DOE/JPL
Contract No. 954836-78/1
Distribution Category UC-63

DELAYED FRACTURE OF SILICON

Silicon Sheet Growth Development for the Large
Area Silicon Sheet Task of the Low Cost Silicon
Solar Array Project

Final Report

by

T-J Chen and W.J. Knapp

March 31, 1978

Materials Department
School of Engineering and Applied Science
University of California
Los Angeles, California 90024

This work was performed for the Jet Propulsion Laboratory, California Institute of Technology, under NAS 7-100 for the U.S. Energy Research and Development Administration, Division of Solar Energy.

The JPL Low Cost Silicon Solar Array Project is funded by DOE and forms part of the DOE Photovoltaic Conversion Program to initiate a major effort toward the development of low cost solar arrays.

(NASA-CR-157313) DELAYED FRACTURE OF SILICON: SILICON SHEET GROWTH DEVELOPMENT FOR THE LARGE AREA SILICON SHEET TASK OF THE LOW COST SILICON SOLAR ARRAY PROJECT Final Report (California Univ.) 16 p HC A02/MF G3/44 N78-28606 Unclas 27081

TABLE OF CONTENTS

SUMMARY

Bar specimens were cut from ingots of single crystal silicon, and acid-etched prior to testing. Artificial surface flaws were introduced in specimens by indentation with a Knoop hardness tester. The specimens were loaded in four-point bending to 95% of the nominal fracture stress, while keeping the surface area,containing the flaw, wet with test liquids. No evidence of delayed fracture, and, therefore stress corrosion, of single crystal silicon was observed for liquid environments including water, acetone and aqueous solutions of $NaC\ell$, NH_4OH, and HNO_3, when tested with a flaw parallel to a (110) surface. The fracture toughness was calculated to be $K_{IC} = 0.591 \times 10^6$ $N/m^{3/2}$.

ACKNOWLEDGEMENT

We wish to express our appreciation for the valuable assistance of Dr. M.H. Leipold, Jr., and Dr. C.P. Chen, in providing and preparing specimens, in photographing fracture surfaces, and for their helpful advice.

DELAYED FRACTURE OF SILICON

I. INTRODUCTION

It is recognized that the fracture behavior of most Brittle Materials is markedly environment-sensitive; for example, delayed fracture (static fatigue) of a brittle element under imposed load (and residual stresses) may be caused by stress corrosion, or, by adsorption of an active species, and the resulting crack propagation. In the use of such elements in systems requiring significant structural performance, consideration of the effects of chemical environment on possible delayed fracture is of great importance.

The purpose of this study was to investigate the effects of several environments on delayed fracture of single crystal silicon. Silicon materials are receiving intensive study for use in photovoltaic energy conversion systems. The question of the sensitivity of silicon to stress corrosion with atmospheric water, organic liquids, acid and alkaline aqueous solutions, for instance, has not been previously-resolved, and may well be of considerable importance for the design of full-scale systems. In this investigation bar specimens, cut from single crystal silicon, were to be subjected to static loading under several selected environments.

II. PRIOR WORK

Certain environment-sensitive fracture characteristics of ceramics glasses, and other brittle materials have been recognized for many years. It is well known that delayed fracture of silicate glasses and crystalline ceramics often is explained by stress corrosion reaction with atmospheric water since similar tests in vacuo or in completely dry air show an elimination or reduction of delayed fracture. In studies of delayed fracture of an alumina ceramic, Chen and Knapp [1] found that the mean time to fracture, of statically-loaded specimens, was increased by about four orders of magnitude when the specimens were tested in dry argon rather than in moist air (50% relative humidity). An experimental procedure was adapted by Wiederhorn [2] to measure the propagation rate of cracks in glass and ceramics; he reported a thousand-fold increase in crack propagation velocity at a given stress intensity, when exposed to water instead of dry nitrogen. In studies of related properties, Westwood [3] has found a correlation between the hardness and zeta-potential of a non-metallic solid in a liquid environment, which indicates that the hardness is greatest when the zeta-potential is zero. Correspondingly, hardness is reported to be influenced by the pH of an aqueous environment. Westwood also explained the variation of hardness of a soda-lime-silicate glass in aqueous solutions by the variation of induced surface potential. In addition, correlations are made [3] between the drilling rate and machining rates of non-metallic solids and the zeta-potential. The use of alcohols, in connection with the drilling or machining of ceramics and rocks, has been found advantageous and is explained in terms of their effect on the zeta-potential. The effect of straigth chain organic alcohols and alkanes on crack propagation in various glasses also was studied by Freiman [4].

From the general aspects of environment-sensitive fracture, it can be assumed that surface-active environments will have little or no effect on the propagation of fast moving cracks in ceramic solids, but can be expected to influence greatly the propagation rate of slowly moving cracks. If the propagation rate is increased by an active environment, the effect usually is associated with (i) a stress corrosion process in which the stress enhances the rate of corrosion at the crack tip relative to the sides, thus sharpening and deepening the crack, and/or with (ii) a lowering of the surface free energy by the adsorption of an active species, which reduces the energy contribution during fracture associated with new surface (Rebinder effect [5]). In the case of ceramics, the result of most prior studies have been explained best by assuming a stress corrosion process, but not all prior results can be understood in terms of this model.

In the case of single crystal silicon, no prior investigations of delayed fracture are known to the authors. Jaccodine [8] has measured the fractured energy of silicon in the (111) planes, and has estimated values for the (100) and (110) planes.

III. EXPERIMENTAL PROCEDURES

Specimens

The specimens used in this study were rectangular bars of single crystal silicon, approximately 2.54 cm x 0.30 cm x 0.20 cm in size. The specimens were cut, using a diamond saw (O.D. type), from ingots of single crystal silicon, grown in-house at JPL by the Czochralski method, and mostly oriented as shown in Figure 1. A smaller number of specimens were tested with the (100) surface in tension. The surfaces of the specimens were treated, prior to load-testing, by etching in an aqueous solution comprised of HNO_3 (15.8N), HF (28.8N), and $HC_2H_3O_2$ (17.5N), in the proportions 1:2:3, for 1.0 minute at room temperature. In certain specimens, an artificial flaw was introduced in the mid-point of a tensile surface, following the method of Petrovic and Mendiratta [9], with a Knoop hardness-testing indentor. Figure 1 gives a schematic representation of the location and orientation of a crack produced by Knoop-indentation; when a 100g load is used, the characteristic length of the major axis of the crack ranges from 40-60μm. The indentation is always made in the surface to be under tensile stress, with the major axis of the crack normal to the direction of tensile stress.

Load-testing

(1) Short time loading

Specimens both with and without indentiations were loaded in this part of the experimentation, using a four-point bending test fixture (Figure 2), with an Instron mechanical testing machine. The loading rate was 0.005"/min. Deflections under loading were recorded.

(2) Delayed fracture

Only indented specimens were used, for delayed fracture testing, with a modified four-point bending test fixture (Figure 3). A constant load, corresponding to 95% of the nominal fracture stress for short time loading, was applied for durations up to two weeks. During loading, the surface regions of the specimen containing the indentor-produced crack was kept wet with a test liquid by means of a tissue wick, as shown in Figure 3. A timing clock, actuated by a contact microswitch, monitored the time under load.

(3) Incremental loading

With certain specimens, a long period (more than one week) of static loading (at 95% of the nominal fracture stress) transpired without failure. To attempt to obtain failure data on incremental loading procedure was initiated by a load producing 80% of the nominal fracture

---

* Specimens were prepared and supplied by C.P. Chen, of the Jet Propulsion Laboratory.

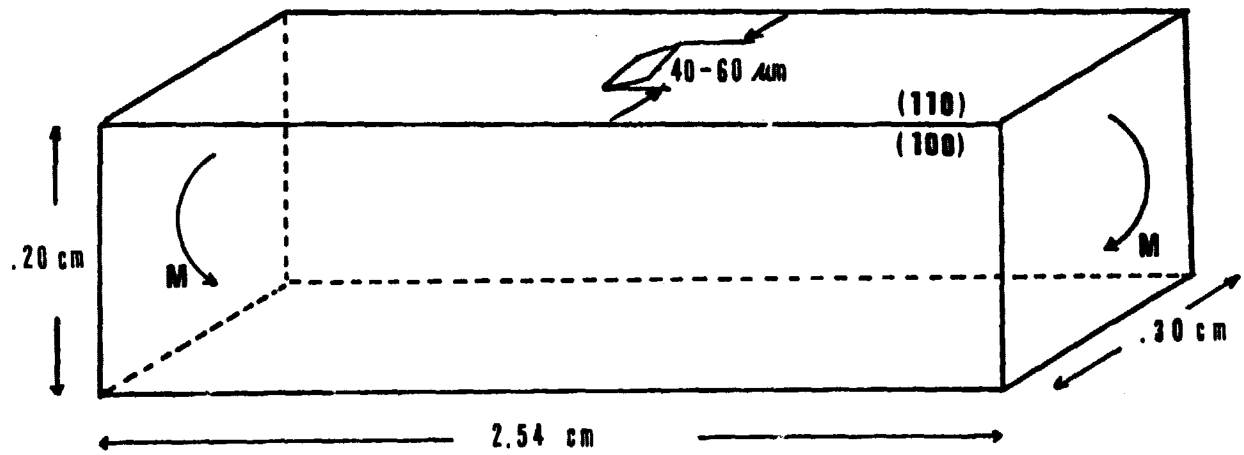

Figure 1. Schematic repres-ntation of a silicon specimen with a Knoop indentation.

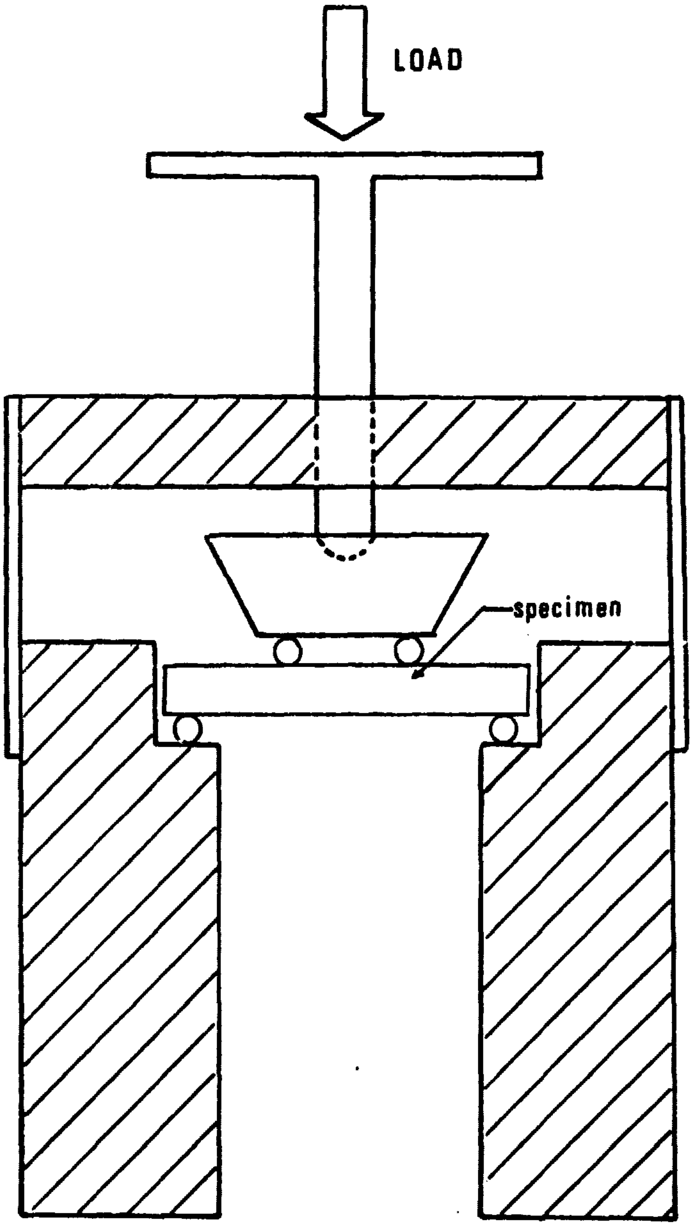

Figure 2. The test fixture used for short time loadings.

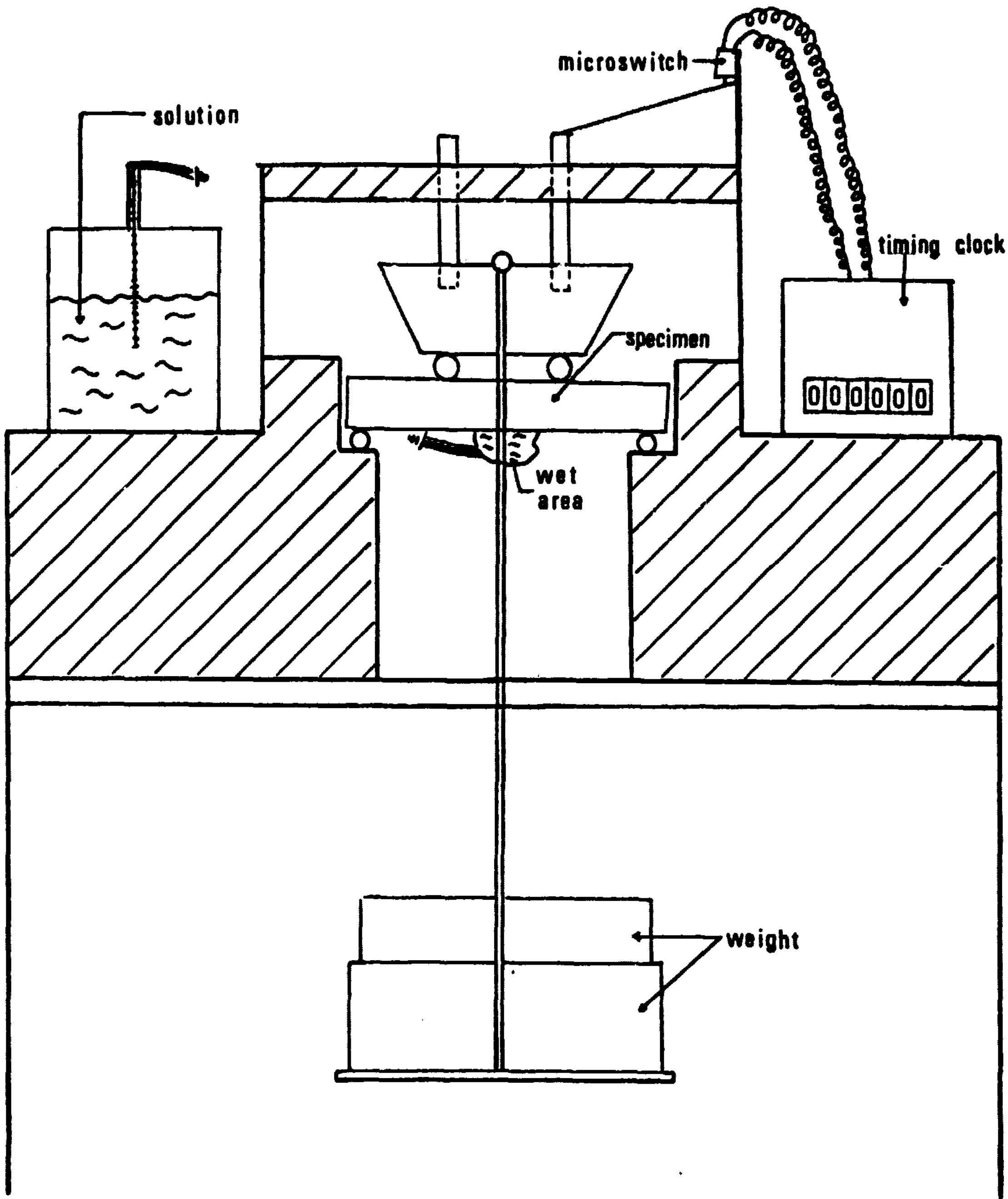

Figure 3. The fixture used for delayed fracture testing.

stress, followed by additional loads of 2.5% of the nominal fracture stress each 24 hours thereafter. This type of loading was used in an effort to cause delayed fracture by increasing the level of stress.

Environmental conditions

As mentioned above, test liquids were applied to surface regions, containing artificial flaws, of specimens tested for delayed fracture, using wicks. Liquids used for this testing were: distilled water, aqueous solution of NaCℓ(10g/l), NH_4OH(1.75M), HNO_3(2.76M), and acetone. All load-testing was conducted at room temperature.

IV. EXPERIMENTAL RESULTS

(1) Short time loading

Fracture stress data, under short time loading, were obtained for specimens with artificial surface flaws (produced by Knoop indentation), and for specimens without artificial surface flaws. The results for ten specimens without indentations are given in Table I and Figure 4, and indicate a mean modulus of rupture of 190.2 MN/m^2 (27,58_ psi), with a highest value of 281.9 MN/m^2 (40,890 psi), a lowest value of 133.8 MN/m^2 (19,400 psi), and a standard deviation of ±40.1 MN/m^2 (5813 psi), or coefficient of variation of 21%. A typical fracture pattern for these specimens (without indentations) is shown in Figure 5.

Fracture stress results for thirteen specimens with artificial surface flaws (indented with a Knoop tester) are given in Table II and Figure 6. Modulus of rupture values for indented specimens indicate a mean of 104.7 MN/m^2 (15,190 psi), a high of 116.5 MN/m^2 (16,890 psi), a low of 89.4 MN/m^2 (12,970 psi) and a standard deviation of ±7.2 MN/m^2 (1038 psi), or coefficient of variation of 6.8%. A typical fracture surface for indented specimens is shown in Figure 7.

(2) Delayed fracture tests

No significant evidence of delayed fracture was obtained for any of the specimens tested in this study. All specimens were indented before load-testing. Eleven specimens in contact with liquid water were loaded to 95% of the nominal (short time) fracture stress; although five of these specimen fractured immediately, upon application of the

TABLE I

Fracture Stress of Silicon Specimens without Indentations under Short Time Loading

Rank	Fracture Stress		Cumulative Fracture probability
(i)	(psi)	(MN/m^2)	(i/1+N)
1	19392	133.70	0.091
2	23787	164.01	0.182
3	24360	167.96	0.273
4	25166	173.51	0.364
5	25688	177.11	0.455
6	25945	178.88	0.545
7	29032	200.17	0.636
8	30288	208.83	0.727
9	31265	215.56	0.818
10	40892	281.94	0.909

Mean = 190.18 $\frac{MN}{m^2}$ (27,583 psi)

Standard deviation = 40.08 $\frac{MN}{m^2}$ (5,813 psi)

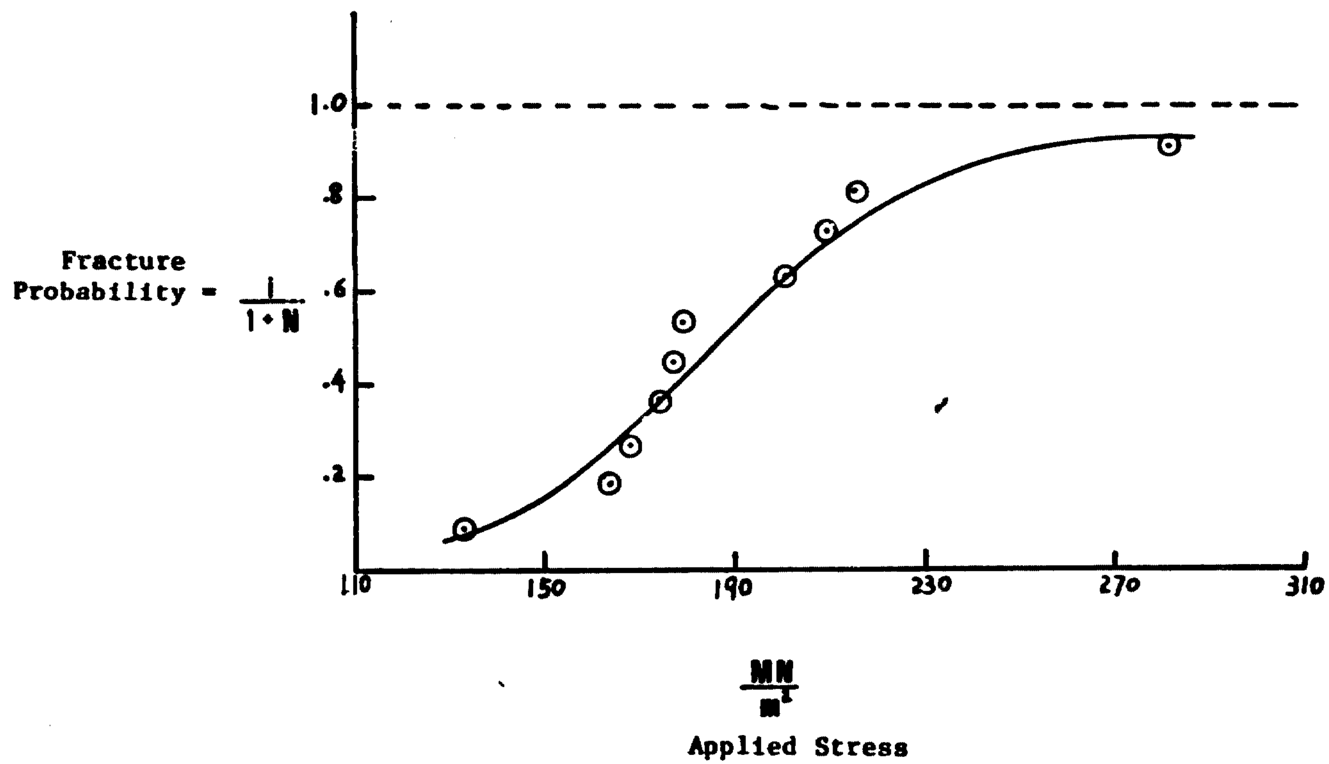

Figure 4. Fracture probability of specimens without indentations under short time loading.

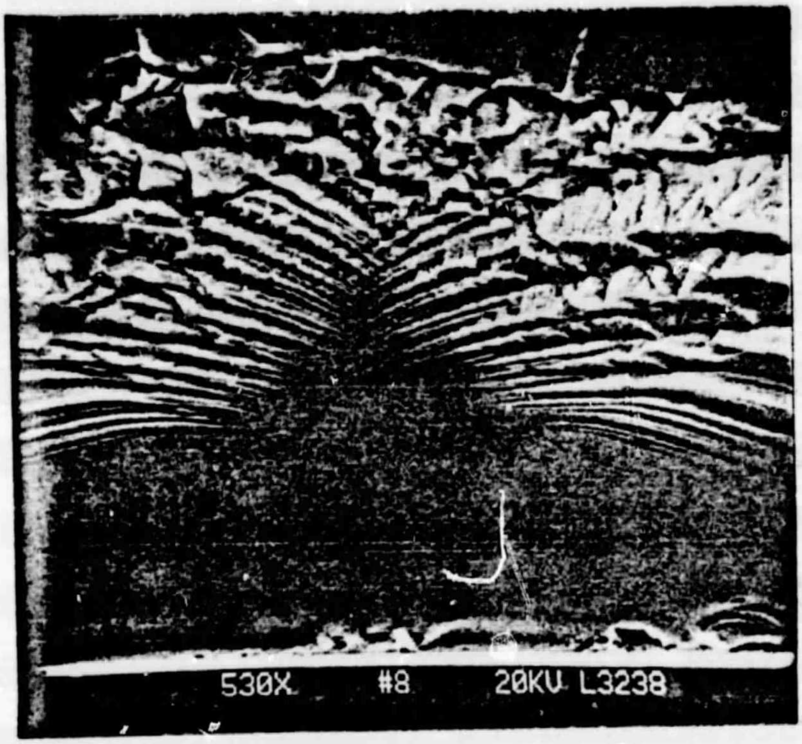

FIGURE 5. A typical fracture surface of a specimen, without an indentation, under short time loading.

TABLE II

Fracture Stress of Silicon Specimens with Indentations under Short Time Loading

Rank	Fracture Stress		Cumulative Fracture probability
(i)	(psi)	(MN/m^2)	(i/1+N)
1	12969	89.42	0.071
2	13851	95.50	0.143
3	14751	101.70	0.214
4	14800	102.04	0.286
5	14834	102.28	0.357
6	14863	102.48	0.429
7	15290	105.42	0.5
8	15362	105.92	0.571
9	15668	108.03	0.643
10	15718	108.37	0.714
11	15980	110.18	0.786
12	16438	113.34	0.857
13	16894	116.48	0.929

Mean = 104.70 $\frac{MN}{m^2}$ (15,186 psi)

Standard deviation = 7.16 $\frac{MN}{m^2}$ (1,038 psi)

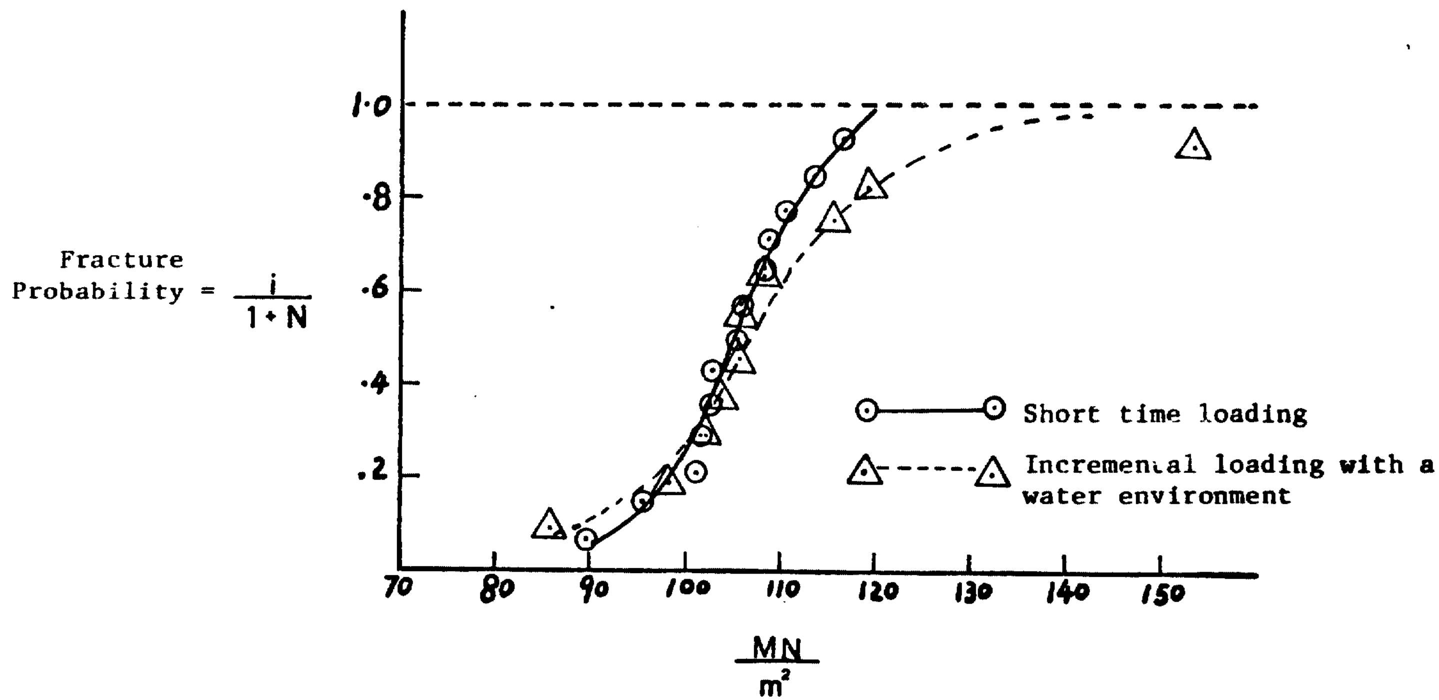

Figure 6. Fracture probability of indented specimens versus applied stress.

FIGURE 7. A typical fracture surface of a specimen, with an indentation, under a short time loading.

load, the balance of the specimens continued to support the load after a period of two weeks. It was found that small vibrations, such as those produced by jarring the test stand, caused immediate fracture of some specimens.

In addition, the several specimens tested each in contact with salt water, dilute solutions of NH_4OH and HNO_3, and acetone, showed no indication of delayed fracture, and, therefore, no stress corrosion.

(3) Incremental loading tests

Results for the incremental loading of ten indented specimens in contact with water are given in Table III and Figure 6, and indicate a mean modulus of rupture of 109.5 MN/m^2 (15,890 psi), high and low values of 153.5 MN/m^2 (22,260 psi) and 85.8 MN/m^2 (12,450 psi) respectively, a standard deviation of ± 17.9 MN/m^2 (2,600 psi), or coefficient of variation of 16%. It may be noted that these results are similar to those obtained for short time loading of indented specimens (Table II).

V. DISCUSSION OF THE RESULTS

It was concluded, from these results, that no delayed fracture of single crystal silicon occurs, under an applied stress of 95% of the nominal fracture (short time) stress, for periods of two weeks in liquid environments including water, acetone, and aqueous solutions of $NaC\ell$, NH_4OH and HNO_3. Little, or no, stress corrosion appears to occur in such periods of study. It is interesting to compare the fracture probability curves (Figure 6) for short time loading, and for incremental loading (over extended time periods) of specimens wetted with water. These curves are quite similar, and there is no evidence of a stress corrosion effect due to water.

It is of additional interest to note certain fracture characterisitcs of single crystal silicon, especially in regards to the use of a Knoop indentor to introduce artificial cracks. The data for short time loading indicate, as may be expected, that the standard deviation of fracture stress is considerably reduced by introducing controlled artificial cracks with a Knoop indentor. The fracture surfaces of specimens show distinctive

TABLE III

Fracture Stress of Silicon Specimens with Indendations under Incremental Loading with a Water Environment

Rank	Fracture Stress		% of nominal fracture	Cumulative Fracture probability
(i)	(psi)	(MN/m^2)	%	(i/1+N)
1	12445	85.81	82	0.091
2	14248	98.24	94	0.182
3	14792	101.99	97	0.273
4	14964	103.17	99	0.364
5	15247	105.12	100	0.455
6	15309	105.55	100	0.545
7	15571	107.36	103	0.636
8	16780	115.69	110	0.727
9	17251	118.94	114	0.818
10	22259	153.47	147	0.909

Mean = $109.33 \frac{MN}{m^2}$ (15,886 psi)

Standard deviation = $17.91 \frac{MN}{m^2}$ (2,597 psi) characteristics for specimens with, and without, indentations. A Knoop indentation produces a crack with a circular leading edge, as may be seen in Figure 8.

The experimental data for short time load testing can be used to calculate the fracture toughness (K_{IC}) of single crystal silicon, using the following relation of Petrovic et al [10]:

$$K_{IC} = \sigma_c M(\pi a/Q)^{\frac{1}{2}} \qquad (1)$$

where σ_c is the maximum outer-fiber tensile stress, M is a numerical factor related to flaw and specimen geometry, a is the flaw depth, and Q is given by

$$Q^{\frac{1}{2}} = \int_0^{\pi/2} [\sin^2\theta + \left(\frac{a}{c}\right)^2 \cos^2\theta]^{\frac{1}{2}} \, d\theta \qquad (2)$$

where $Q^{\frac{1}{2}}$ is the elliptic integral. For a typical indented specimen (specimen #14, Fig. 9) the values of

$Q^{\frac{1}{2}} = 1.6$
$a = 22.1 \times 10^{-6}$m
$c = 21.0 \times 10^{-6}$m (major axis of the indentation)

were obtained, leading to a calculation of the fracture toughness

$$K_{IC} = 0.591 \times 10^6 \ N/m^{3/2}$$

The Young's modulus of elasticity (E) for single crystal silicon was calculated, from the data for short time loadings, to be

$$E = 8.96 \times 10^4 \ MN/m^2 \ (13 \times 10^6 \ psi)$$

It is felt that the above value is lower than the true value, because the displacement under load was taken as the crosshead displacement of the testing machine.

Examination of a number of fractured specimens confirmed that the plane of fracture was (111) in each case. Most specimens were loaded against the (110) surfaces, as shown in Figure 10A, whereas certain specimens were

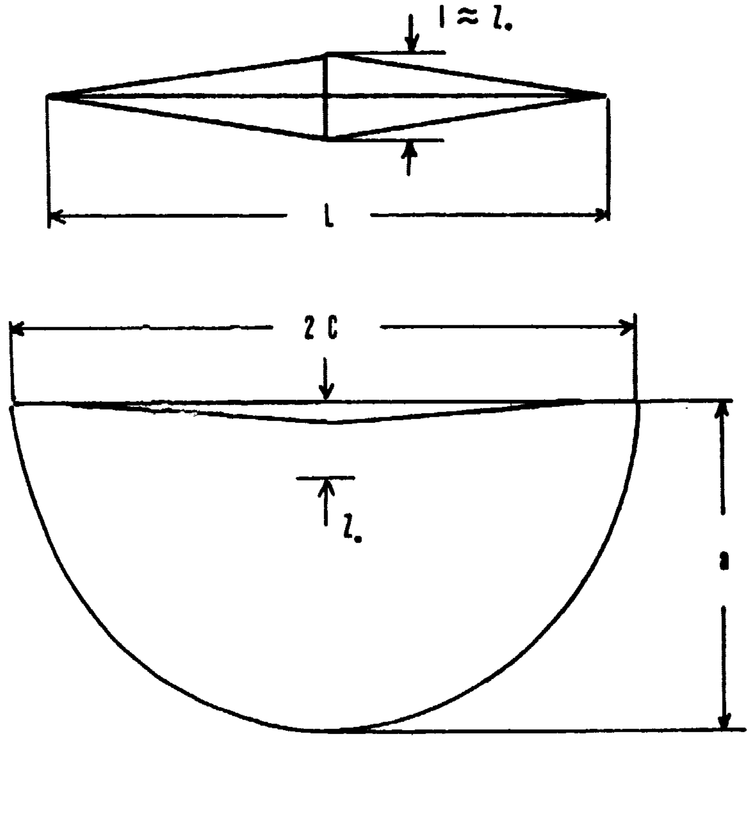

Figure 8. Schematic representation of a Knoop indentation and the corresponding circular crack.

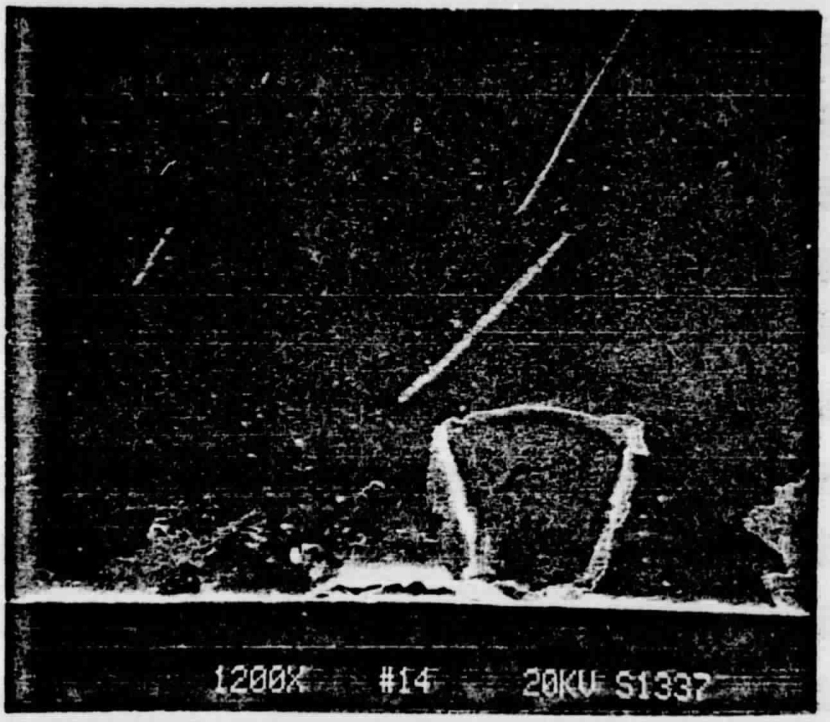

FIGURE 9. A semicircular crack produced by Knoop indentation.

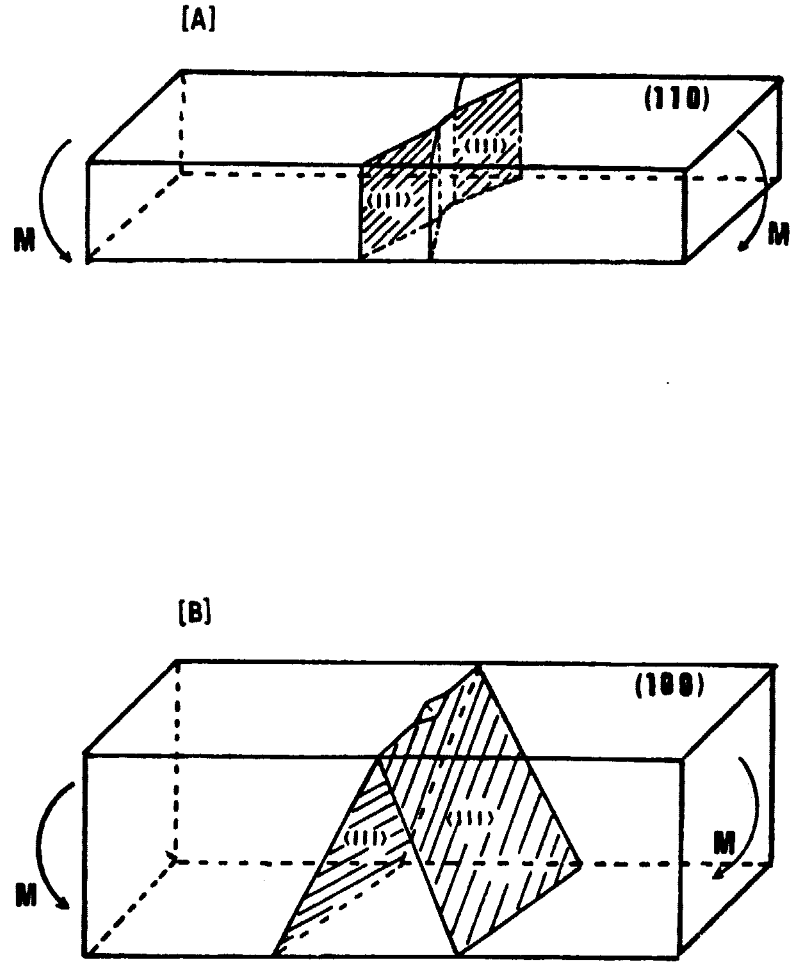

Figure 10. Schematic representation of the fracture planes (111) from loading on (A) (110), and (B) (100) surfaces.

loaded against the (100) surfaces (Figure 10B); fracture followed (111) planes in both types of loading.

VI. CONCLUSIONS

It was concluded, from the results of this study, that

(1) there is no evidence of delayed fracture (and stress corrosion) of single crystal silicon on liquid environments including water, acetone, and aqueous solutions of NaCℓ, NH_4OH and HNO_3 when tested with a flaw parallel to a (110) surface.

(2) the fracture toughness of silicon, is calculated to be $K_{IC} = 0.591 \times 10^6\ N/m^{3/2}$.

(3) fracture occurs most readily along (111) planes, as shown by tests with specimens of different orientations.

VII. RECOMMENDATIONS FOR FUTURE WORK

(1) Although no evidence of delayed fracture, and, therefore stress corrosion, was observed for the environmental influences of this study, it seems likely that corrosive liquids for silicon remain to be identified. Additional liquids, such as other organic liquids, acids and alkalis should be evaluated.

(2) The fracture of silicon under several stress states, including compression,and combined stress, should be studied. Possible types of loading may include that producing twisting, and one developing equibiaxial tension.

(3) The influence of flaw orientation on the fracture of silicon is a study topic of importance.

(4) The fracture of silicon over a range of temperatures should be investigated.

REFERENCES

1. (a) C.P. Chen and W.J. Knapp, "Fatigue Fracture of an Alumina Ceramic at Several Temperatures," pp. 691-707 in Fracture Mechanics of Ceramics, Vol. 2, Edited by R.C. Bradt, D.P.H. Hasselman, and F.F. Lange, Plenum Press, New York, 1974.

   (b) C.P. Chen and W.J. Knapp, "Delayed Fracture of an Alumina Ceramic" J. Am. Ceramic Soc., 60[1-2] (Jan.-Feb. 1977).

2. S.M. Wiederhorn, "Influence of Water Vapor on Crack Propagation in Soda-Lime Glass," J.Am.Ceramic Soc. 50[8] 407-14 (1967).

3. A.R.C. Westwood, "Control and Application of Environment-Sensitive Fracture Processes," J. Materials Science, 9[11] 1871-95 (1974).

4. S.W.Freiman, "Effect of Organic Liquids on Crack Propagation in Glass," NRL Report 7825, Naval Research Laboratory, Washington, D.C., October 17, 1974.

5. P.A. Rebinder, L.A. Schreiner and S.F. Zhigach, "Hardness Reducers in Rock Drilling," (Academy of Science, USSR, Moscow, 1944).

6. J.E. Ritter, Jr. and J.A. Meisel, "Strength and Failure Predictions ofr Glass and Ceramics," J. Am. Ceramic Soc. 59 (11-12) 478-81 (1976).

7. S.M. Widerhorn, "A Chemical Interpretation of Static Fatigue," J. Am. Ceramic Soc., 55(2) 81-85 (1972).

8. R.J. Jaccodine, "Surface Energy of Germanium and Silicon," J. Electrochemical Soc., 110(6) 524-7 (1963.

9. J.J. Petrovic and M.G. Mendiratta, "Mixed-Mode Fracture from Controlled Surface Flaws in Hot-Pressed Si_3N_4," J. Am. Ceramic Soc., 59 (3-4), 163-7 (1976).

10. J.J. Petrovic, L.A. Jacobson, P.K. Talty, and A.K, Vasudevan, "Controlled Surface Flaws in Hot-Pressed Si_3N_4," J. Am. Ceramic Soc., 58 (3-4) 113-6 (1975).