.com.sg

Rio de Janeiro: Elsevier Science, Rua Sete de Setembro 111/16 Andar, 20050-002 Centro, Rio de Janeiro - RJ, Brazil; phone: (+55) (21) 509 5340; fax: (+55) (21) 507 1991; e-mail: elsevier@campus.com.br [Note (Latin America): for orders, claims and help desk information, please contact the Regional Sales Office in New York as listed above]

Back Issues. Back issues of all previously published volumes are available direct from Elsevier Science Offices (Oxford and New York). Complete volumes and single issues can be purchased for 1998–2002. Earlier issues are available in high quality photo-duplicated copies as complete volumes only. Back volumes on microfilm are available from UMI, 300 North Zeeb Road, Ann Arbor, MI 48106, USA

USA mailing notice: *Journal of the Mechanics and Physics of Solids* (ISSN 0022-5096) is published monthly by Elsevier Science Ltd (P.O. Box 211, 1000 AE Amsterdam, The Netherlands). Annual subscription price in the USA US$ 3183 (valid in North, Central and South America), including air speed delivery. Periodical postage rate paid at Jamaica, NY 11431.

USA POSTMASTER: Send address changes to *Journal of the Mechanics and Physics of Solids*, Publications Expediting Inc., 200 Meacham Ave, Elmont, NY 11003.

AIRFREIGHT AND MAILING in the USA by Publications Expediting Inc., 200 Meacham Avenue, Elmont, NY 11003.

Copyright © 2003 Elsevier Science Ltd

VOLUME 51 NUMBER 8, AUGUST 2003 ISSN 0022-5096

JOURNAL OF THE MECHANICS AND PHYSICS OF SOLIDS

EDITORS

L. B. FREUND
Brown University
Division of Engineering

J. R. WILLIS
Centre for Mathematical Sciences
Department of Applied Mathematics
and Theoretical Physics

EDITORIAL ADVISERS

R. HILL (Editor-in-Chief 1952–68)—Cambridge, U.K.

M. C. BOYCE—Cambridge, U.S.A.
R. J. CLIFTON—Providence, U.S.A.
H. HORII—Tokyo, Japan
R. D. JAMES—Minneapolis, U.S.A.
J. R. RICE—Cambridge, U.S.A.
E. VAN DER GIESSEN—Groningen, The Netherlands
N. A. FLECK—Cambridge, U.K.
J. W. HUTCHINSON—Cambridge, U.S.A.
M. ORTIZ—Pasadena, U.S.A.
P. SUQUET—Marseille, France





PERGAMON

Also available on SCIENCE DIRECT® www.sciencedirect.com

Boeing Ex. 1019, p. 22 of 22
Boeing v. Regents Univ. Cal.