AD-A240 978

Office of Naval Research

Contract N00014-90-J-1726

Technical Report 2

Fracture Studies of Diamond Films on Silicon

by

J. J. Mecholsky, Y. L. Tsai, and W. R. Drawl

Prepared for Publication

in

Journal of Applied Physics

Department of Materials Science and Engineering
University of Florida
Gainesville, FL 32611

91-11418

August 28, 1991

91 9 24 064

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED	1b. RESTRICTIVE MARKINGS
2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION/AVAILABILITY OF REPORT UNLIMITED
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE	
4. PERFORMING ORGANIZATION REPORT NUMBER(S)	5. MONITORING ORGANIZATION REPORT NUMBER(S) N00014-90-J-1726
6a. NAME OF PERFORMING ORGANIZATION University of Florida — 6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION ONR / Dr. Robert Schwartz
6c. ADDRESS (City, State, and ZIP Code) 256A Rhines Hall Gainesville, FL 32611	7b. ADDRESS (City, State, and ZIP Code) Code 3/3 Naval Weapons Center China Lake, CA 93555-6001
8a. NAME OF FUNDING/SPONSORING ORGANIZATION ONR — 8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
8c. ADDRESS (City, State, and ZIP Code) 800 North Quincy Street Arlington, VA 22217-5000	10. SOURCE OF FUNDING NUMBERS PROGRAM ELEMENT NO / PROJECT NO / TASK NO / WORK UNIT NO

11. TITLE (Include Security Classification)
Fracture Studies of Diamond Films on Silicon (U)

12. PERSONAL AUTHOR(S)
J. J. Mecholsky, Jr., T. L. Tsai, and W. R. Drawl

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Technical	FROM ____ TO ____	91-8-28	17

16. SUPPLEMENTARY NOTATION

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	This document has been approved for public release and sale; its distribution is unlimited.

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

Diamond coatings were prepared on silicon substrates for fracture studies. Two thicknesses of coatings were evaluated: 6 m and 12 m. The diamond films increased the strength of the silicon for the same size fracture initiating crack and thus caused an apparent toughness increase from 1.1 $MPam^{1/2}$ for the uncoated silicon to about 1.6 $MPam^{1/2}$ for the 12 m coated silicon. Fractography showed that the indentation impression on the coated surface was altered by the coating, but this did not alter the formation of the radial crack beneath the surface so that indentation fracture mechanics can be used for thin coatings with thicknesses below 12 m. Fractography also showed that the coatings separated from the substrate under and near the indentation site, but was still intact away from the indentation. Most of the fracture in the diamond coating was transgranular indicating good intergranular adhesion.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT XX UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS	21. ABSTRACT SECURITY CLASSIFICATION UNCLASSIFIED
22a. NAME OF RESPONSIBLE INDIVIDUAL	22b. TELEPHONE (Include Area Code) — 22c. OFFICE SYMBOL

DD FORM 1473, 84 MAR — 83 APR edition may be used until exhausted. All other editions are obsolete. — SECURITY CLASSIFICATION OF THIS PAGE

Sub. J.A.P.

Fracture studies of diamond films on silicon

J. J. Mecholsky, Jr. and Y. L. Tsai
Department of Materials Science & Engineering, University of Florida, Gainesville, FL 32605

W. R. Drawl
Materials Research Laboratory, Pennsylvania State University, University Park, PA 16802

ABSTRACT

Diamond coatings were prepared on silicon substrates for fracture studies. Two thicknesses of coatings were evaluated: 6 µm and 12 µm. The diamond films increased the strength of the silicon for the same size fracture initiating crack and thus caused an apparent toughness increase from 1.1 $MPam^{1/2}$ for the uncoated silicon to about 1.6 $MPam^{1/2}$ for the 12 µm coated silicon. Fractography showed that the indentation impression on the coated surface was altered by the coating, but this did not alter the formation of the radial crack beneath the surface so that indentation fracture mechanics can be used for thin coatings with thicknesses below 12µm. Fractography also showed that the coatings separated from the substrate under and near the indentation site, but was still intact away from the indentation. Most of the fracture in the diamond coating was transgranular indicating good intergranular adhesion.

Fracture studies of diamond films on silicc n

J. J. Mecholsky, Jr. and Y. L. Tsai
Department of Materials Science & Engineering, University of Florida, Gainesville, FL 32605

W. R. Drawl
Materials Research Laboratory, Pennsylvania State University, University Park, PA 16802

Diamond coatings were prepared on silicon substrates for fracture studies. Two thicknesses of coatings were evaluated: 6 μm and 12 μm. The diamond films increased the strength of the silicon for the same size fracture initiating crack and thus caused an apparent toughness increase from 1.1 $MPam^{1/2}$ for the uncoated silicon to about 1.6 $MPam^{1/2}$ for the 12 μm coated silicon. Fractography showed that the indentation impression on the coated surface was altered by the coating, but this did not alter the formation of the radial crack beneath the surface so that indentation fracture mechanics can be used for thin coatings with thicknesses below 12μm. Fractography also showed that the coatings separated from the substrate under and near the indentation site, but was still intact away from the indentation. Most of the fracture in the diamond coating was transgranular indicating good intergranular adhesion.

The development of low pressure techniques for the production of diamond films and substrates has encouraged researchers, technologists and industrialists to utilize the unique properties of diamond in a plethora of applications[1]. The potential uses range from coatings for bearings and cutting tools to free standing infrared dome materials[2]. Many of the potential applications involve diamond as a structural material. However, very few studies have been reported on the fracture of diamond[2]. This letter reports on the fracture of microwave-plasma-assisted chemical vapor deposition (MPACVD) of diamond coated silicon substrates. Two thicknesses of diamond coatings are evaluated: nominally 6μm and 12 μm. The diamond films were characterized using Raman spectroscopy. Diamond pyramid indentations were used to control the crack size and location of failure. The strength and toughness of the diamond coated silicon substrates were determined and fractography was used to identify the nature of the fracture.

Single crystal silicon was selected as the substrate for diamond films because it is isostructural with diamond and previous experience is available on the fracture of silicon[3]. Diamond deposition was made utilizing a Toshiba tube type microwave system[1,4]. The system creates a plasma which operates at 2.45 GHz with a maximum output power of 1500 W. The microwave cavity surrounds a 38mm quartz tube which contains the susceptor and substrate. In an attempt to obtain uniform films, all substrates were polished with a mixture of 0.5 μm diamond powder and methanol. All substrates should be considered as seeded.

Two deposition time periods were evaluated: 5h and 10 h.. The deposition conditions were held constant at a gas mixture of 2 % methane in UHP hydrogen, at a gas pressure of 90 Torr, and at a temperature of 1000 °C. The coating rate was approximately 1.2 μm/h.

Raman spectroscopy characterization of the diamond films were obtained. Figure 1 shows typical spectra. The characteristic 1332 cm^{-1} absorption band indicates that sp^3 carbon to carbon bonding is present. The sp^2 bonded carbon is shown as an absorption band between 1380 cm^{-1} and 650 cm^{-1}. The observed band between 1400 cm^{-1} and 1600 cm^{-1} is considered negligible[5].

In order to study the fracture properties, the coated silicon substrates were indented with a Vickers diamond at indentation loads of 3, 5, 7 and 9 kg. loads and then fractured in three point flexure. The toughness, K_c, was calculated from the indentation strength and load[6]:

$$K_c = \eta \, (E/H)^{1/8} \, [\sigma \, P^{1/3}]^{3/4} \qquad (1)$$

where E is the elastic modulus, H is the hardness, η is a constant (0.59), σ is the stress at fracture and P is the indentation load. For the purposes of this calculation, it was assumed that the diamond coating would not change the E & H values of the silicon appreciably. A measure of the toughness was also calculated from the observed crack size on the fracture surface using a fracture mechanics equation modified to account for the (local) residual stress associated with the indentation process[7,8].

$$K_c = 1.65\, \sigma\, (c)^{1/2} \qquad (2)$$

where c is $[a \cdot b]^{1/2}$; a is the depth and b is the half width of a semi-elliptical crack; 1.65 accounts for the shape, location and other constants in the fracture mechanics expression. This latter constant assumes that the crack is small relative to the thickness of the bar and that local residual tensile stresses (from the indentation process) are present.

In Figure 2, we see the strength results for the fracture of bars coated for 5 hours and 10 hours compared to that of silicon bars alone. The graph of logarithm strength, σ, versus logarithm indentation load, P, for the silicon without coating[3] follows the expected behavior, i.e., $\sigma\text{-}P^{-1/3}$ (Eq. 1). The diamond coated materials appear to lie above the line for the silicon alone. There are too few data to determine if the same trend is followed, i.e., the σ - $P^{1/3}$ behavior. Notice that the data for the 5h and 10h depositions lie at approximately the same positions. The position of the data indicates an apparent increase in toughness over that of silicon alone. If we examine the values of K_c as a function of indentation load, then we see in Figure 3 a & b that the values are approximately constant for the indentation loads used for the 5 hour and 10 hour coating, respectively. The calculated values for the toughness are presented in Table I. Notice that the 10 hour diamond is about 38 % higher (1.6 $MPam^{1/2}$) than the uncoated silicon[3] (1.2 $MPam^{1/2}$). Of course, this is an apparent toughening because the most likely reason for the increased strength is a residual compressive stress on the surface of the coated bars due to thermal expansion mismatch between the diamond and the silicon.

If we examine the fracture surfaces of the diamond coated silicon, we notice several important features. First, for example, in Figure 4, we notice that a well-formed radial crack is present on the fracture surface under the fracture initiating indentation site. It does not appear much different than those formed on uncoated silicon (Figure 4a). If we examine the surface of the indentation site (Figure 5 a), then we see that there is more crushing than expected and a well formed surface trace[3,6] does not appear. However, for higher indentation loads, the crack sizes and shapes formed do not differ, on the average, from that of silicon alone[3]. For the lowest indentation load, i.e., 29.4 N, well formed cracks did not form and the diamond coating appeared intact. Notice the higher than expected strengths (from σ-$P^{-1/3}$ behavior) for the lowest indentation loads for the 5h and 10 h depositions (Figure 2). Apparently the diamond coating does not greatly affect the formation of large cracks, but will inhibit the formation of smaller cracks. The implications of the present results is that investigators who only sample the strength for as-deposited films should observe higher strengths, which should be drastically reduced if surface damage occurs either by intentional indentation or unintentional impact. This type of behavior would result in a large scatter in strength data. Thus, the reasonable explanation for the strength increase observed for the indentation load range used, here, is the presence of residual compressive stress and not the limitation of crack sizes. We can estimate the magnitude of this stress by calculating the difference between the observed strength and the expected strength from the crack size (using fracture mechanics). This calculation results in a residual compressive stress of about 30 MPa. This estimate from fractographic data is consistent with classical laminate plate theory calculations of the residual stress (40 MPa) for a composite[9].

Second, the fracture in the diamond is primarily transgranular (Figure 4 c-d and Figure 5 b-c), implying that the inter-grain adherence is relatively strong. Third, in Figure 4 c, notice that the diamond layer separates from the substrate during fracture near the initial damage due to the indentation. This separation does not occur elsewhere in the material (Figure 4d). Thus, it appears that the stress state under the indenter is such that separation is enhanced. We know from previous studies that lateral cracks can indeed form under the indentation site and proceed approximately parallel to the surface[10, 11]. This result also implies that the coating-substrate adherence is mostly mechanical.

In a few limited cases, the diamond coating did not completely cover the Si surface. For these cases, the strengths were comparable to uncoated Si. Thus, it appears that a certain amount of contiguity is needed for successful strengthening. This finding is consistent with, and supports the compressive stress layer strengthening proposed here. These few samples were not counted in the strength and fracture studies reported here.

The conclusions from this study are as follows:

1. Relatively thin diamond coatings increase the strength and apparent toughness of silicon substrates due to residual compressive stress and not the prevention of crack growth for large impact loads.
2. When the coating process is successful, transgranular fracture should be expected. Of course this is dependent on the deposition technique (processing), substrate composition and surface roughness.
3. Diamond indentation techniques are applicable to study the fracture behavior of diamond coated films. Both low loads and high loads should be used in order to sample a range of crack sizes. Strength studies without controlled crack initiation may suggest misleading results.

ACKNOWLEDGEMENTS: The authors thank Diane S. Knight (PSU) for the Raman spectroscopy characterization, Zheng Chen (UF) for the laminated plate theory calculations, Dr. Robert Schwartz (NWC) for technical discussions and ONR as well as the Diamond And Related Materials Consortium of the Penn State University for partial financial support.

REFEKENCES:

1.K. E. Spear, "Diamond - Ceramic Coating of the Future", J. Am. Ceram. Soc., 72[2] 171-91 (1989).

2. J. E. Field, "Strength and Fracture Properties of Diamond", pp. 282-324 in The Properties of Diamond, ed. J. E. Field, Academic Press, NY (1979).

3.Y. L. Tsai and J. J. Mecholsky, Jr., "Fractal Fracture of Single Crystal Silicon", J. Mater. Res., 6[6] 1248- 63 (1991).

4.A. R. Badzian, T. Badzian, R. Roy, R. Messier and K. Spear, Mater. Res. Bull. XXIII, 531 (1989).

5.D. S. Knight and W. B. White, "Characterization of Diamond Films by Raman Spectroscopy", J. Mater. Res. (1990).

6.P. Chantikul, G. R. Anstis, B. R. Lawn, and D. B. Marshall, J. Am. Ceram. Soc. 64 (9), 539-543 (1981).

7.R. F. Cook and B. R. Lawn, J. Am. Ceram. Soc. 66[11] C-200-201(1983).

8.Y-S. Chou, J. J. Mecholsky, Jr., and M. R. Silsbee, "Fracture Toughness of Macro-Defect-Free Cement Using Small Crack Techniques", J.Mater.Res. 5[8] 1774-80 (1990).

9.Z. Hashin and B. W. Rosen, Fiber Composites Analysis and Design V.I, Composites, Materials and Laminates , DOT/FAA/CT -85/6 (1983).

10.C. Rossington, A. G. Evans, D. B. Marshall and B. T. Khuri-Yakub, "Measurements of Adherence of Residually Stressed Thin Films by Indentation. II. Experiments with ZnO/Si", J. Appl. Phys 56[10] 2639-2644 (1984).

11.P. H. Korbrin and A. B. Harker, "The Effects of Thin Compressive Films on Indentation Fracture Toughness Measurements", J. Mater. Res. (1990).

Table I. Strength & Toughness of Diamond Coated Silicon

Condition	Indentation Load (N)	Fracture Stress(MPa)	Crack Size c (µm)	Toughness K_{IC} (MPa$\sqrt{m}$) Eq.(1)	Toughness K_{IC} (MPa$\sqrt{m}$) Eq.(2)
10 hour deposition (≈12µm)	29.4	161.8	47	2.9	1.8
	29.4	152.8	41	2.8	1.6
	49.0	68.7	235	1.7	1.7
	49.0	54.5	263	1.4	1.5
	68.6	62.2	267	1.8	1.7
	88.2	58.3	213	1.8	1.4
			average	2.1±0.6	1.6±0.2
5 hour deposition (≈6µm)	29.4	99.3	70	2.0	1.4
	29.4	129.2	55	2.4	1.6
	49.0	68.3	159	1.7	1.4
	49.0	49.5	254	1.3	1.3
	68.6	63.9	219	1.8	1.6
	68.6	66.3	175	1.8	1.5
	88.2	46.0	362	1.5	[illegible]
	88.2	71.0	133	2.0	1.4
			average	1.8±0.3	1.4±0.[illegible]

FIGURE CAPTIONS

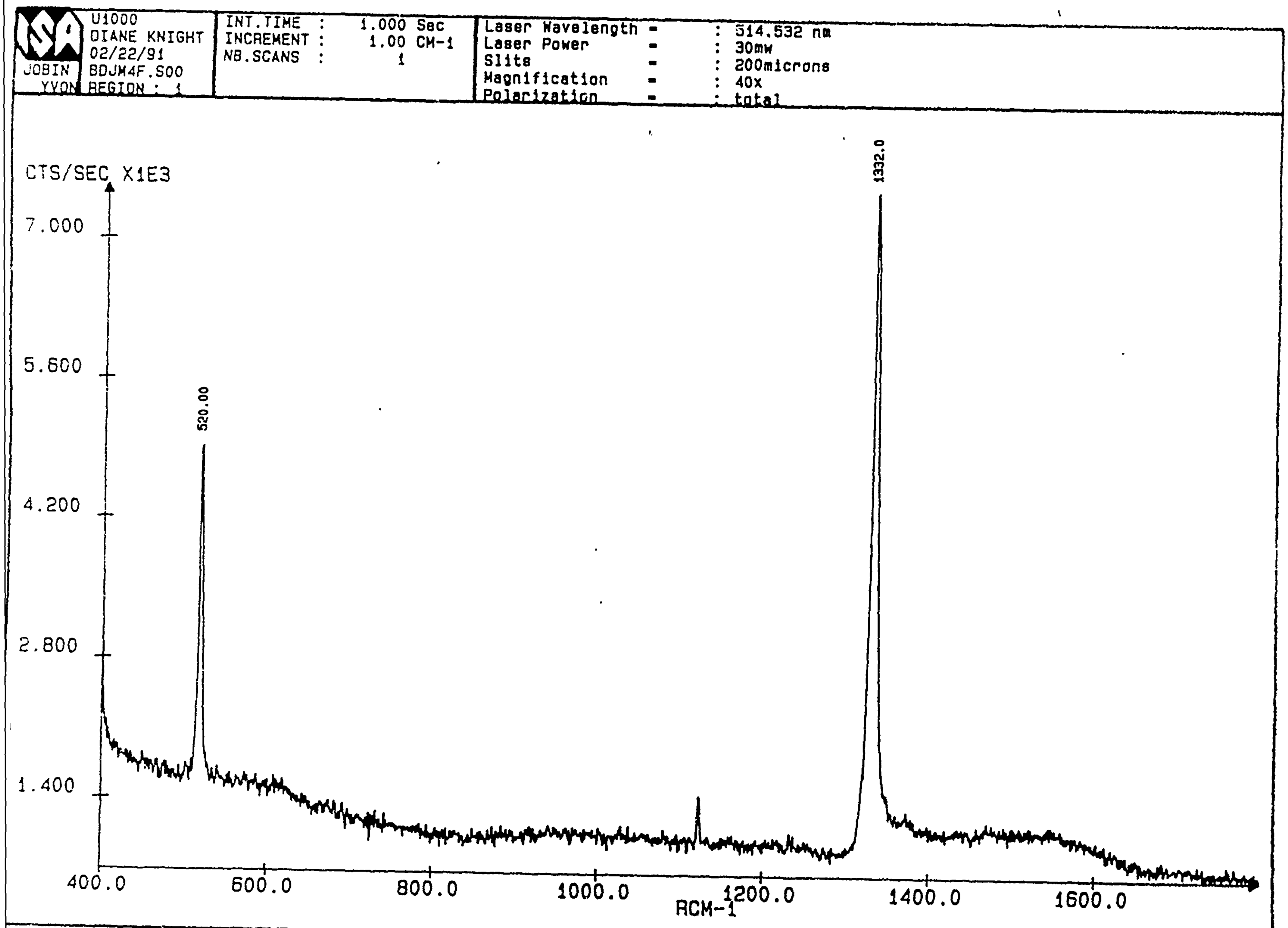
Figure 1 - Raman Spectra of Diamond Coating on A Silicon Substrate. The absorption band at 1332 cm^{-1} represents sp^3 carbon to carbon bonding. The broad band between 1400 cm^{-1} and 1650 cm^{-1} is indicative of sp^2 bonded carbon. In this sample for this figure as well as the other cases examined minimal sp^2 bonding is present. The bands at 520 cm^{-1} and 1100 cm^{-1} represent the substrate and room lights, respectively.

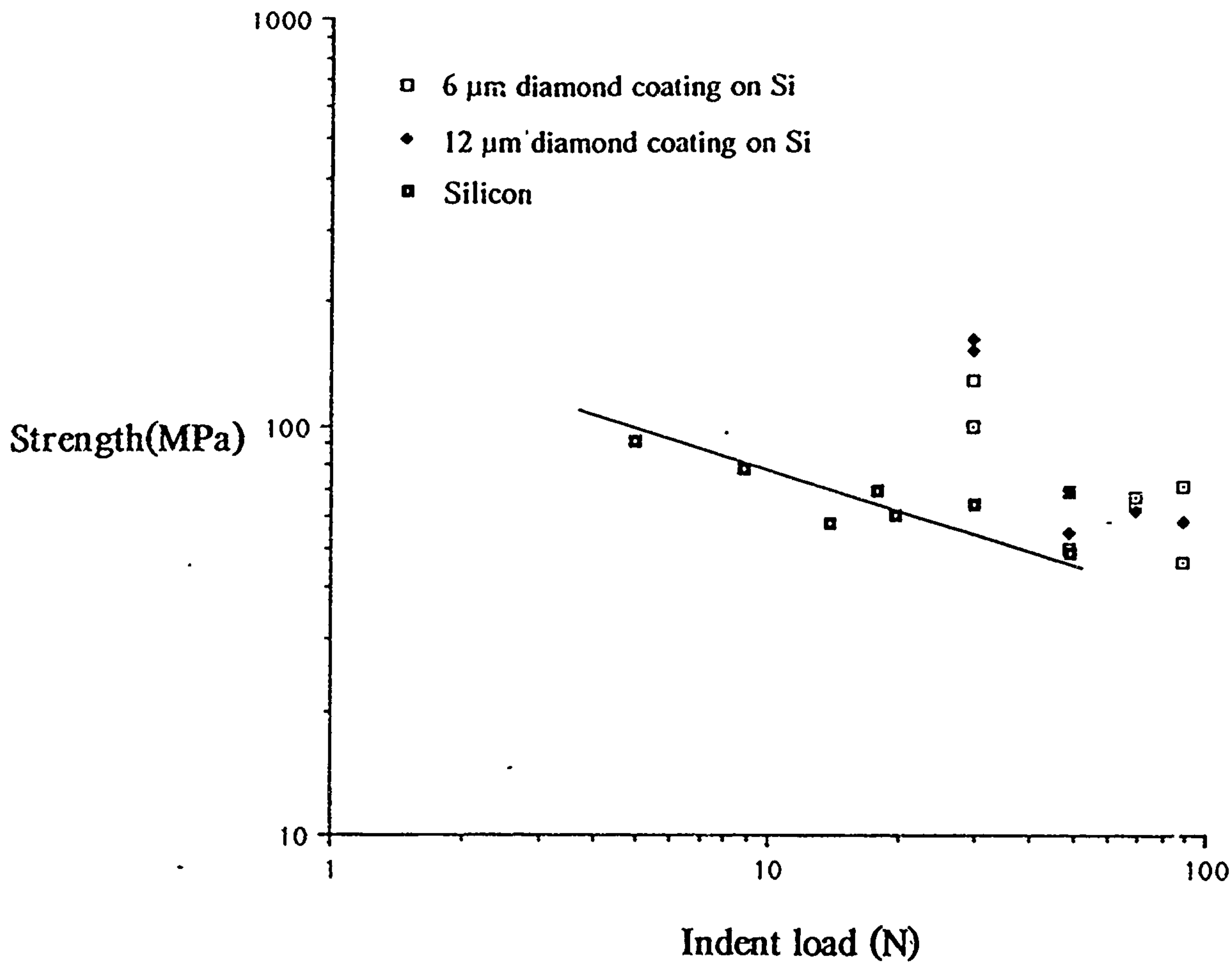
Figure 2 - Strength as a Function of Indentation Load for Diamond Coated Silicon. The 5 h deposition and10 h deposition are shown by the symbols. The solid line represents the data for uncoated silicon (cf. ref 3). Data above that line indicates a strength increase for the same size crack, i.e., an apparent toughness increase.

Figure 3 - Toughness as a Function of Indentation Load for Diamond Coated Silicon : (a) 5 h deposition and (b) 10 h deposition. The nearly constant value of toughness implies that indentation fracture mechanics applies to this material.

Figure 4 - Fractographs of Silicon and Diamond Coated Silicon.(A) optical fractograph showing the trace of the radial crack on the fracture surface for uncoated silicon. . (B) scanning electron micrograph shows the trace of the radial crack on the fracture surface of a (5hour) diamond coated silicon bar; The arrows in (A) and (B) indicate the location of the approximate center of the indentation point.(C) shows the separation of the film from the substrate in the region of the indentation crack. Notice the transgranular nature of the fracture. (d) shows a region away from the indentation region that is still attached. In both (C) and (D), "C" indicates the diamond film and "Si" is the silicon substrate.

Figure 5 - Scanning Electron Micrograph of Diamond Coated Silicon. (A) Trace of the indentation impression on the diamond film and the silicon substrate. Notice that the impression region is not well formed and does not appear as a diamond pyramid hardness as expected. However, also notice there are still cracks which emanate from the crushed zone and form radial cracks to act as sites for fracture initiation (Figure 4 B.). (B.) and (C) show the cracks (arrows) from the top surface; these regions show many transgranular features, e.g. the arrows in (C).


JOBIN YVON
U1000
DIANE KNIGHT
02/22/91
BDJM4F.S00
REGION : 1
INT.TIME : 1.000 Sec
INCREMENT : 1.00 CM-1
NB.SCANS : 1
Laser Wavelength = : 514.532 nm
Laser Power = : 30mw
Slits = : 200microns
Magnification = : 40x
Polarization = : total
CTS/SEC X1E3
7.000
5.600
4.200
2.800
1.400
520.00
1332.0
400.0
600.0
800.0
1000.0
1200.0
1400.0
1600.0
RCM-1



1000
6 μm diamond coating on Si
12 μm diamond coating on Si
Silicon
Strength(MPa)
100
10
1
10
100
Indent load (N)

Data from "Shour Diamond CVD data"

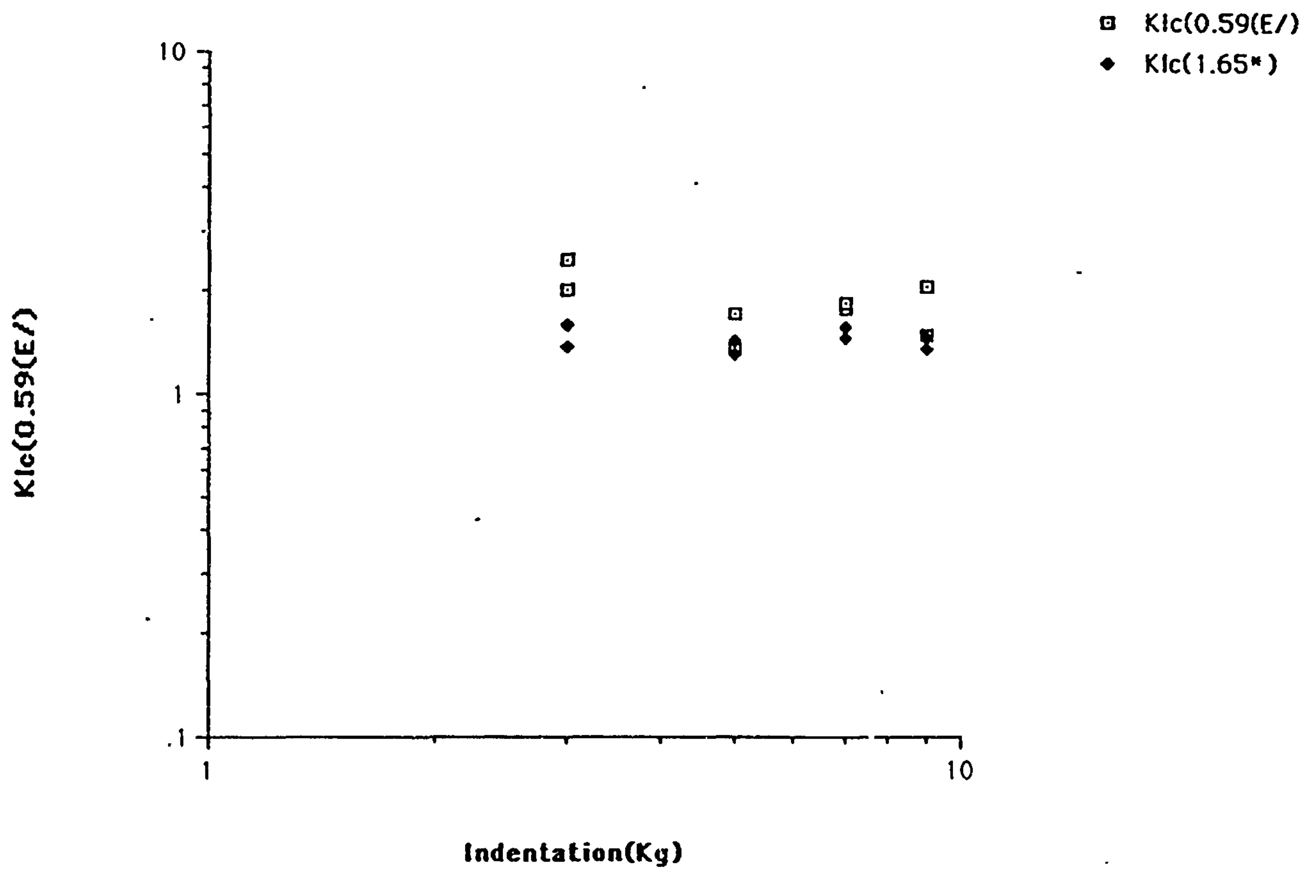


Fig. 3 (a)

Data from "10hour Diamond CVD data"

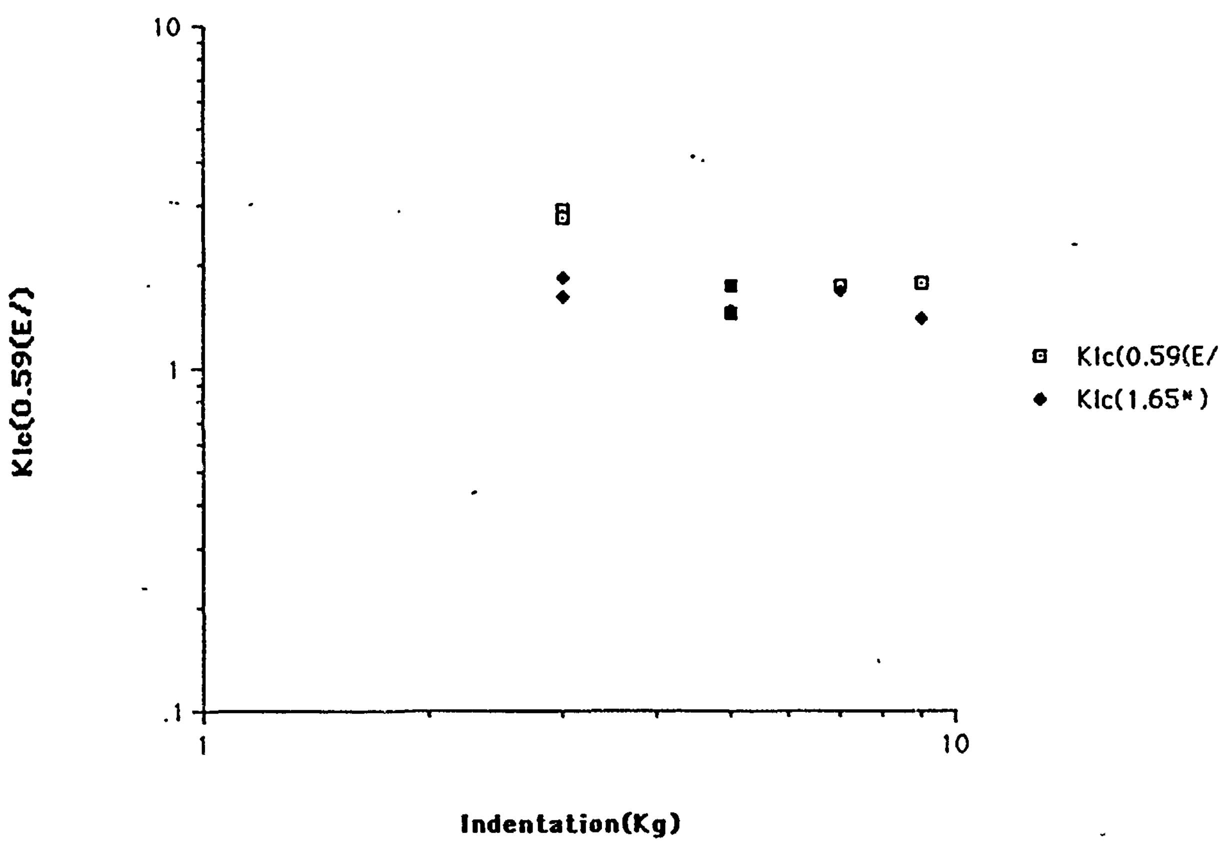
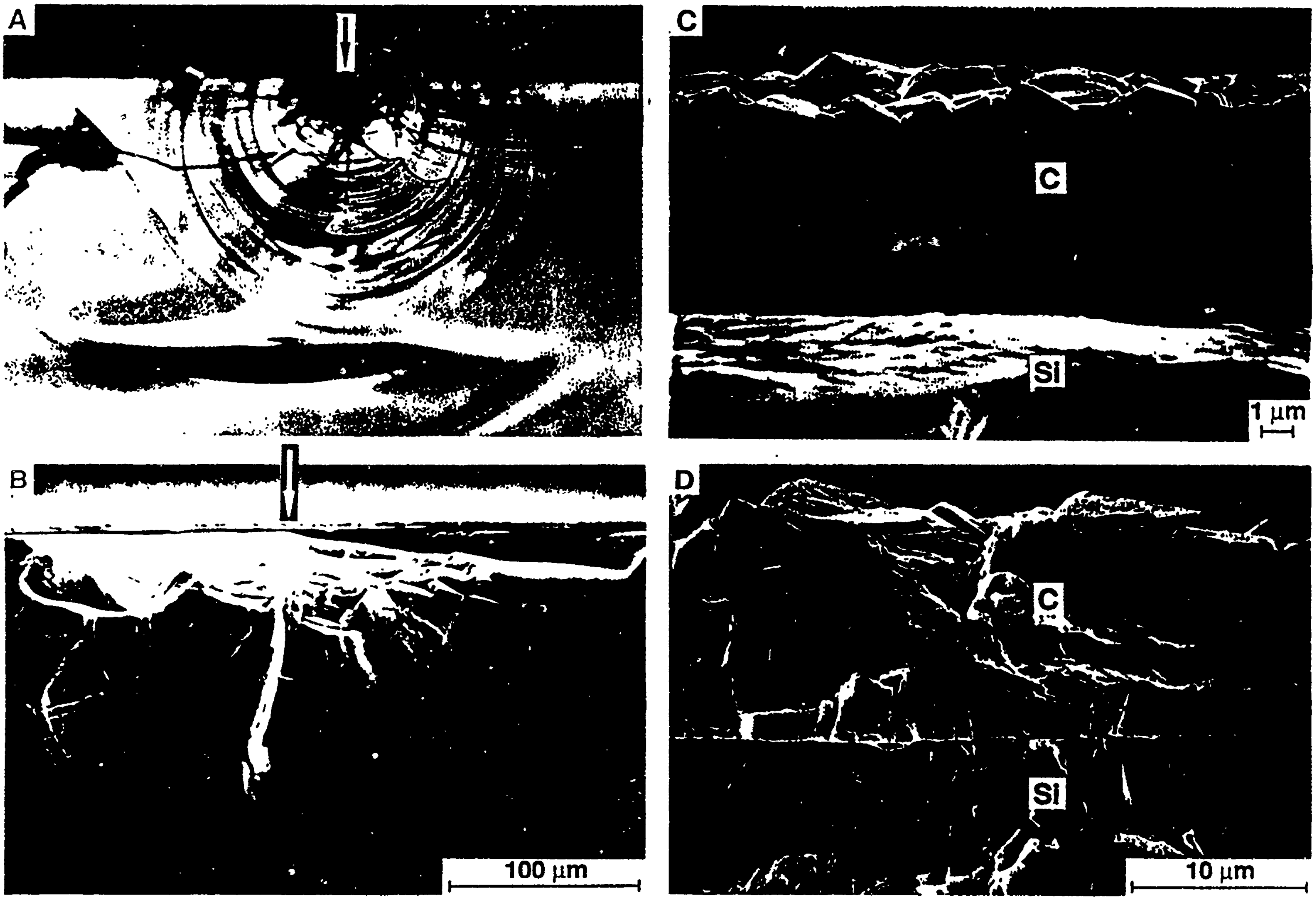
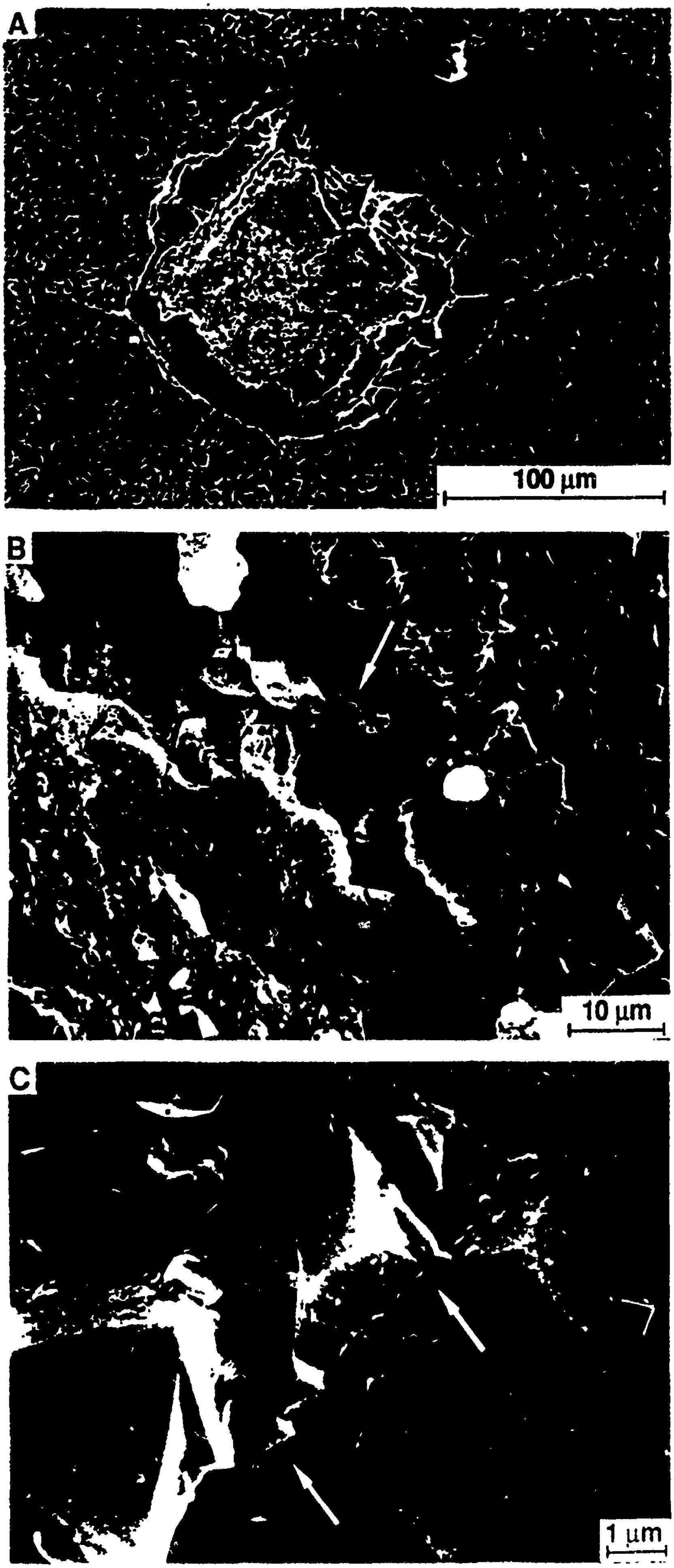


Fig 3(b)


A
B
100 μm
C
C
Si
1 μm
D
C
Si
10 μm


A
100 µm
B
10 µm
C
1 µm