13th Workshop on Crystalline Solar Cell Materials and Processes
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Failure of Silicon:
Crack Formation and Propagation

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with thanks to

C. L. Muhlstein *(Penn State)* **and E. A. Stach** *(NCEM, LBNL)*

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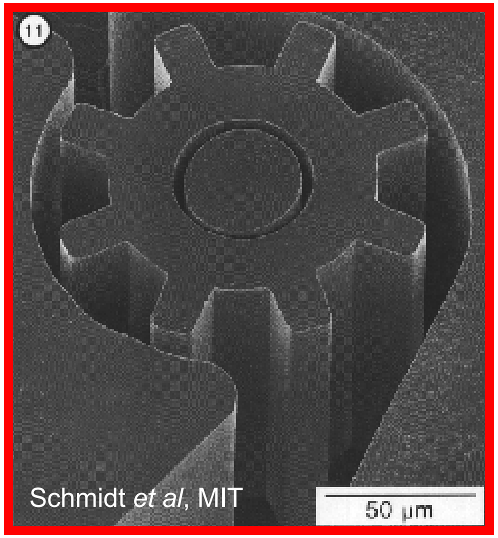
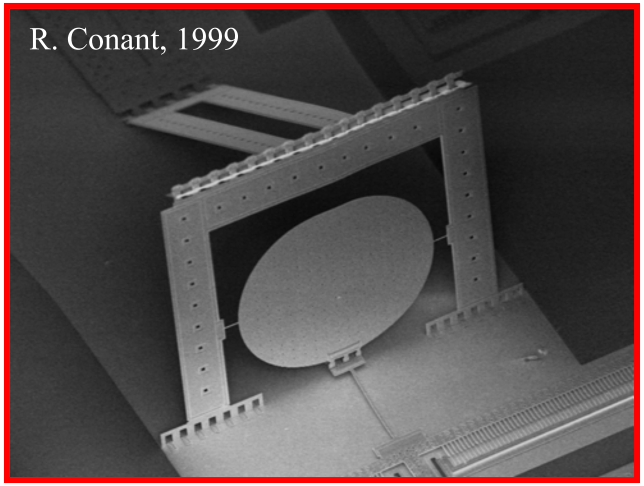
MEMS, Microsystems and Micromachines



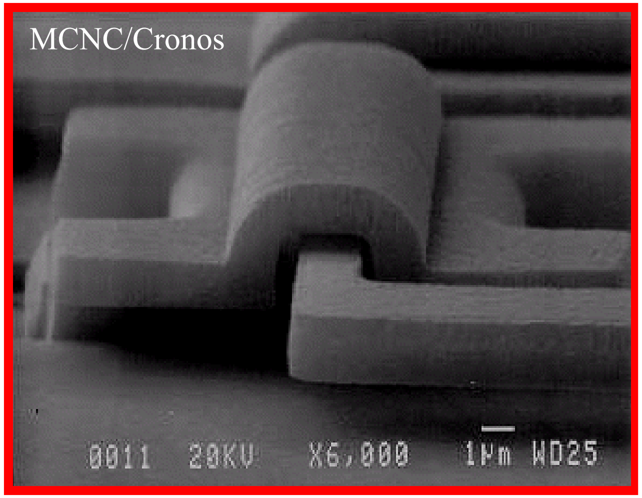
microturbine,


R. Conant, 1999

micron-scale
moveable mirrors


©1997 UW-Madison

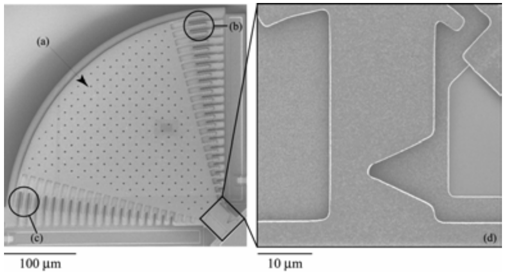
series of gears

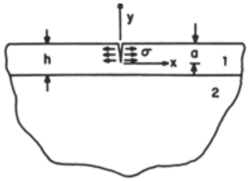

MCNC/Cronos

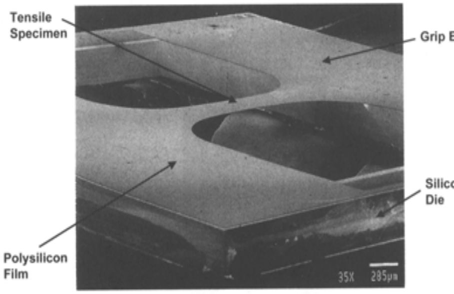
microhinge

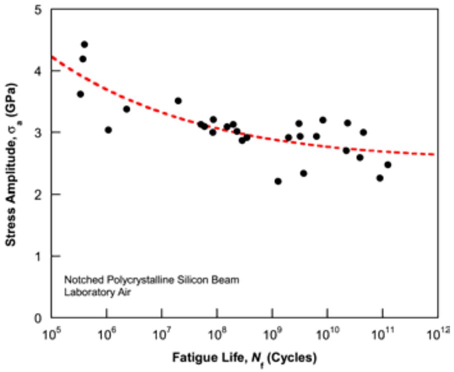
Outline

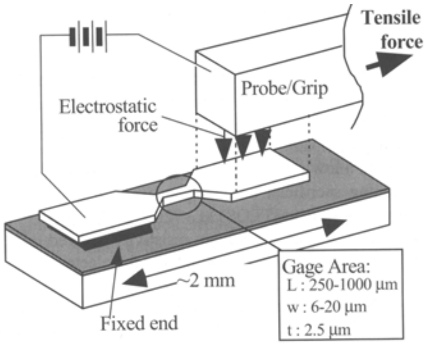
- Mechanical properties of silicon
- Brittle fracture of silicon
- Strength vs. fracture toughness
- Delayed failure of thin-film silicon
- Role of the native oxide layer
- Suppression/prediction of fracture

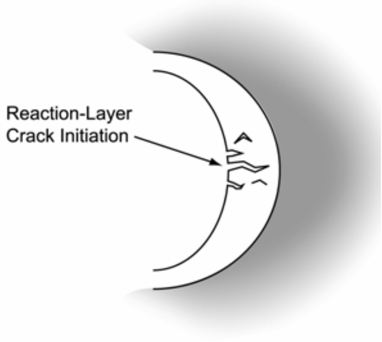


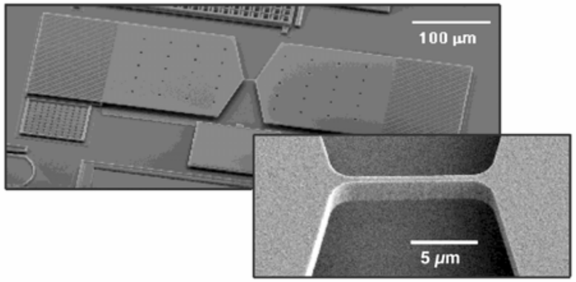


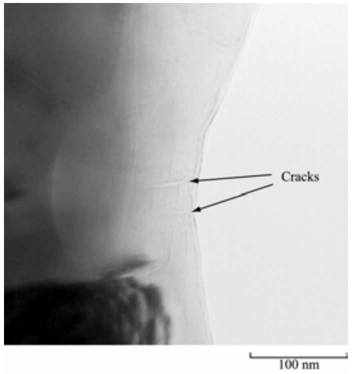






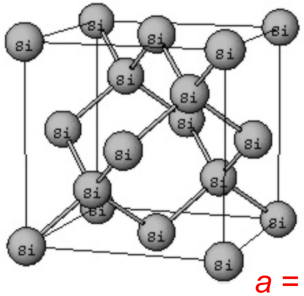






Ductile vs. Brittle Properties of Silicon

- crystal structure
  - diamond cubic structure (face-centered cubic)

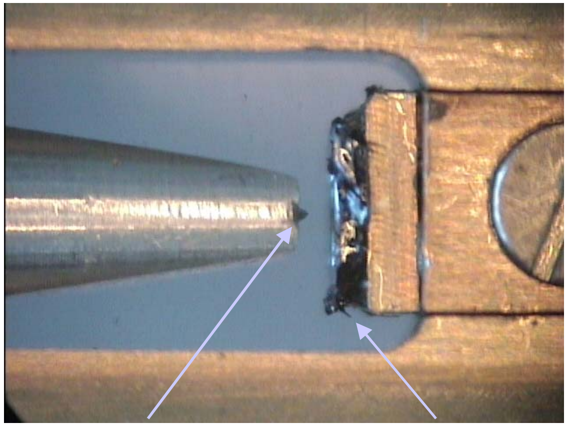


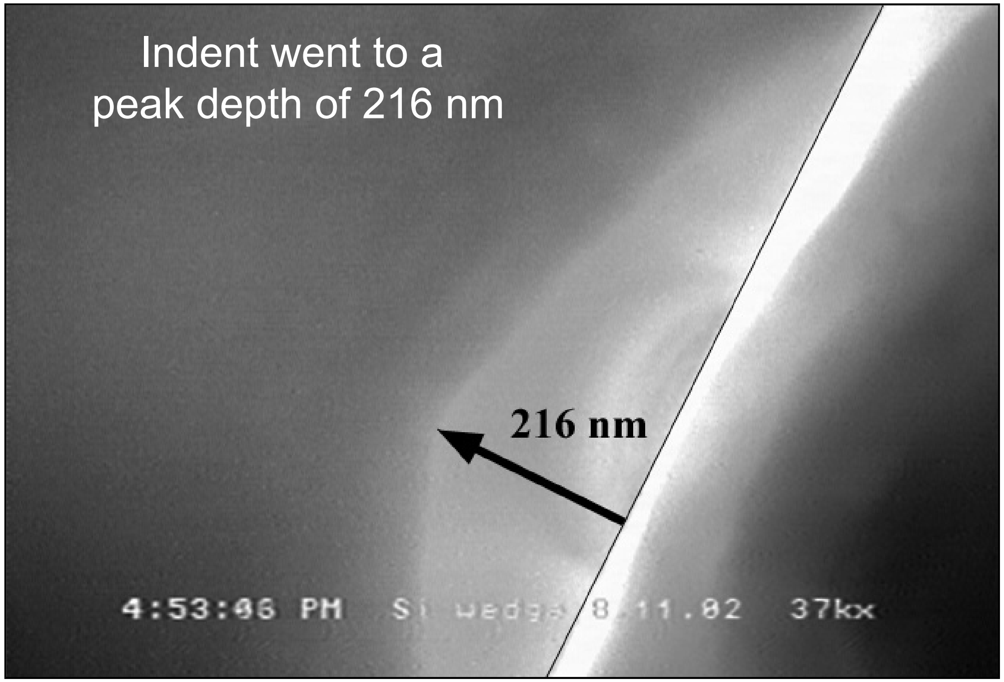
a = 0.534 nm

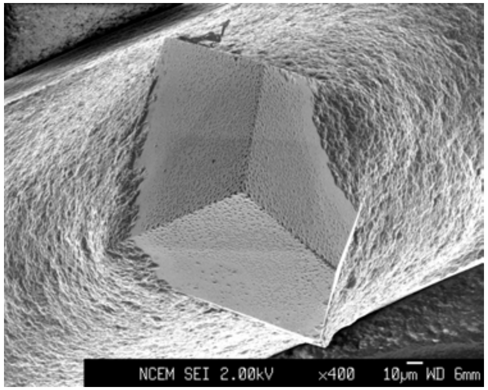
- brittle-to-ductile transition (DBTT at ~500°C)
  - below the DBTT (or at high strain rates), Si is completely brittle
    - dislocations not mobile, Si fractures by cleavage on {111} planes
    - fracture strengths ~ 1 to 20 GPa in single-crystal silicon
    - fracture strengths ~ 3 to 5 GPa in polycrystalline silicon
  - above the DBTT, silicon becomes gradually ductile
    - glide motion of (*a*/2)<110> dislocations on {111} planes
    - dissociation into (*a*/6)<112> Shockley partials with 4-6 nm stacking faults
    - heterogeneous dislocation nucleation in “dislocation-free” crystals

      e.g., at surfaces or due to deformation-induced amorphous Si
    - solid-solution hardening by impurity solutes, e.g., oxygen, nitrogen

Mobile Dislocations in Silicon at 25°C




Indent went to a peak depth of 216 nm



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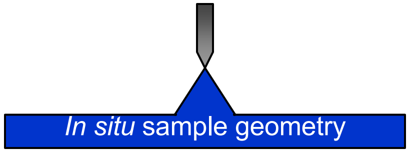
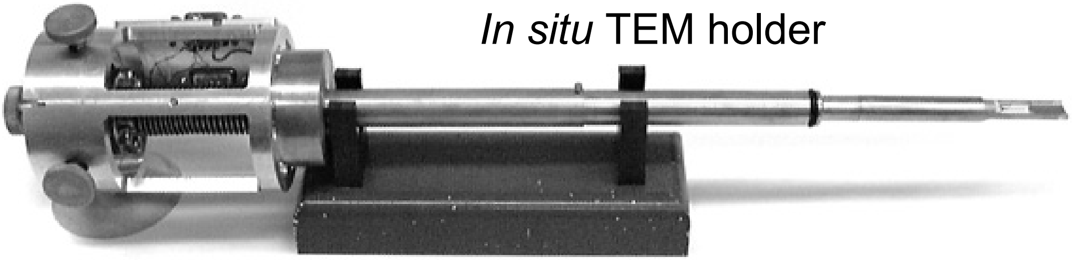

In situ sample geometry

- no phase transformations
- large plastic extrusions of the diamond cubic phase
- dislocation nucleation easier than phase transformation


In situ TEM holder

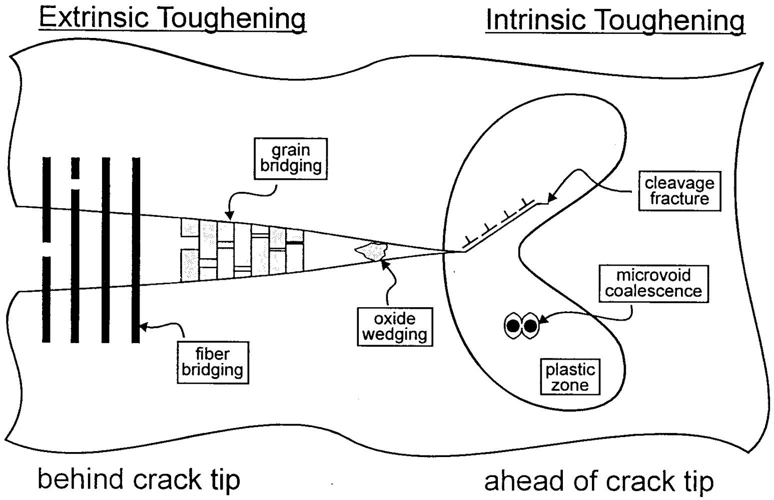
Wall & Dahmen, 1997

Minor, Stach, *et al*., Phys. Rev. Lett.., 2003

Modes of Failure in Silicon

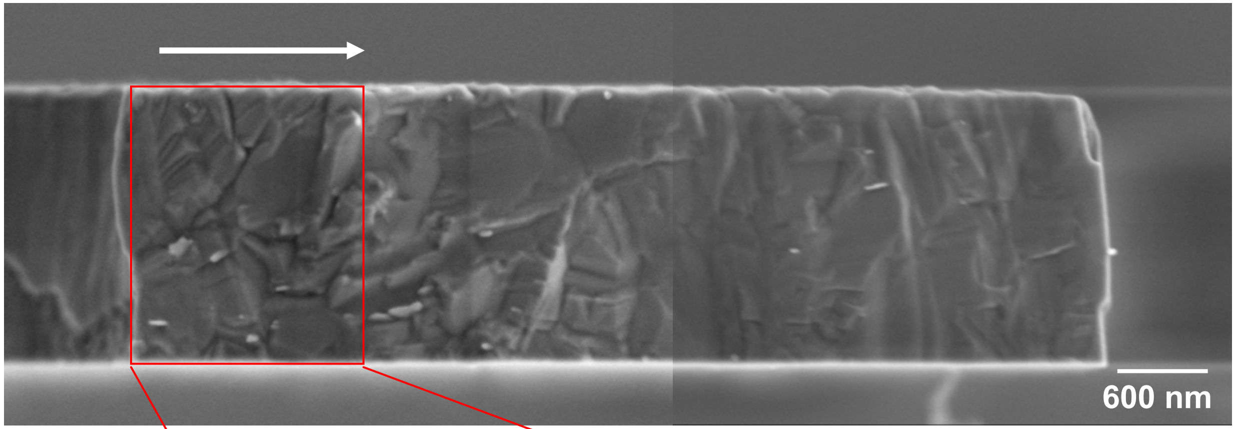
- Brittle (catastrophic) fracture
  - catastrophic transgranular cleavage fracture on {111} planes
  - evidence for {110} cleavage for “low energy/velocity” fractures
- Sustained-load cracking (delayed fracture)
  - no evidence for delayed fracture from subcritical crack growth, e.g., due to stress-corrosion cracking, in *bulk* silicon below the DBTT (<500°C)
  - evidence for moisture-induced cracking in *thin film* silicon
- Cyclic fatigue failure (delayed fracture)
  - no evidence for delayed fracture from fatigue cracking under alternating loads in *bulk* silicon below the DBTT
  - strong evidence of premature fatigue failure of *thin film* silicon

What affects resistance to brittle fracture? in silicon?

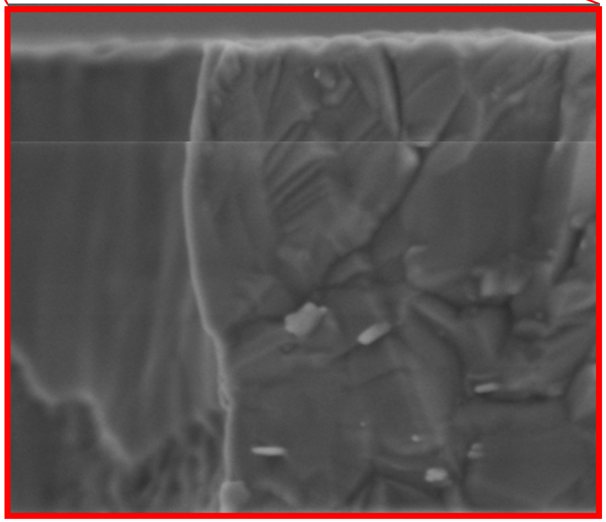


- Intrinsic factors
  - bond rupture
  - plasticity, i.e., mobile dislocations
  - defect (crack) population
- Toughening mechanisms
  - intrinsic mechanisms (ahead of crack tip)
    - microstructure, e.g., second phases
  - extrinsic (crack-tip shielding) mechanisms (behind crack tip)
    - crack bridging (intergranular cracking)
    - microcrack toughening (from dilation and reduced stiffness)
    - residual stresses (compressive for toughening)

Brittle Fracture of Silicon



transgranular
cleavage
fracture

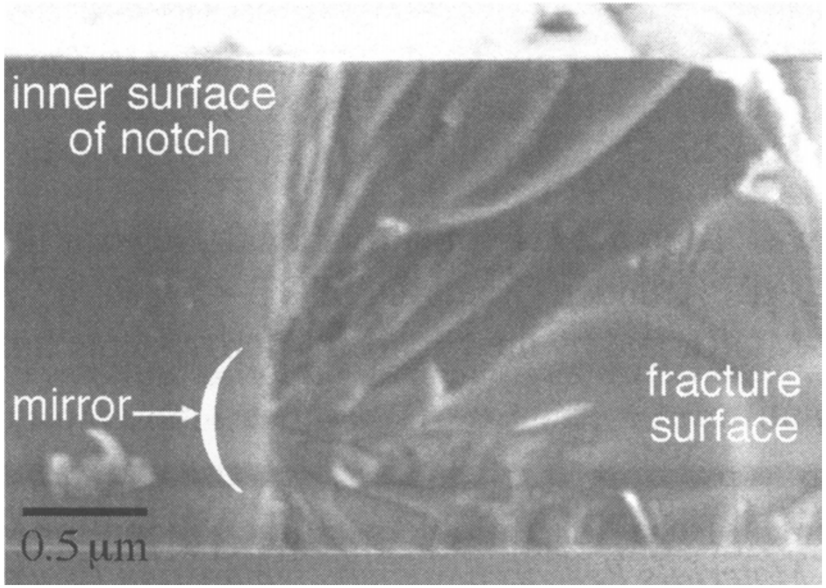


{110}

cleavage

Muhlstein, Brown, Ritchie, *Sensors & Actuators,* 2001

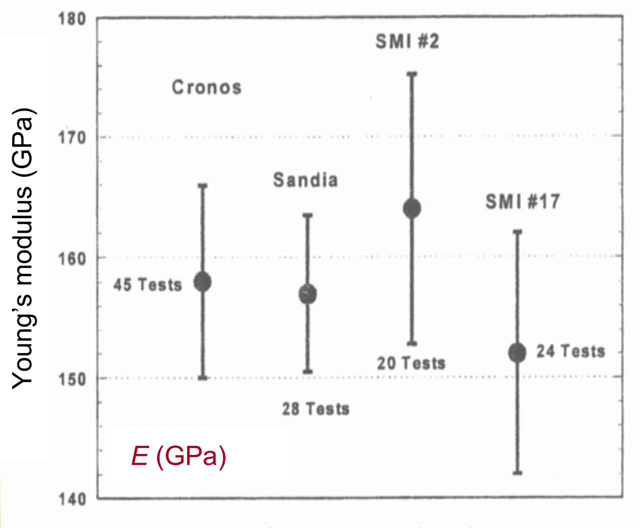
{111} cleavage



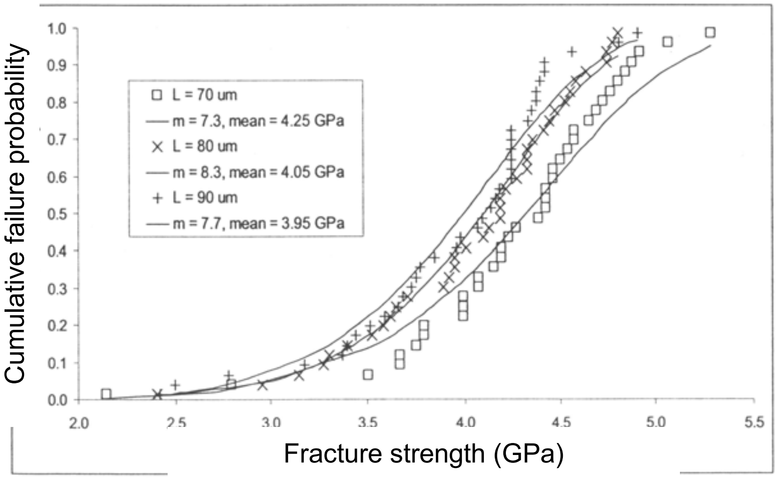
Ballarini *et al*., ASTM STP 1413, 2001

Brittle Fracture of Silicon

- elastic modulus
  - *E* ~ 160 GPa
- high fracture strengths
  - 1 to 20 GPa in single-crystal silicon
  - 3 to 5 GPa in polycrystalline silicon
  - dependent on *defect size*, loading mode, specimen size, orientation, test method
  - probability of fracture dependent on “weakest-link” (Weibull) statistics
- low fracture toughness
  - K_c ~ 1 MPa√m in polysilicon thin films
  - K_c ~ 0.7-1.3 MPa√m in single-crystal films
  - dependent on specimen type, orientation and investigator
  - *independent of microstructure*



Sharpe *et al*., ASTM STP 1413, 2001



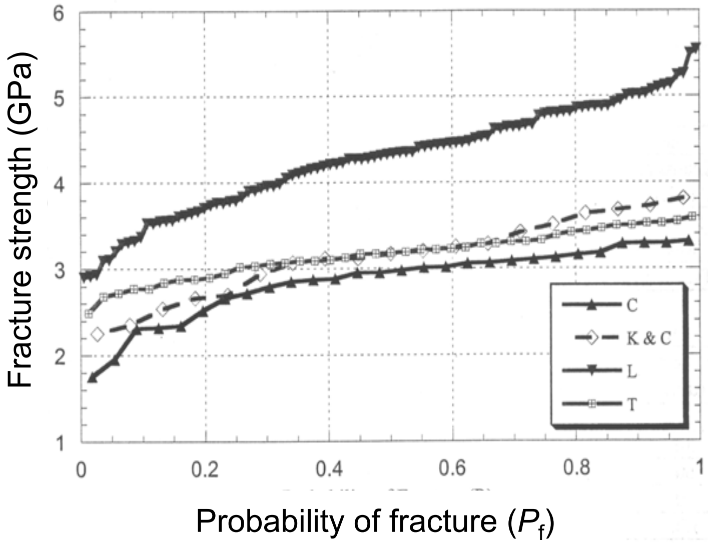
Johnson *et al*., ASTM STP 1413, 2001

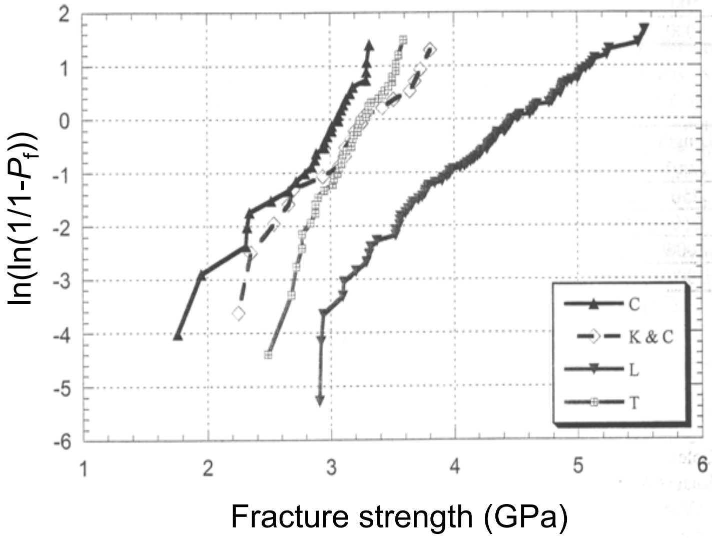
Probability of Brittle Fracture in Silicon

- brittle fracture of silicon governed solely by the rupture of Si-Si bonds at the crack tip
  - K_c is independent of microstructure
- except variations due to orientation (in single-crystal Si) and experimental error, *fracture strength depends on the defect population*
- The probability of failure, P_F, can thus best be described in terms of “weakest-link” statistics

$$P_F(\sigma) = 1 - \exp\left[-\int_0^V \left[dV \left(\frac{\sigma - \sigma_u}{\sigma_o}\right)^m N \right]\right]$$

- where σ_U is the lower bound fracture strength, σ_o is the “scale parameter”, *m* is the Weibull modulus, and *V* is the volume of the sample





LaVan *et al.*, ASTM STP 1413, 2001

Strength vs. Fracture Toughness

- fracture strength/strain subject to extreme variability – not a material property
- more fundamental parameter is the fracture toughness - K_c or G_c
  - where K_c is the critical value of the stress intenisty K to cause fracture

$$K_c = Q\,\sigma_F\,(\pi a_c)^{1/2}$$

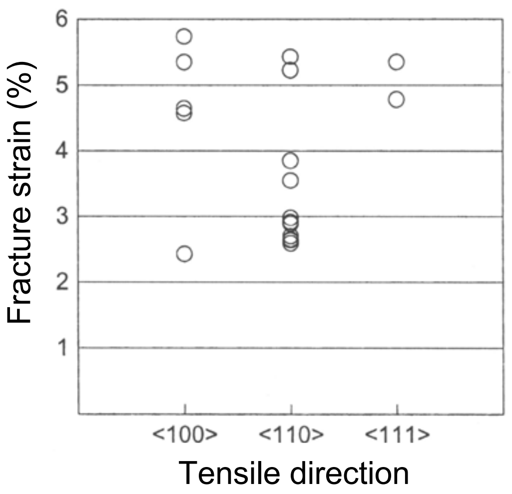
σ_F is the fracture strength
a_c is the critical crack size
Q is a geometry factor (~unity)

  - and G_c is the strain energy release rate

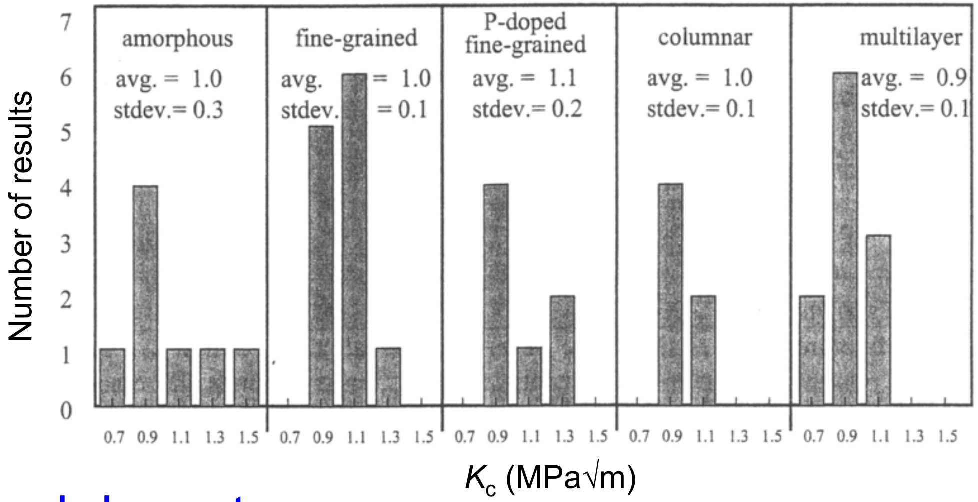
$$G_c = (K_c)^2/E$$

E is Young's modulus

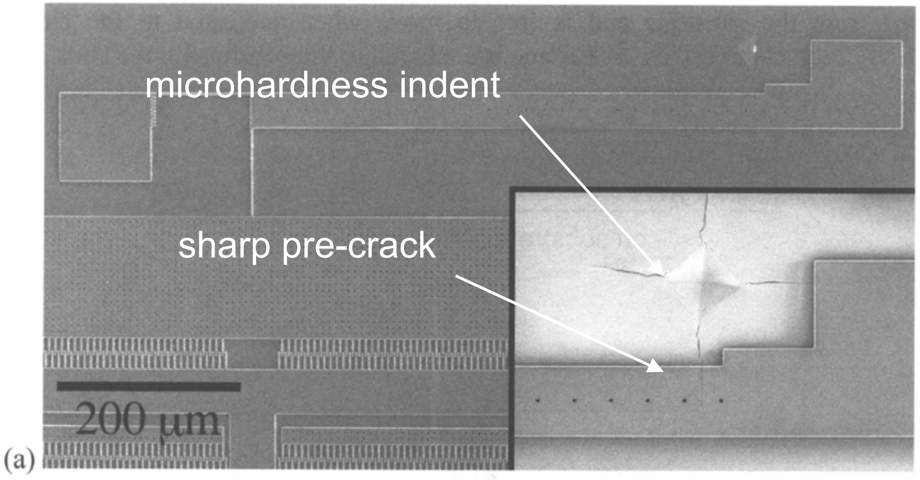
- K_c = 1 MPa√m in Si and is independent of microstructure and dopant

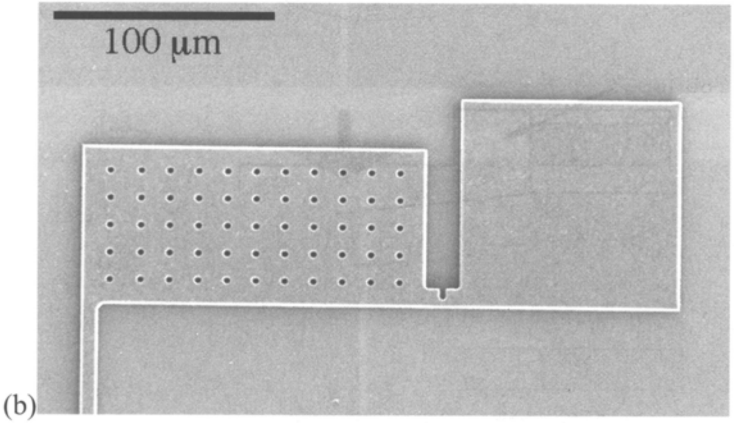


Ballarini *et al.*, ASTM STP 1413, 2001

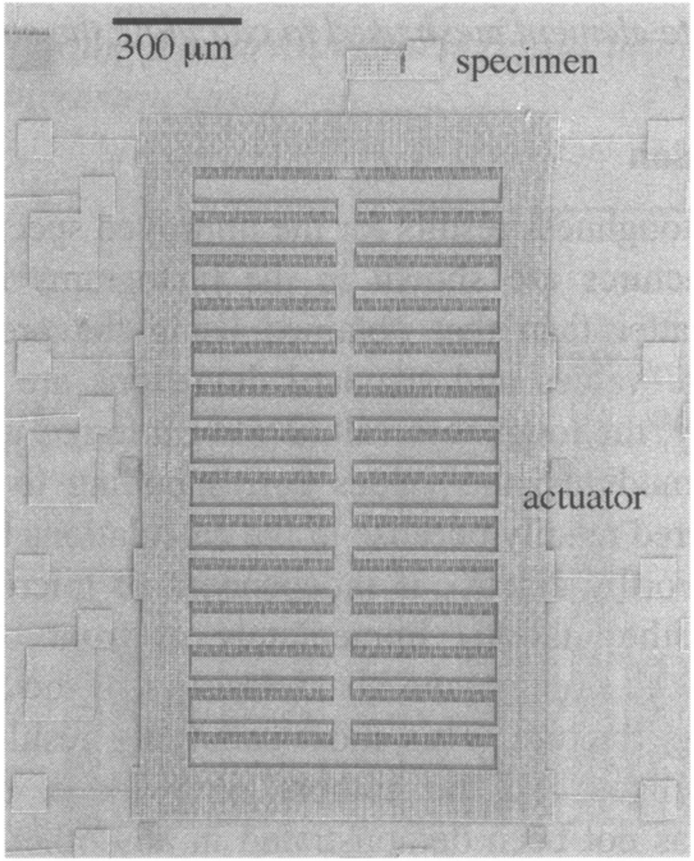


Measurement of Fracture Toughness





$$K_c = Q\,\sigma_F\,(\pi a_c)^{1/2}$$



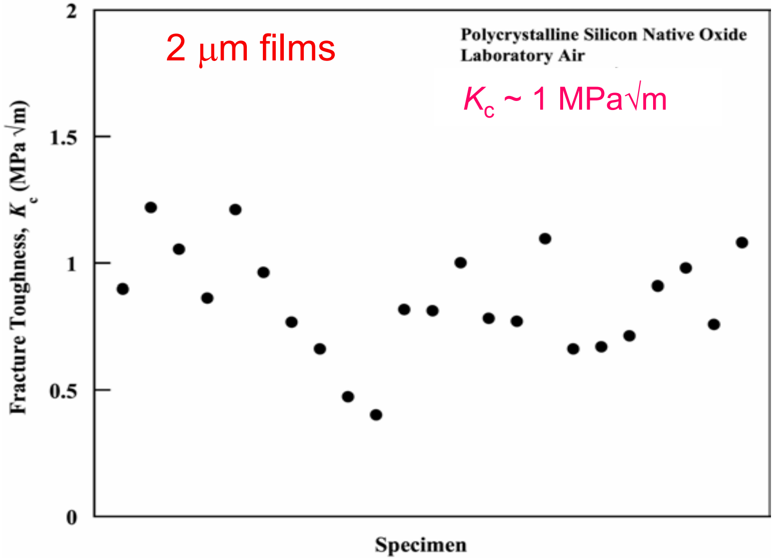
- measurement of the fracture toughness of thin-film silicon using MEMS

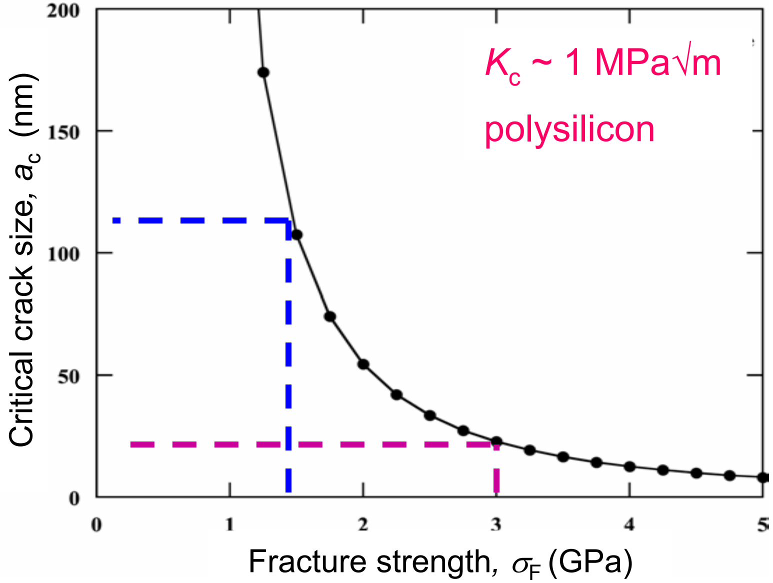
Ballarini *et al.*, ASTM STP 1413, 2001

Fracture Mechanics Approach

- low fracture toughness K_c in silicon
  - 0.7 to 1.3 MPa√m in single-crystal Si
  - 1 MPa√m in polysilicon thin films
- compare with K_c values of:
  - ~0.6 MPa√m in (soda-lime) glass
  - 2 to 3 MPa√m in human teeth (dentin)
  - 3 to 8 MPa√m in alumina ceramics
  - 20 to 200 MPa√m in steels
- from this microstructure-independent K_c value in Si, can:
  - determine the fracture strength, σ_F, as a function of the largest defect size, a_c

$$K_c = Q\,\sigma_F\,(\pi a_c)^{1/2}$$

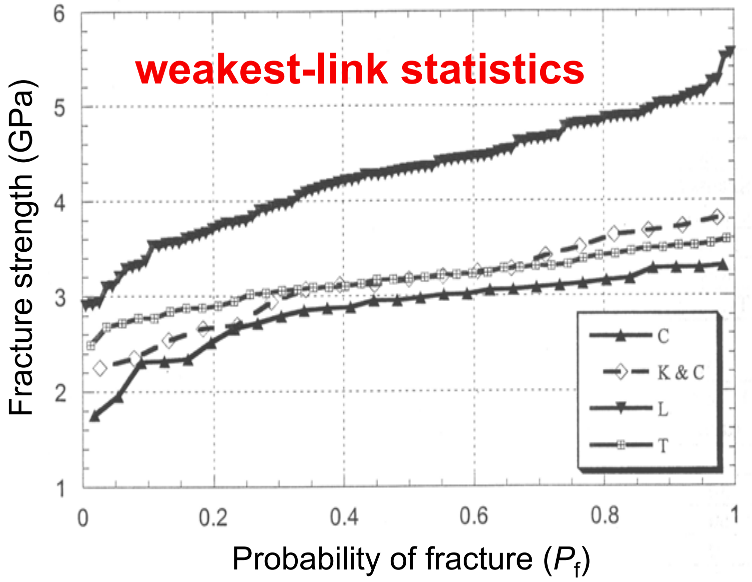


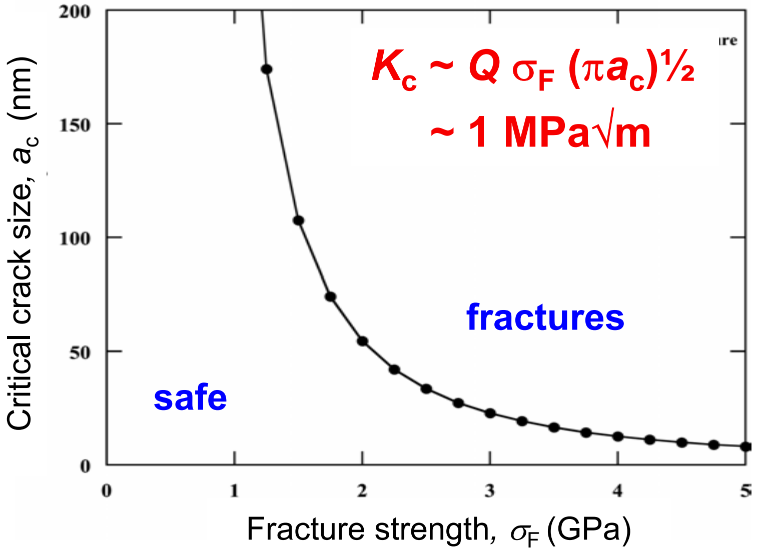


Muhlstein, Stach, Ritchie, *Acta Mat.*, 2002

Prediction of Brittle Fracture in Silicon

- **Probability of brittle fracture depends on defect (crack) population**
  - use fracture strength approach with weakest-link statistics to determine probability of fracture
  - characterize defect population at sub-micron resolution (actually tens of nanometers)
    - X-ray tomography
      (e.g., Xradia, Concord, CA)
    - GHz acoustic microscopy





$K_c \sim Q\,\sigma_F\,(\pi a_c)^{1/2}$

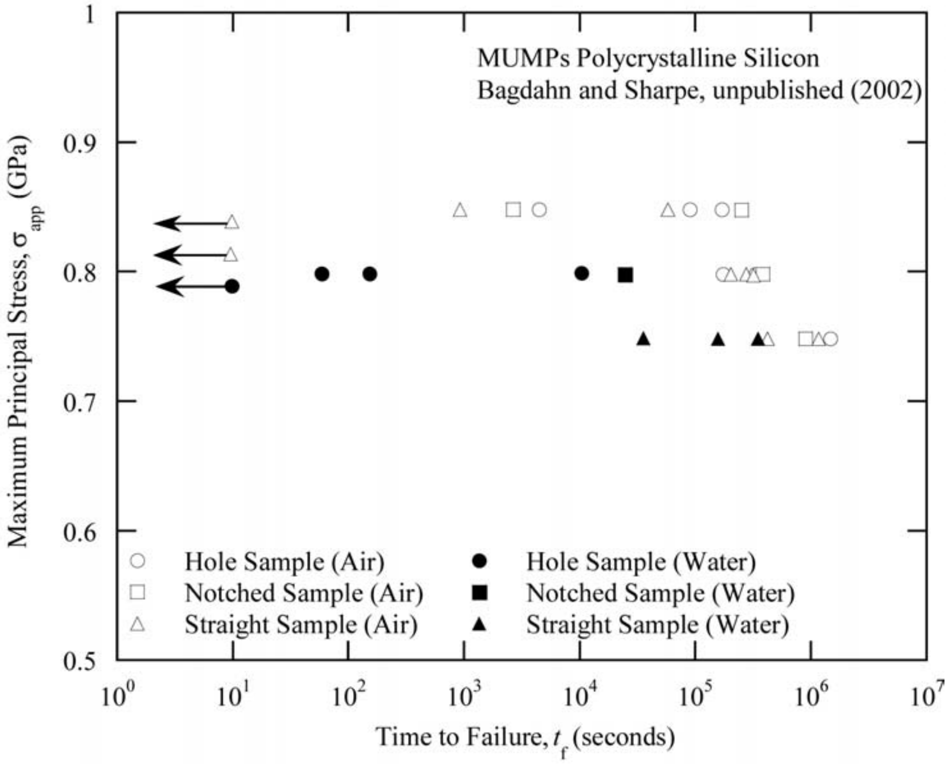
$\sim 1\ \mathrm{MPa}\sqrt{m}$

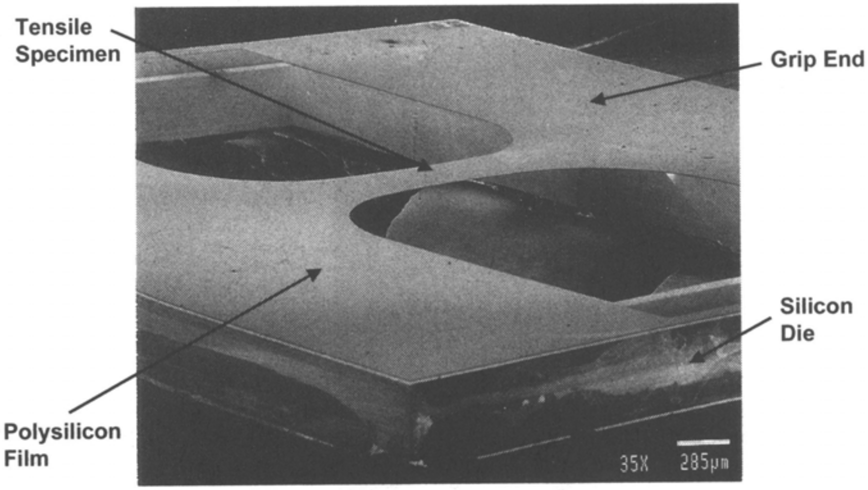
Modes of Failure in Silicon

- Brittle (catastrophic) fracture
  - catastrophic transgranular cleavage fracture on {111} planes
  - evidence for {110} cleavage for "low energy/velocity" fractures
- Sustained-load cracking (delayed fracture)
  - no evidence for delayed fracture from subcritical crack growth, e.g., due to stress-corrosion cracking, in *bulk* silicon below the DBTT (<500°C)
  - evidence for moisture-induced cracking in *thin film* silicon
- Cyclic fatigue failure (delayed fracture)
  - no evidence for delayed fracture from fatigue cracking under alternating loads in *bulk* silicon below the DBTT
  - strong evidence of premature fatigue failure of *thin film* silicon

Environmentally-Assisted Cracking in Polycrystalline Silicon

- micron-scale silicon films display some evidence of time-delayed failure under sustained (non-cyclic) loading





- lives for thin-film silicon are somewhat shorter in water
- no evidence of such time-delayed failure in bulk silicon

Bagdahn and Sharpe (2002) unpublished

Modes of Failure in Silicon

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LPCVD Polysilicon

- composition

  MUMPs process - LPCVD reactor*
  n-type – P doped
  deposited Si and PSG layers
  thermally annealed at ~900°C

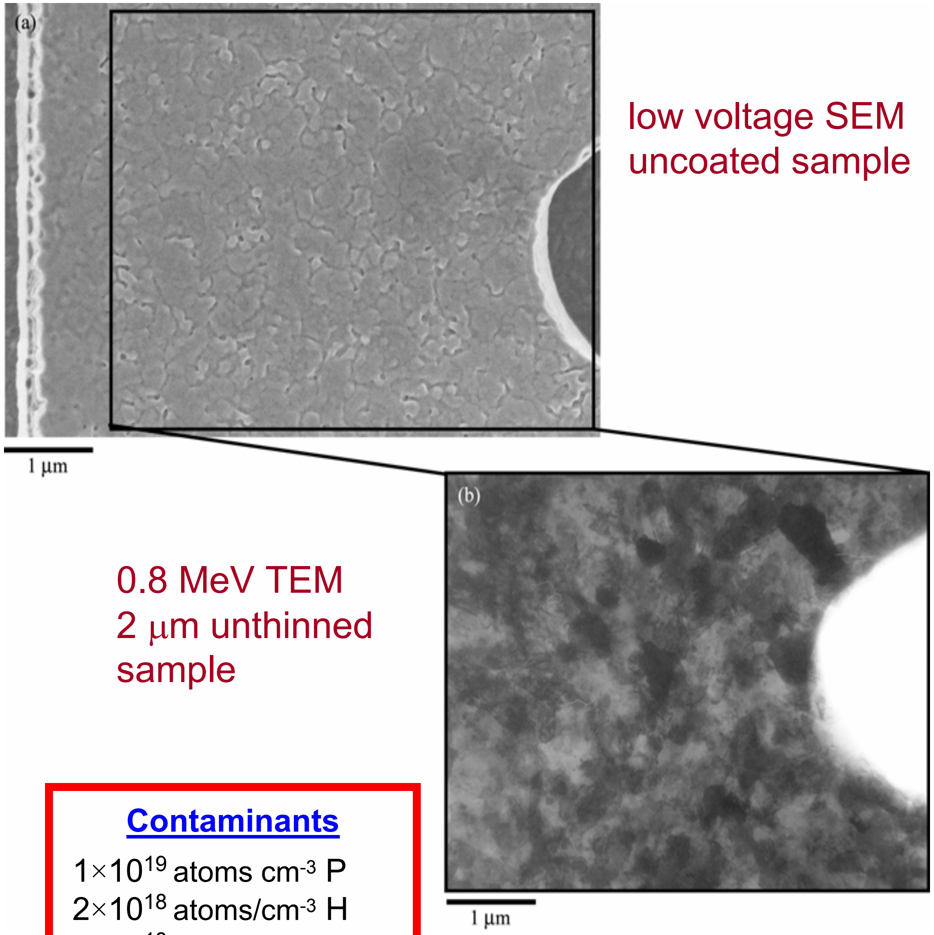
- microstructure

  nominal grain size ~100 nm
  low residual stresses ~ -9 MPa

- mechanical properties

  $E \sim 163$ GPa, $\nu \sim 0.22$
  bending strength, $\sigma_F \sim$ 3 - 5 GPa
  fracture toughness $K_c \sim 1$ MPa$\sqrt{\text{m}}$

*MCNC/JDS Uniphase/Cronos/MEMSCAP



low voltage SEM
uncoated sample

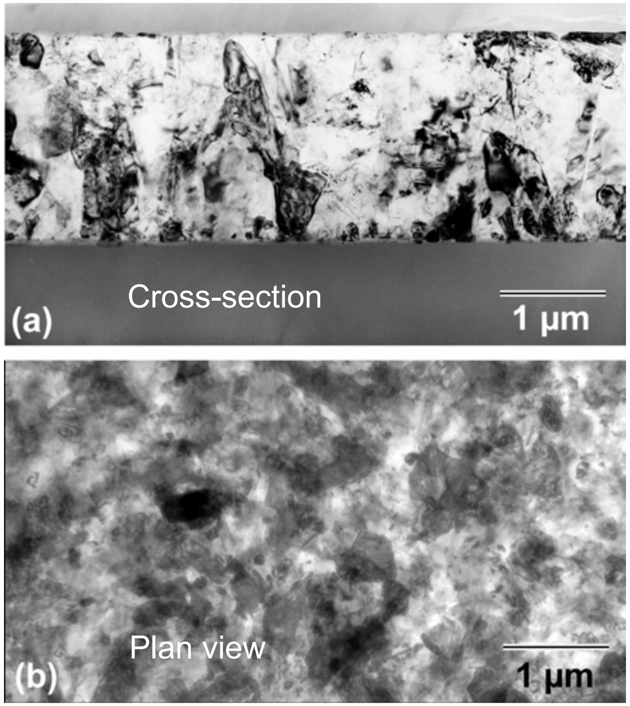
0.8 MeV TEM
2 µm unthinned
sample

Contaminants

1×10^{19} atoms cm^{-3} P
2×10^{18} atoms/cm^{-3} H
1×10^{18} atoms/cm^{-3} O
6×10^{17} atoms/cm^{-3} C

Muhlstein, Brown, Ritchie, *Sensors & Actuators*, 2001

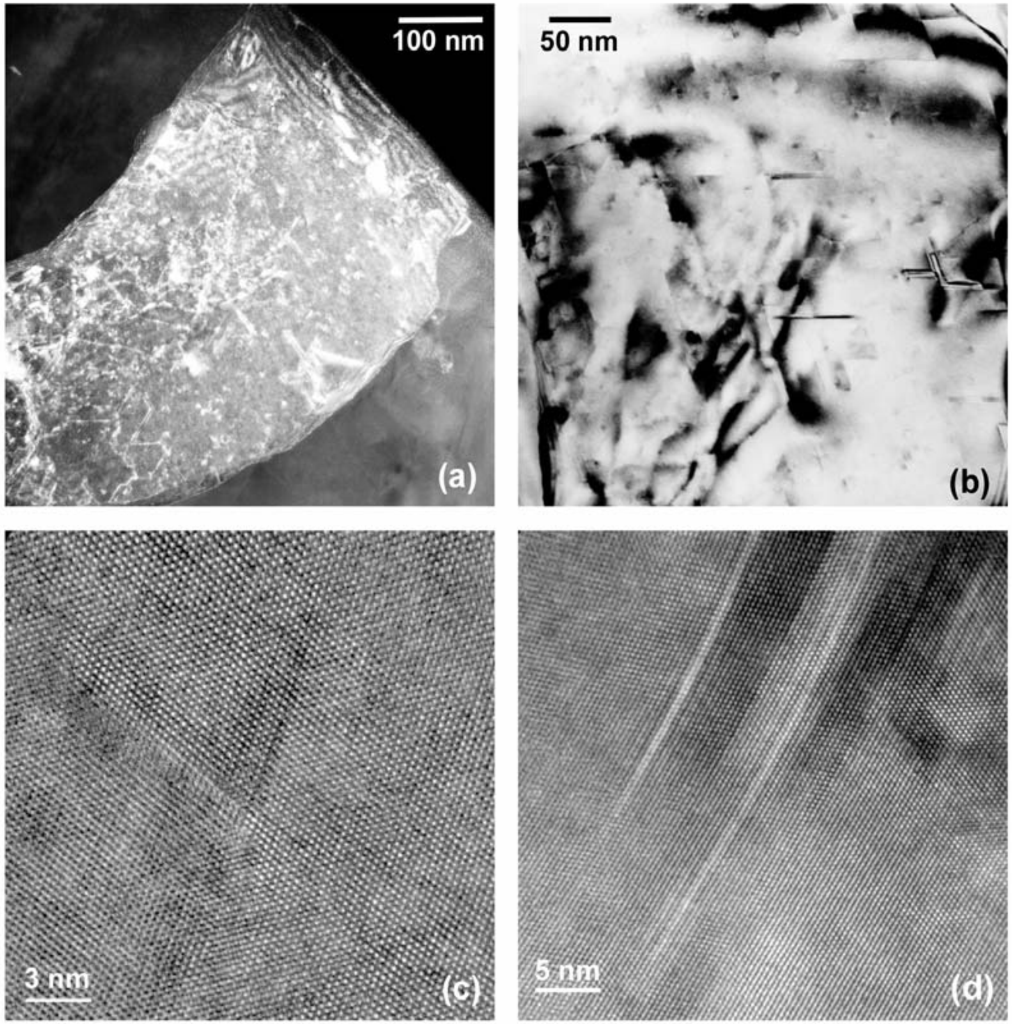
Microstructure of Polysilicon Films



1 MeV HVTEM images

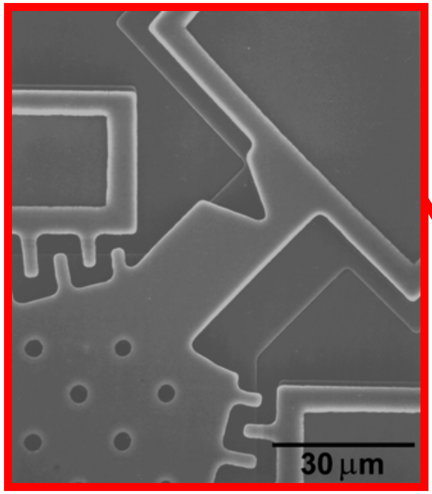
defects in the polysilicon films

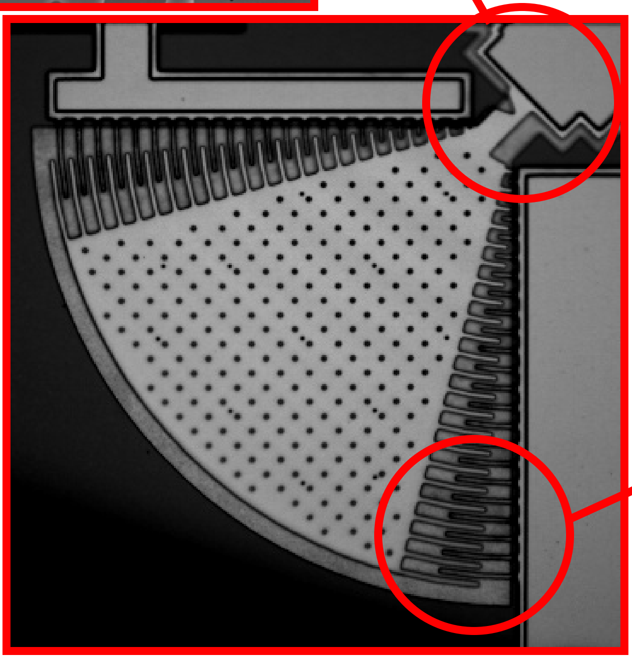
- stacking faults
- Lomer-Cottrell locks
- microtwins



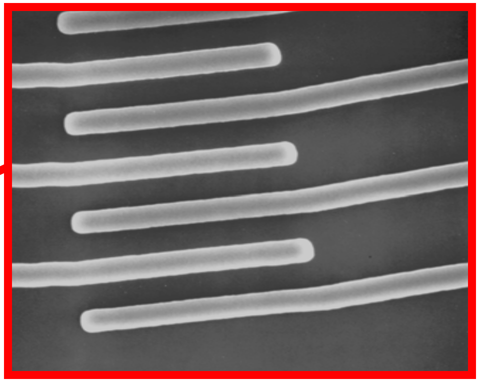
Muhlstein, Stach, Ritchie, *Acta Mater.*, 2002

Electrostatically-Actuated Resonant Fatigue Testing





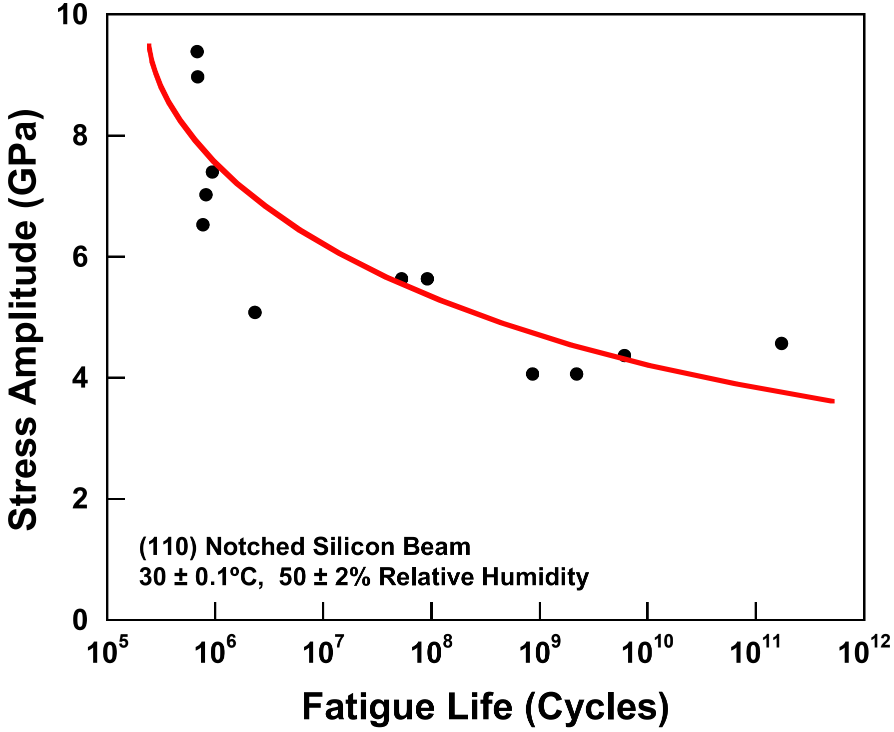
- notched cantilever beam attached to ~300 µm square perforated plate (resonant mass)
- "comb drives" on one side are electrostatically forced to resonate at ~ 40 kHz, with *R* = -1
- other side provides for capacitive sensing of motion, calibrated with machine vision system (Freeman, MIT)
- stress amplitudes determined by finite-element analysis (ANSYS)
- smallest notch root radius (1 – 1.5 µm) achieved by photolithographic masking

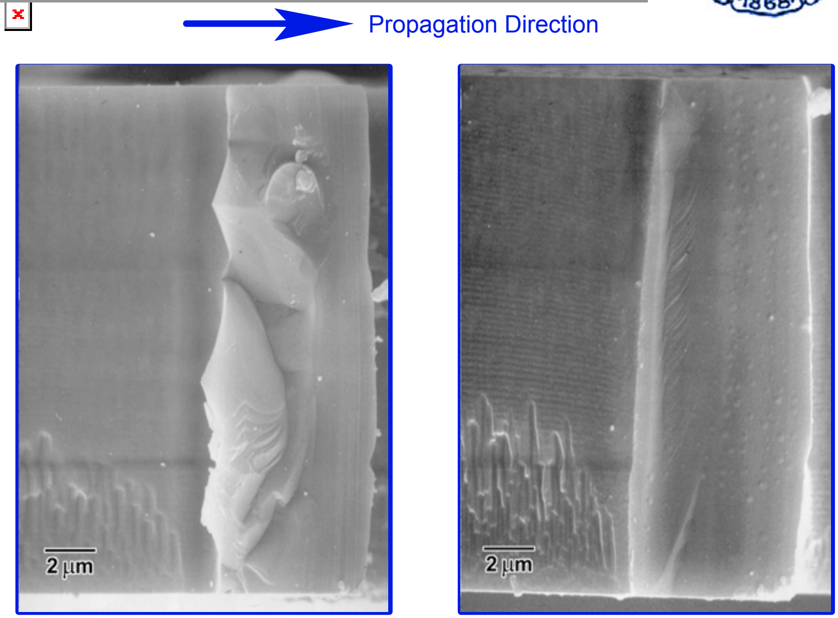


Brown, Van Arsdell, Muhlstein *et al.*

Fatigue of Thin (20 μm) Single Crystal Silicon Films

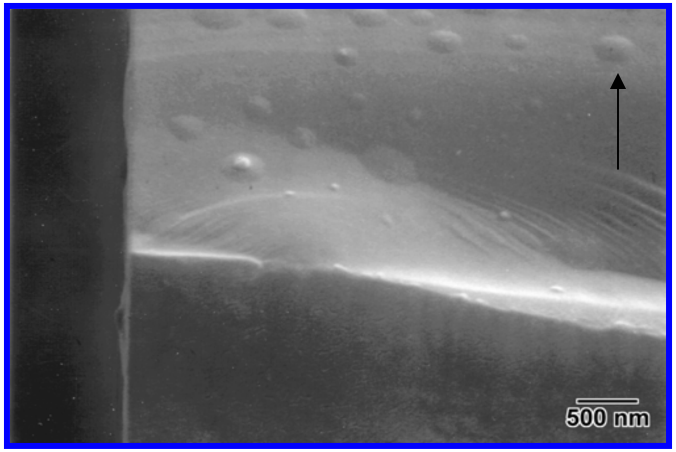
- Micron-scale *p*-type (110) single crystal Si films can fail after 10^9 cycles at (maximum principal) stresses (on 110 plane) of one half the (single cycle) fracture strength
- {110} crack paths suggest mechanisms other than {111} cleavage





20 sec life

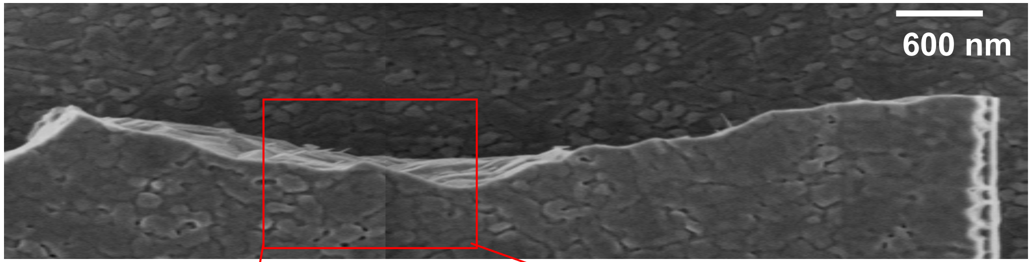
48 day life



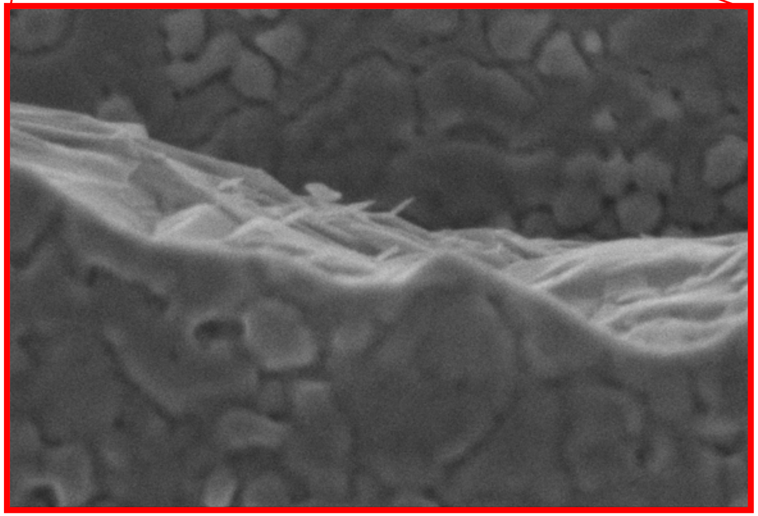
Muhlstein, Brown, Ritchie, *J. MEMS*, 2001.

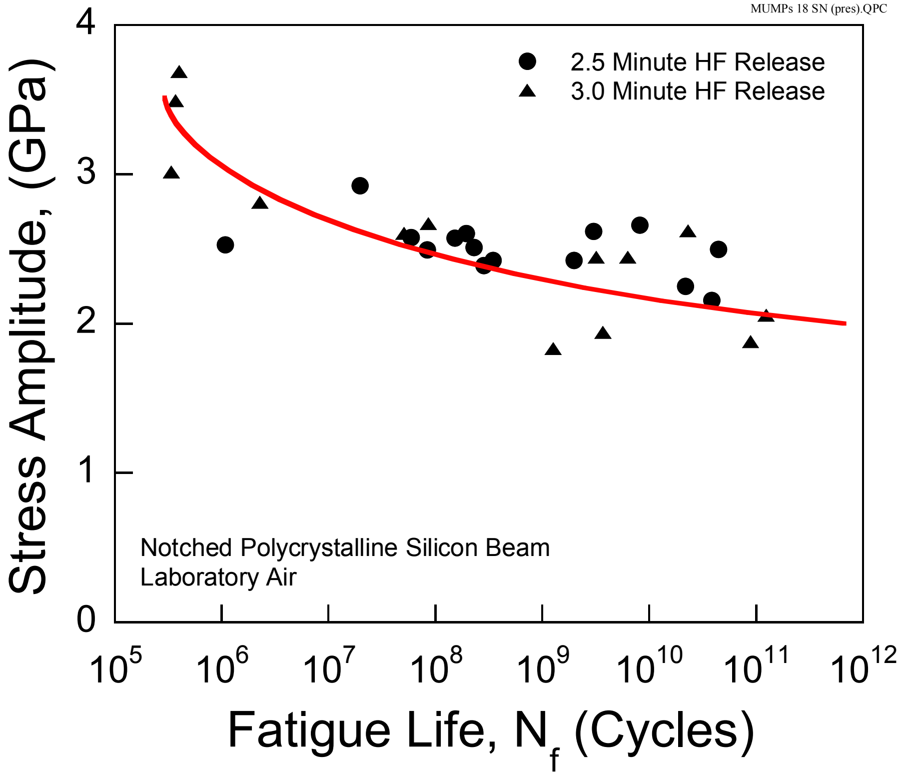
Fatigue of Thin (2 μm) Polycrystalline Silicon Films

- Micron-scale polycrystalline *n*-type Si is susceptible to fatigue failure
- Films can fail after 10^9 cycles at stresses of one half the (single cycle) fracture strength



3.8 x 10^{10} cycles to failure

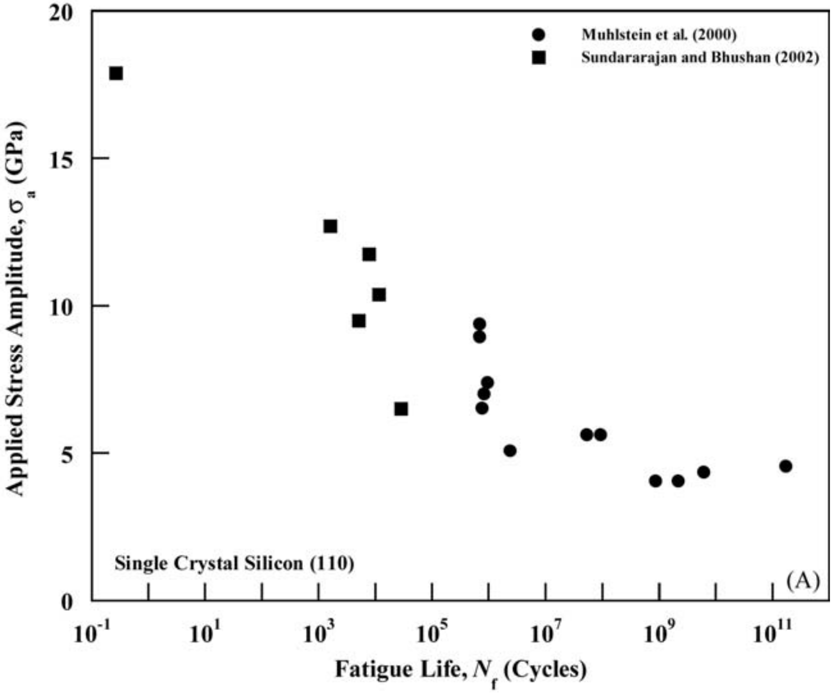




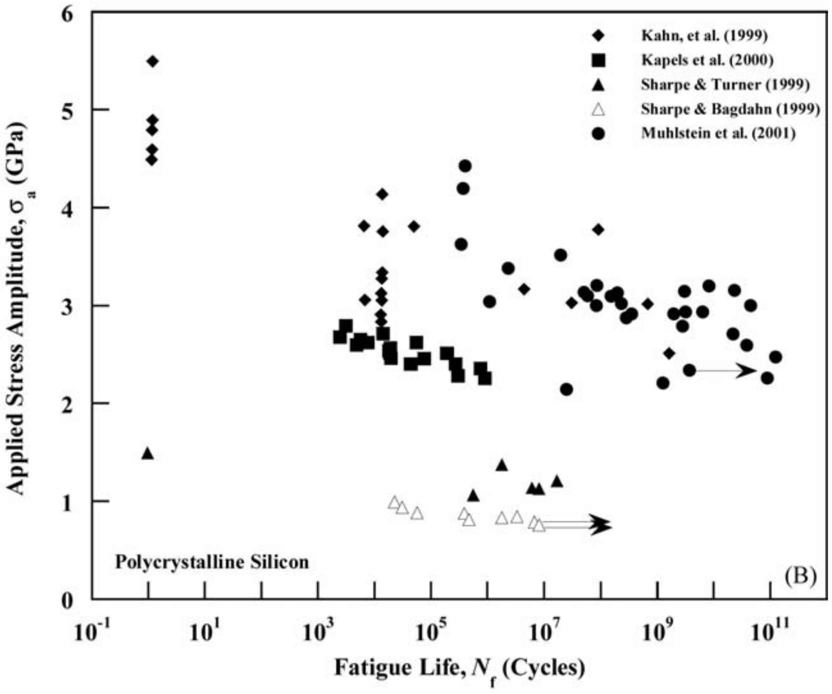
- slivers and debris on fractures consistent with some degree of microcracking

Muhlstein, Brown, Ritchie, *Sensors & Actuators*, 2001

Fatigue of Single Crystal and Polycrystalline Silicon Thin Films



single-crystal (110) silicon

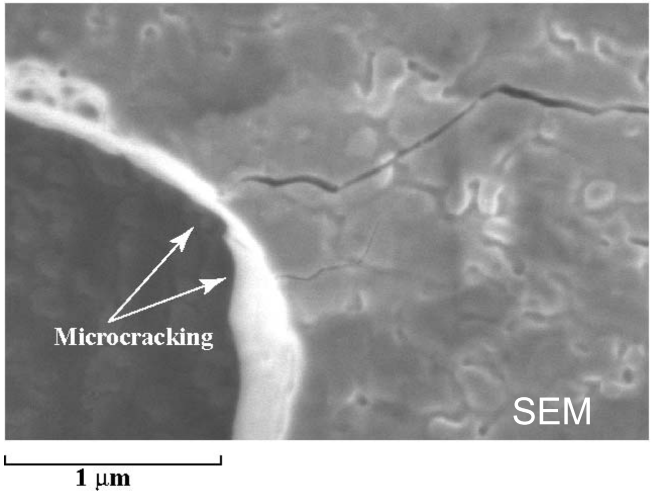


polycrystalline silicon

- Micron-scale silicon films display delayed failure under high-cycle fatigue loading
- No such delayed fatigue failure is seen in bulk silicon

Transgranular Cleavage Fracture

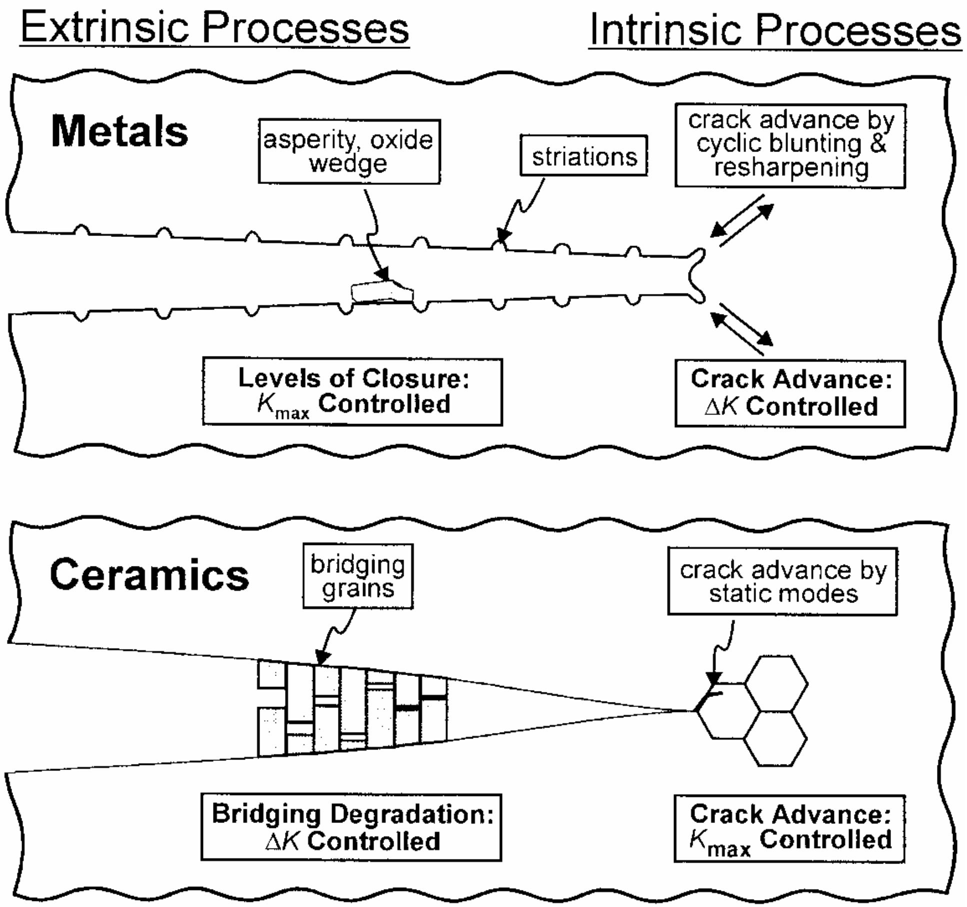
- transgranular cleavage cracking from notch under sustained loads
- some evidence of secondary cracking and multiple microcracking



Muhlstein, Stach, Ritchie, *Acta Mater.*, 2002

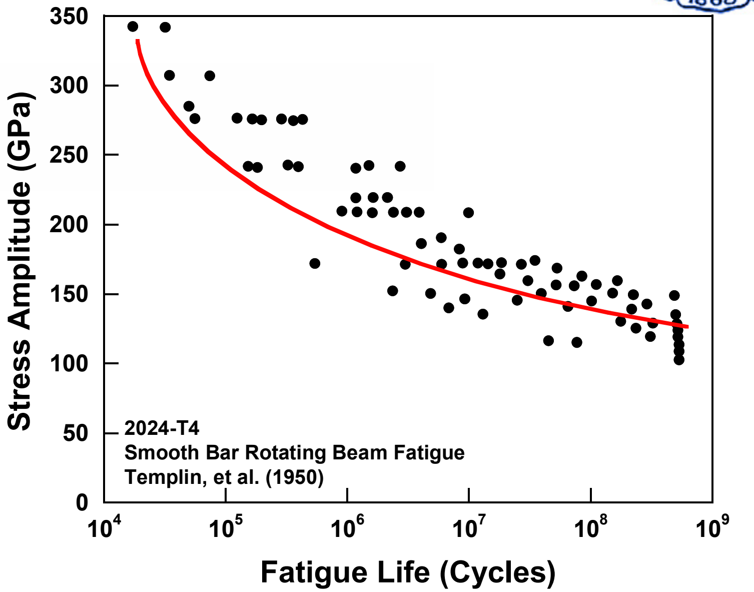
Traditional Fatigue Mechanisms

Bulk ductile materials

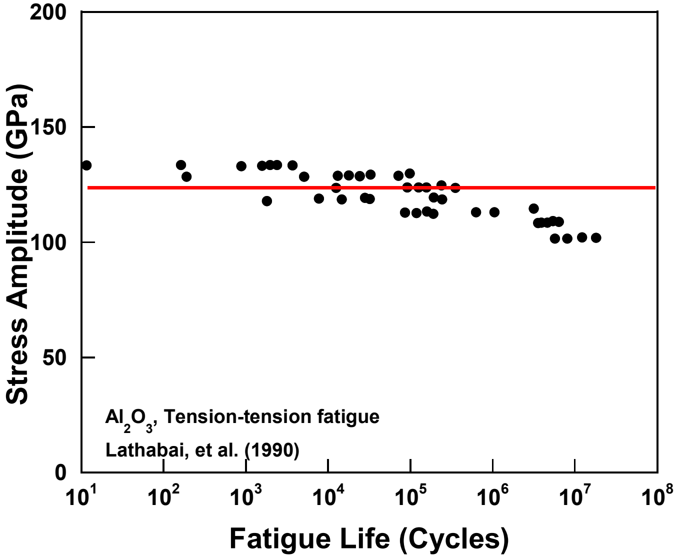


(Ritchie,1989)

Bulk brittle materials



2024-T4
Smooth Bar Rotating Beam Fatigue
Templin, et al. (1950)

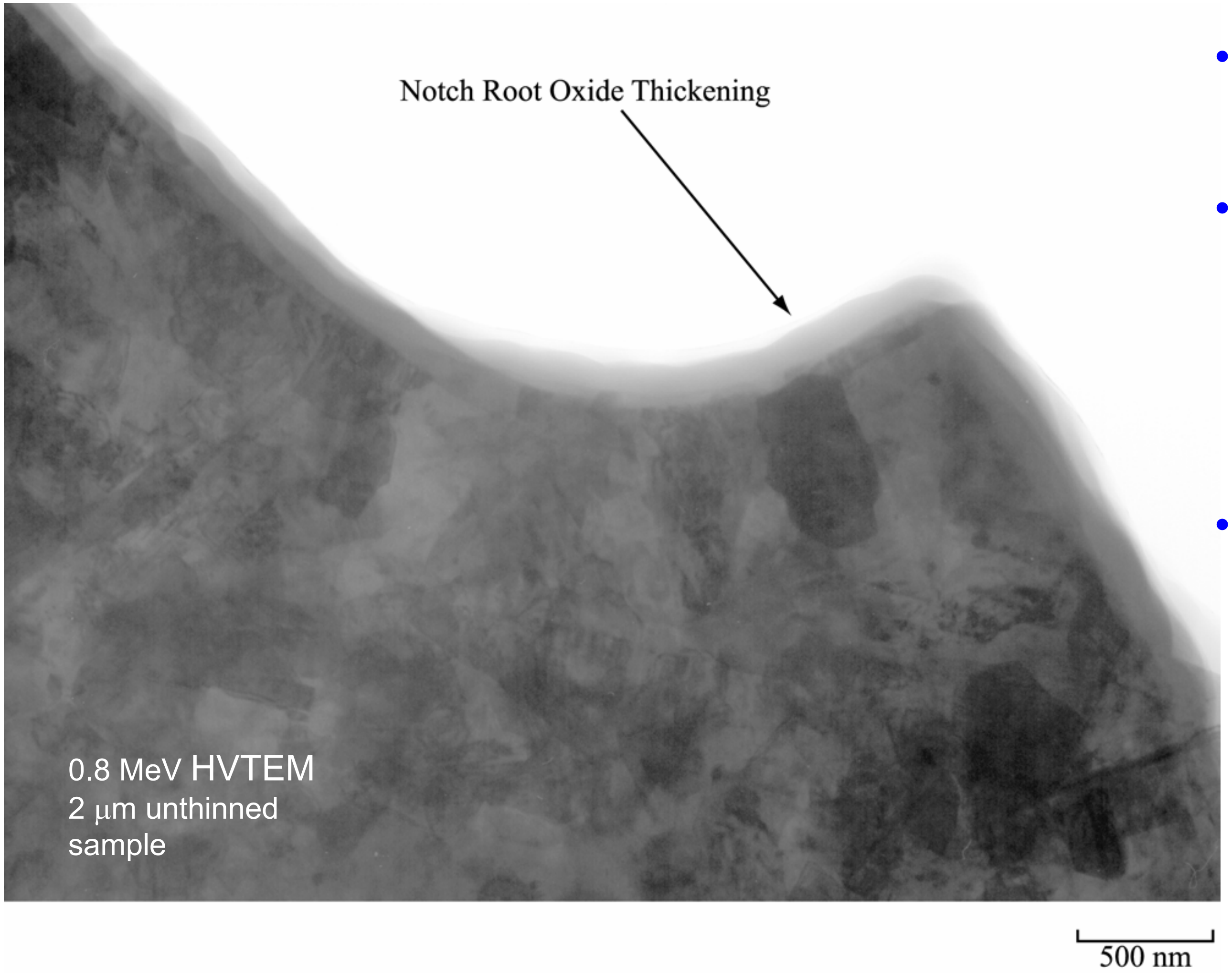


Al_2O_3, Tension-tension fatigue
Lathabai, et al. (1990)

Proposed Mechanisms of Silicon Fatigue

- Dislocation activity in thin films
- Stress-induced phase transformations (*e.g.*, amorphous Si)
- Impurity effects (*e.g.*, precipitates)
- Suppression of crack-tip shielding
- Surface effects (native oxide layer)

Notch Root Oxide Thickening



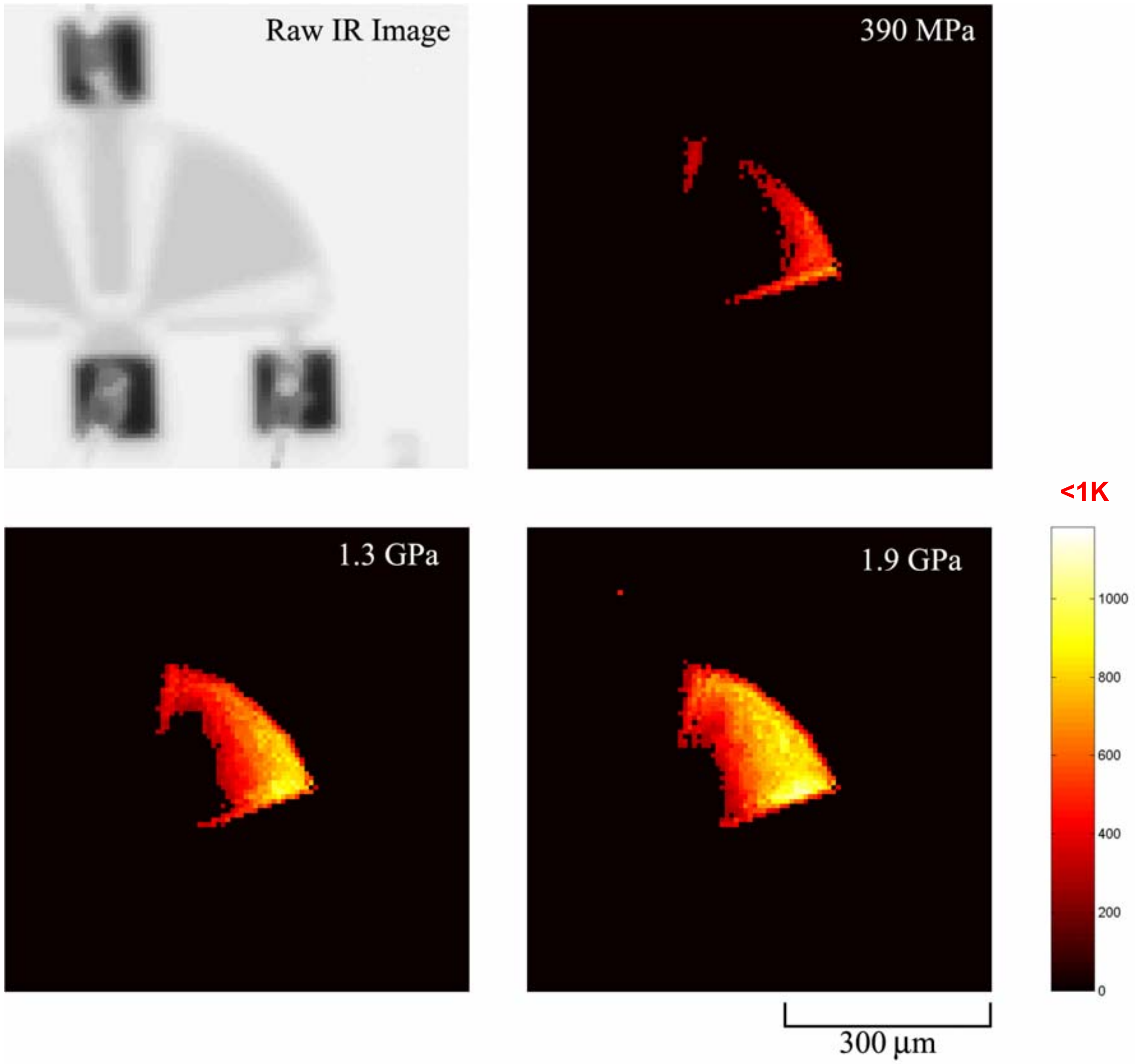
0.8 MeV HVTEM
2 μm unthinned sample

$\sigma_a = 2.26$ GPa, $N_f = 3.56 \times 10^9$ cycles

- native oxide thickness ~30 nm
- *in fatigue*, oxide thickness at notch root seen to thicken three-fold to ~100 nm
- *in sustained loading*, no such thickening is seen

Muhlstein, Stach, Ritchie, *Acta Mat.*, 2002

Thermal vs. Mechanical Oxide Thickening

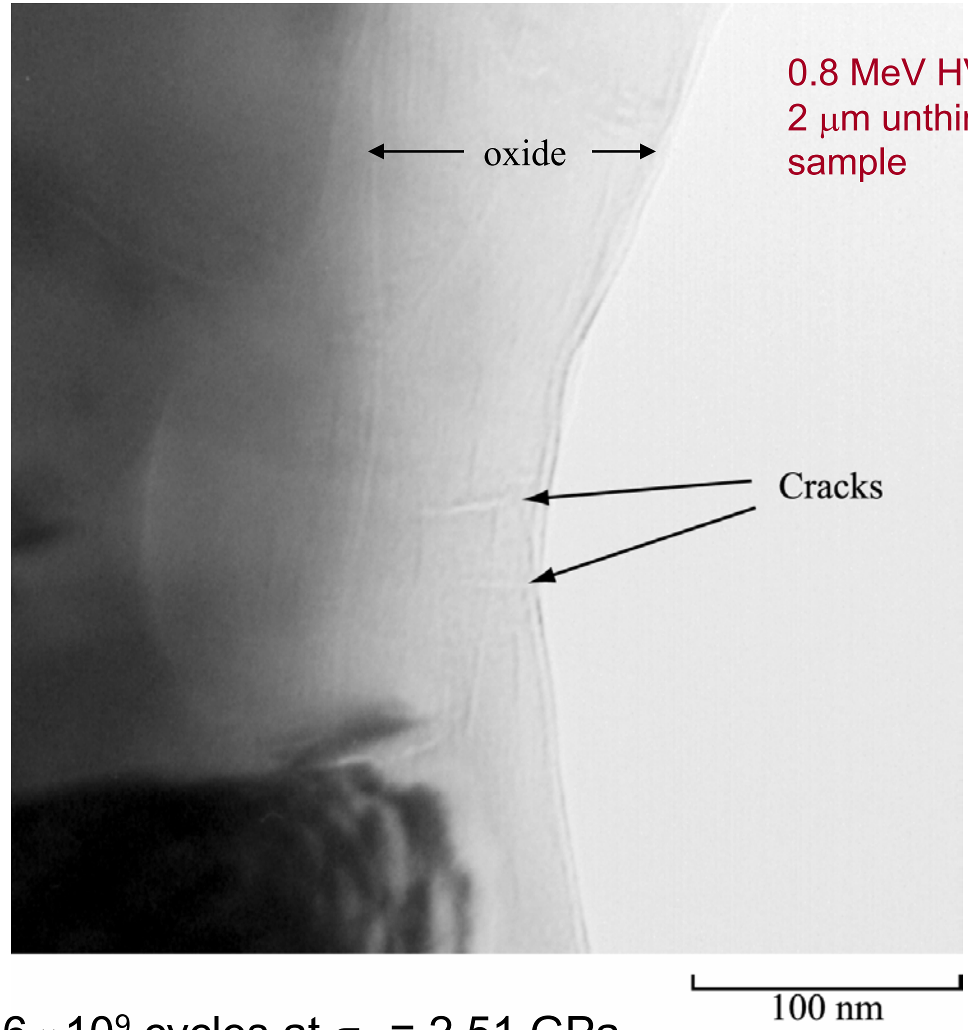


- temperature measured *in situ* at various stresses using a high-resolution IR camera
- IR camera capable of detecting ΔT to within mK with lateral positioning within microns
- small changes in ΔT of the resonant mass due to friction with the air
- notch region shows no change (<1 K) in ΔT during the fatigue test
- *the observed 3-fold thickening of the oxide film in the notch region is promoted by mechanical rather than thermal factors*

Muhlstein, Stach, Ritchie, *Appl. Phys. Lett.*, 2002

Crack Initiation in Notch Root Oxide

- crack initiation in oxide scale during interrupted fatigue test
- evidence of several cracks ~40 – 50 nm in length
- length of cracks consistent with change in resonant frequency
- strongly suggests subcritical cracking in the oxide layer, consistent with proposed model for fatigue



0.8 MeV HVTEM
2 μm unthinned
sample

interrupted after 3.56×10^9 cycles at $\sigma_a = 2.51$ GPa

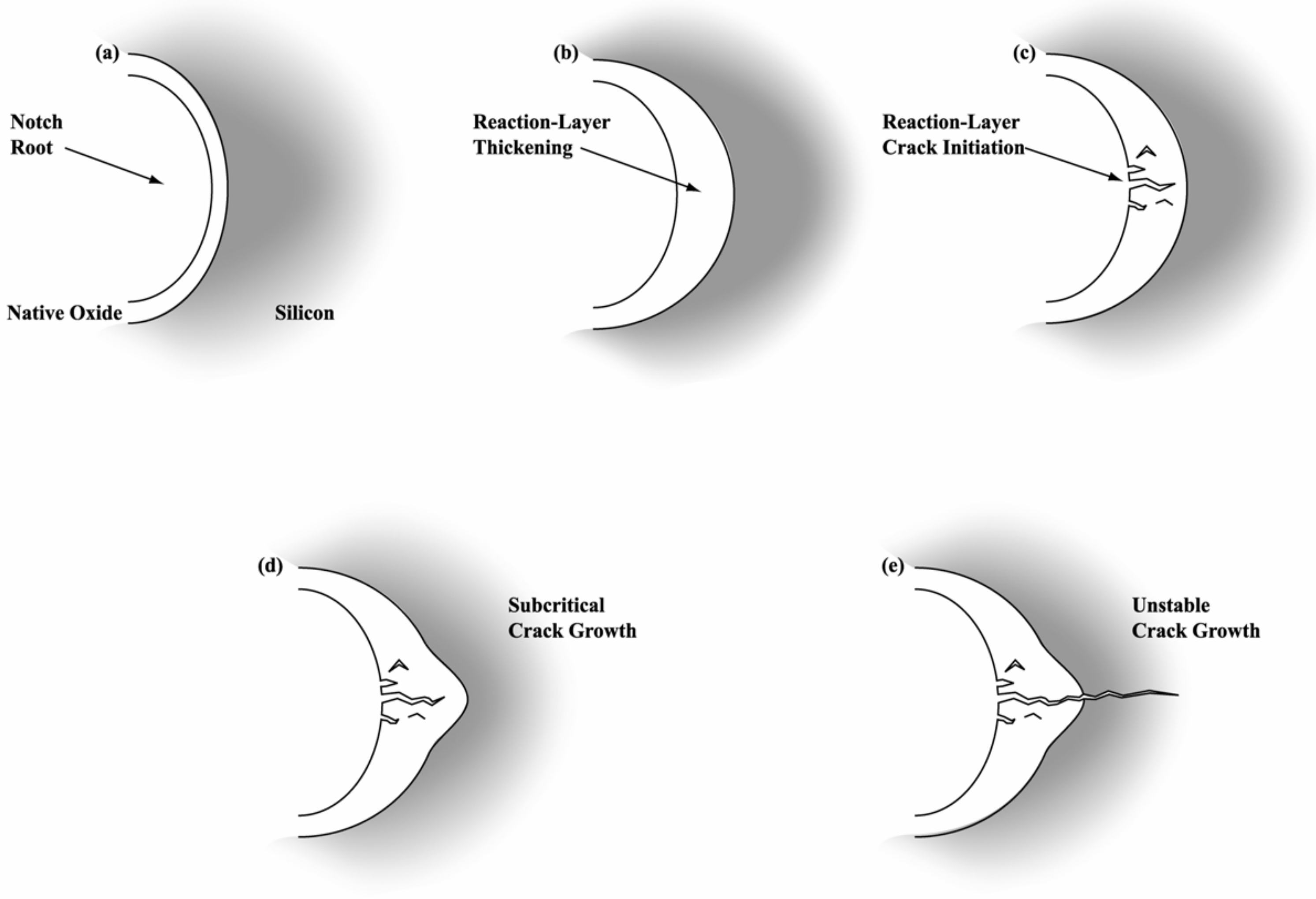
Muhlstein, Stach, Ritchie, *Acta Mater.*, 2002

Relative Crack-Growth Resistance of Si and SiO_2

- Progressive time/cycle dependent fatigue mechanism could involve an alternating process of *oxide formation* and *oxide cracking*. However, the fracture toughnesses of Si and SiO_2 are comparable:
    - Si: $K_c \sim 1\ \mathrm{MPa}\sqrt{\mathrm{m}}$
    - SiO_2: $K_c \sim 0.8 - 1\ \mathrm{MPa}\sqrt{\mathrm{m}}$
- In contrast, the susceptibility of Si and SiO_2 to *environmentally-assisted cracking* in the presence of moisture are quite different, with silica glass being much more prone to stress-corrosion cracking:
    - Si: $K_{Iscc} \sim 1\ \mathrm{MPa}\sqrt{\mathrm{m}}$ (in moisture)
    - SiO_2: $K_{Iscc} \sim 0.25\ \mathrm{MPa}\sqrt{\mathrm{m}}$
- Thus, fatigue mechanism is postulated as a sequential process of:
    - mechanically-induced surface oxide thickening
    - environmentally-assisted oxide cracking
    - final brittle fracture of silicon

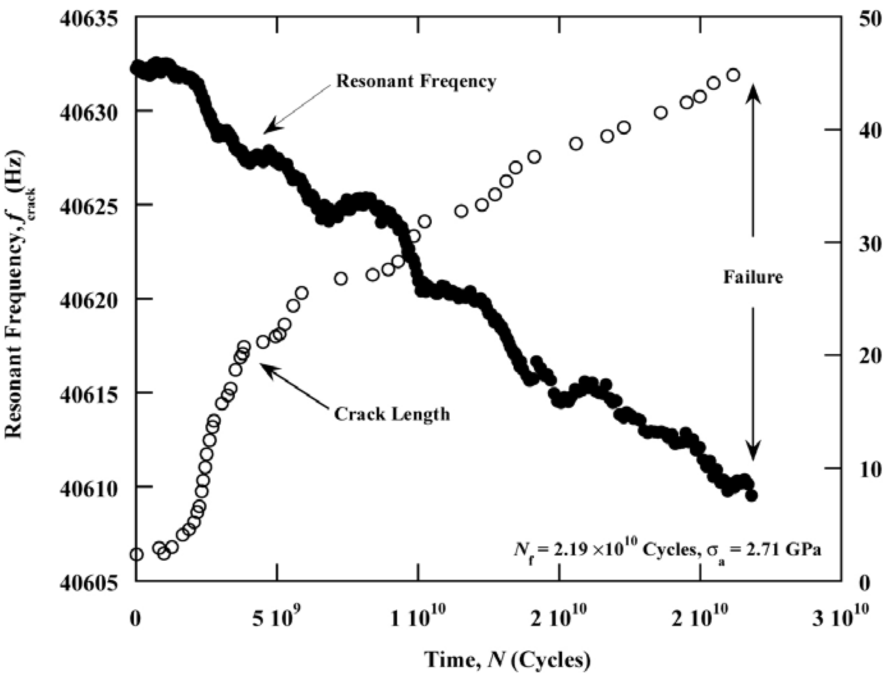
Muhlstein, Stach, Ritchie, *Acta Mater.*, 2002

Silicon Fatigue Mechanism
- Reaction-Layer Fatigue -



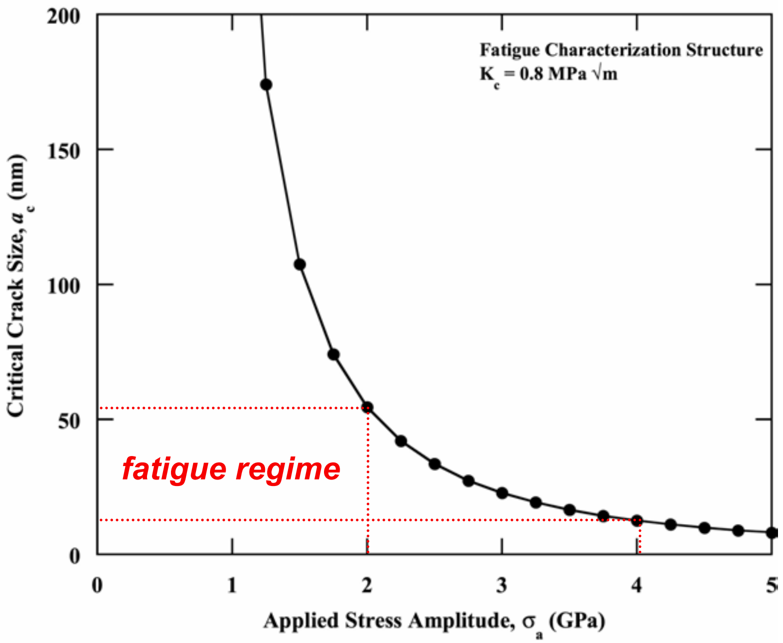
Muhlstein, Stach, Ritchie, *Appl. Phys. Lett.*, 2002

Incipient Cracking during Fatigue Test



- measured change in natural frequency used to compute specimen compliance and hence crack length throughout the test
- for σ_a = 2 – 5 GPa, crack lengths at onset of specimen failure remain less than ~50 nm

$$K_c = Q\,\sigma_F\,(\pi a_c)^{1/2}$$

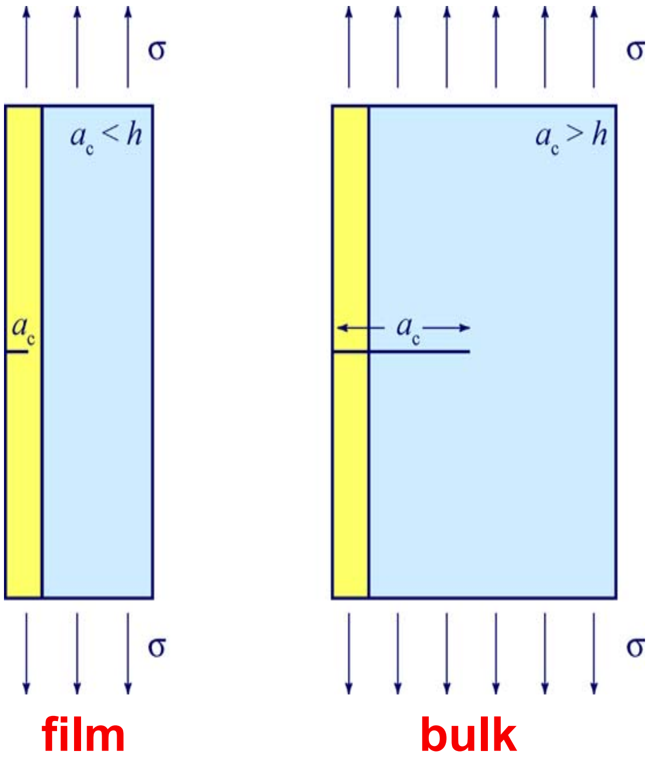


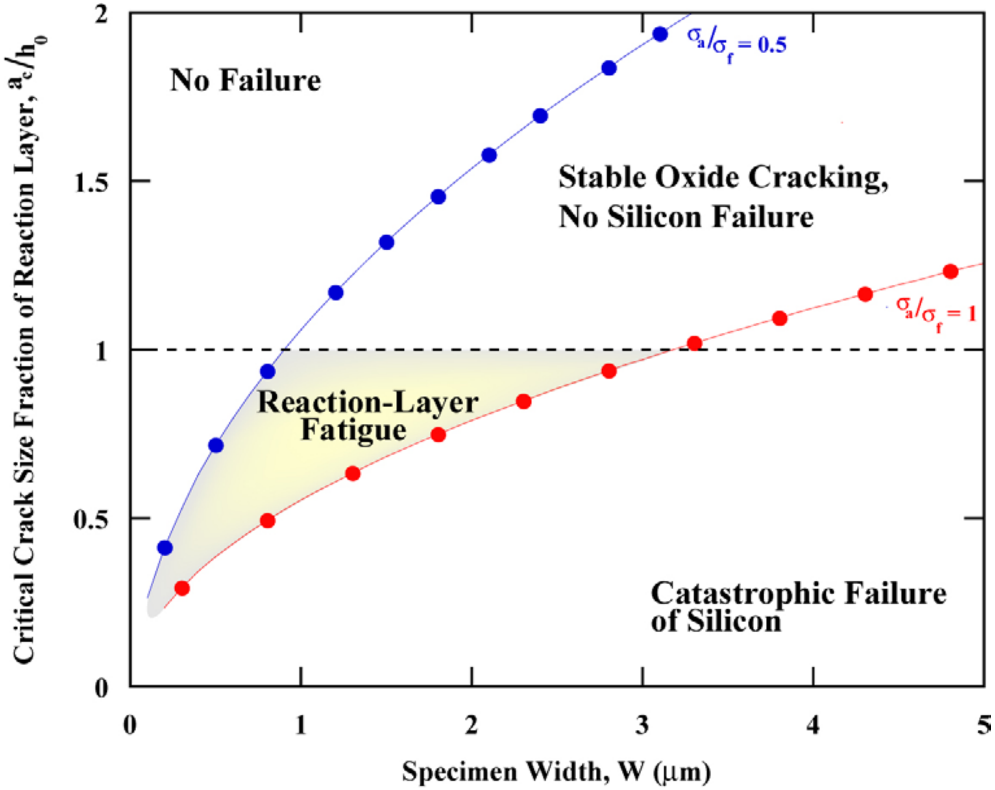
- this suggests that the entire fatigue process, i.e.,
  - crack initiation
  - subcritical crack growth
  - onset of final failure

occurs within the native oxide layer

Muhlstein, Stach, Ritchie, *Acta Mat.*, 2002

Why is Only Thin-Film Silicon Susceptible to Reaction-Layer Fatigue?





- mechanism is active for thin-film and bulk silicon in moist air
- due to low surface-to-volume ratio of bulk materials, the effect is insignificant
- critical crack size for failure can be reached in the oxide layer only for thin-film silicon, i.e., where $a_c < h$

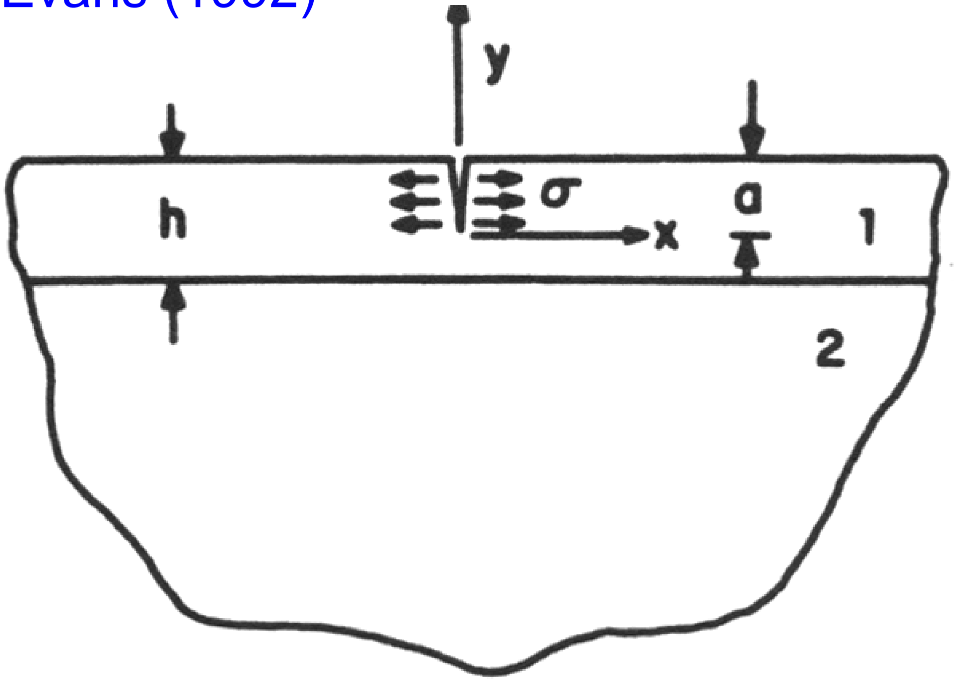
Muhlstein, Ritchie, 2002

Interfacial Crack Solutions: Crack Inside Layer, Normal to Interface

- Beuth (1992)
  - extension of Civilek (1985) and Suo and Hutchinson (1989,1990)
  - dislocation-based fracture mechanics solution
- Ye, Suo, and Evans (1992)

$$\alpha = \frac{\overline{E}_1 - \overline{E}_2}{\overline{E}_1 + \overline{E}_2}$$

$$\beta = \frac{\mu_1(1-2\nu_2) - \mu_2(1-2\nu_1)}{2\mu_1(1-\nu_2) + 2\mu_2(1-\nu_1)}$$

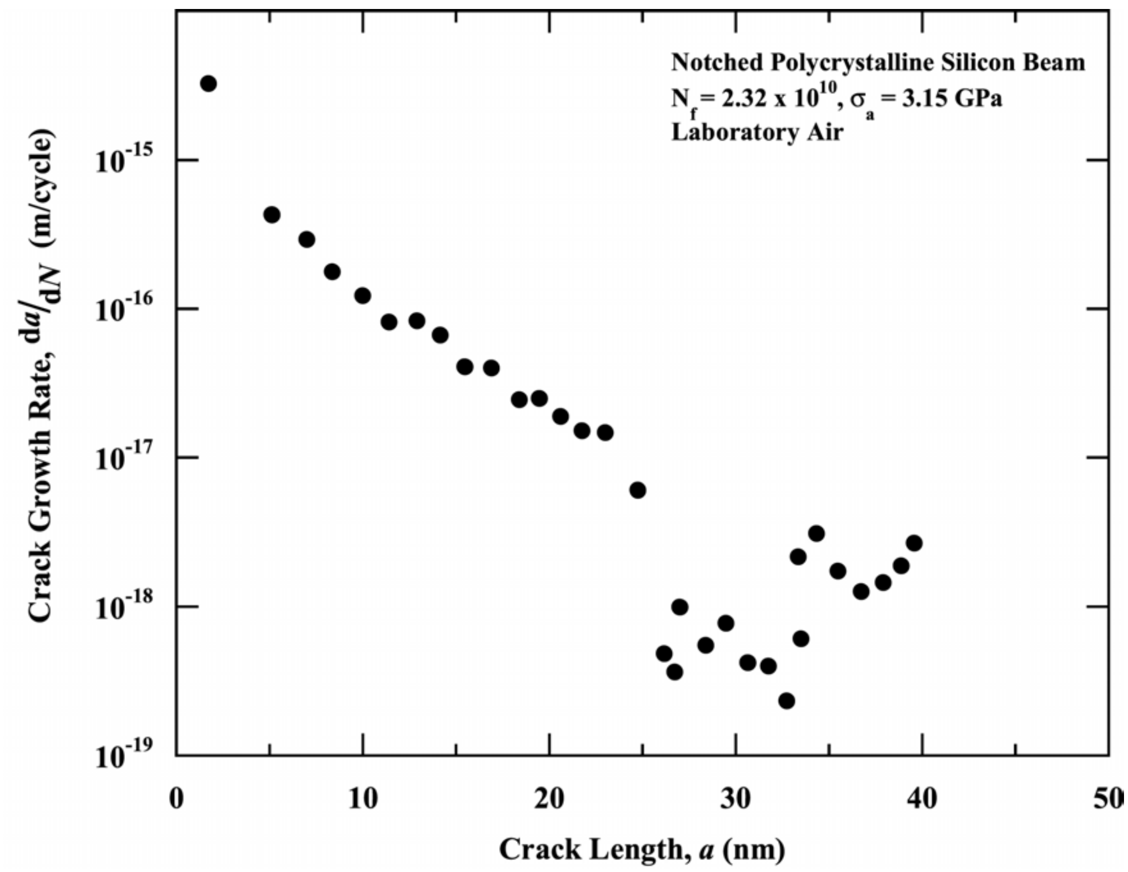


SiO_2/Si

$\alpha = -0.5$

$\beta = -0.2$

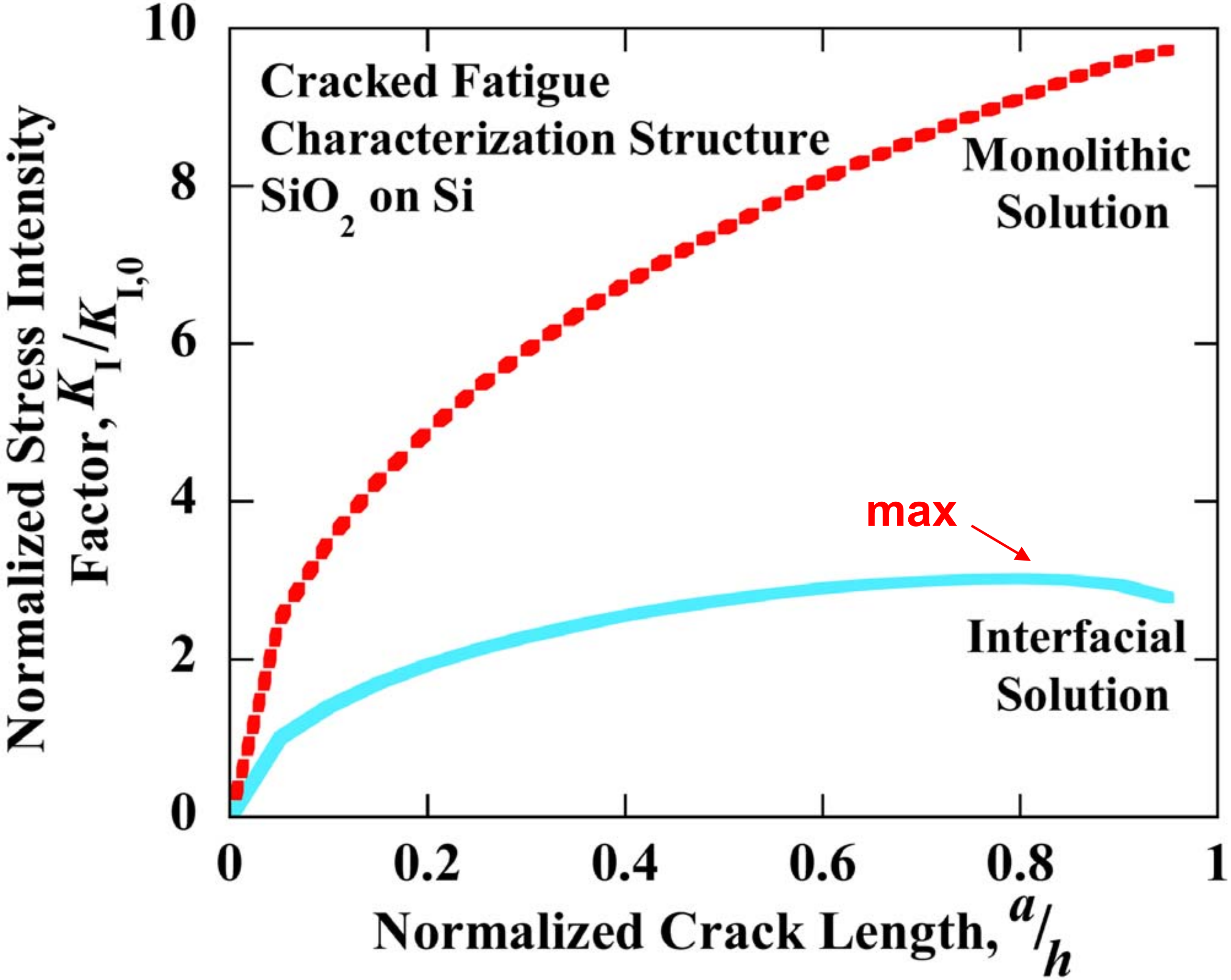
Crack-Growth Rates and Final Failure



- estimated cracking rates display decreasing growth-rate behavior, consistent with:
  - small-crack effects
  - displacement-control conditions
  - residual stresses in film
  - growth toward SiO_2/Si interface

Muhlstein, Stach, Ritchie, *Acta Mat.*, 2002

Solution for Crack in Native Oxide of Si

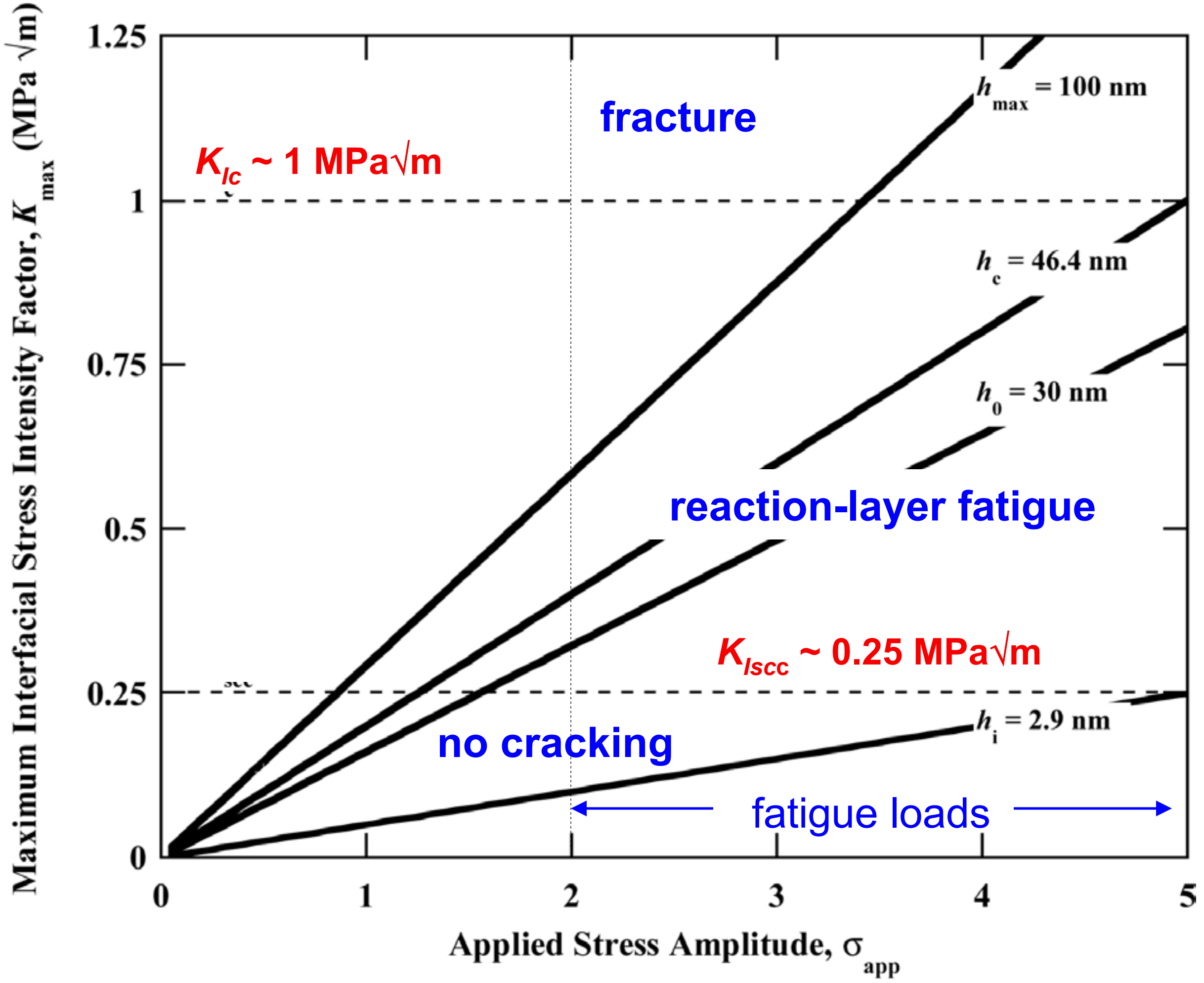


- interfacial solutions for a compliant (cracked) SiO_2 layer on a stiff silicon substrate
- crack-driving force K is $f(a,h)$
- *maximum* K is found at $a_c/h \sim 0.8$

$K_{I,o}$ is the interfacial K where $a/h = 0.05$; $h = 100$ nm

Muhlstein and Ritchie, *Int. J. Fract.*, 2003

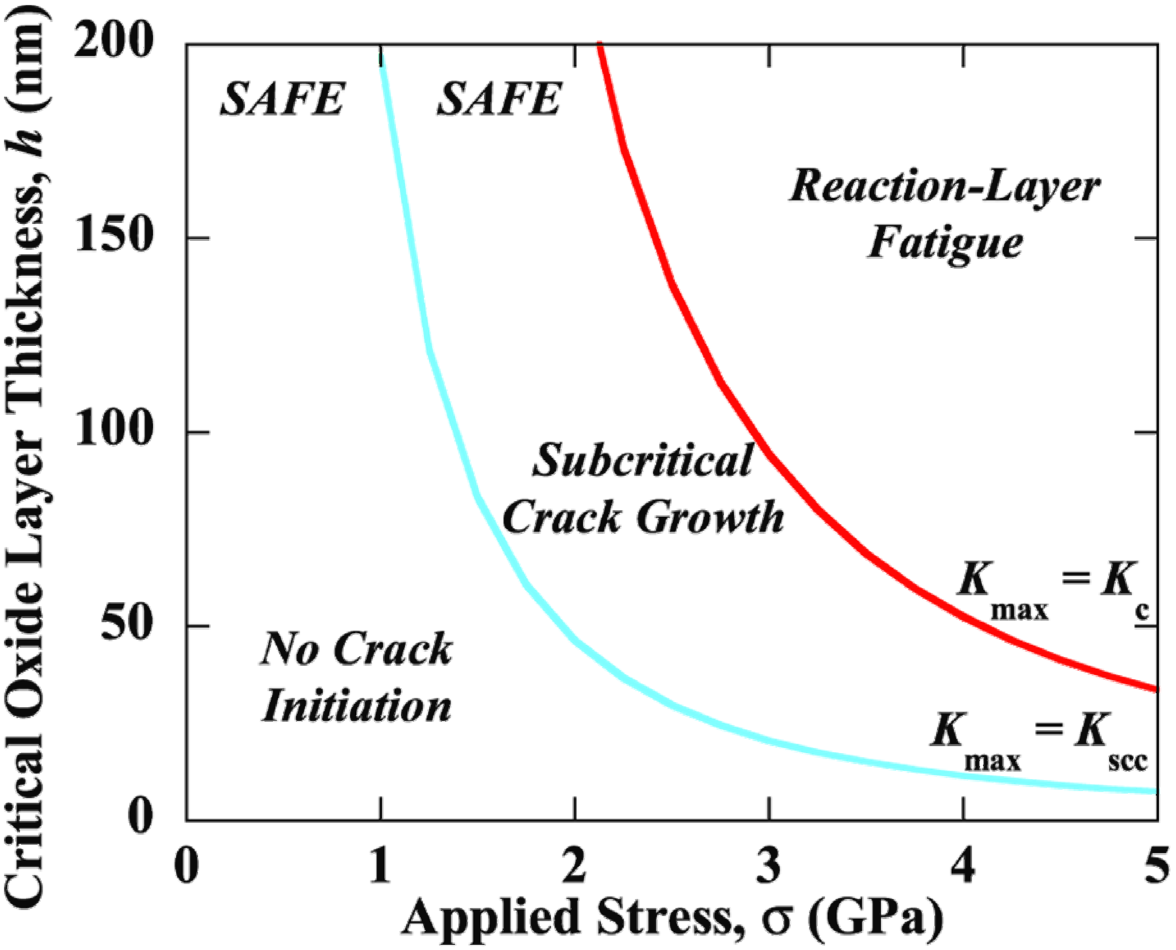
Interfacial Crack-Driving Force



- maximum K at (a/h) ~ 0.8
- in range of fatigue failure, where σ_{app} ~ 2 to 5 GPa, cyclic-induced oxidation *required* for reaction-layer fatigue
- oxide thickness ≥ 46 nm for failure at $\sigma_{app} < 5$ GPa
- oxide thickness ≥ 2.9 nm for crack initiation at $\sigma_{app} < 5$ GPa

Muhlstein and Ritchie, *Int. J. Fract.*, 2003

Bounds for Reaction-Layer Fatigue



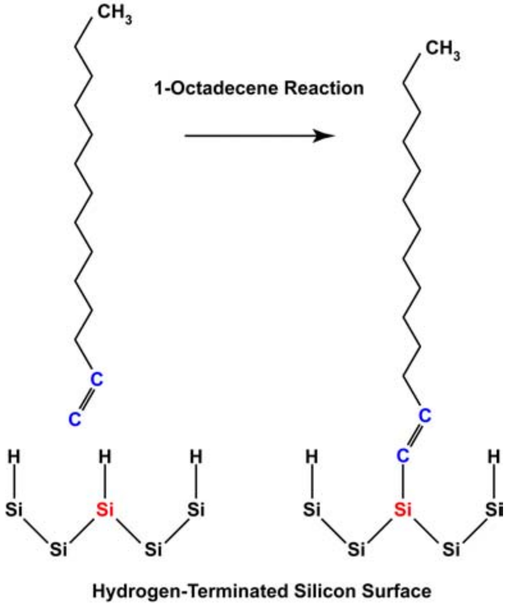
- behavior dependent on reaction-layer thickness
- bounds set by K_{Iscc} and K_c of the oxide
- regimes consist of:
  - no crack initiation in oxide ($K < K_{Iscc}$)
  - cracking in oxide but no failure ($K_{Iscc} < K < K_c$)
  - reaction-layer fatigue ($K > K_c$)

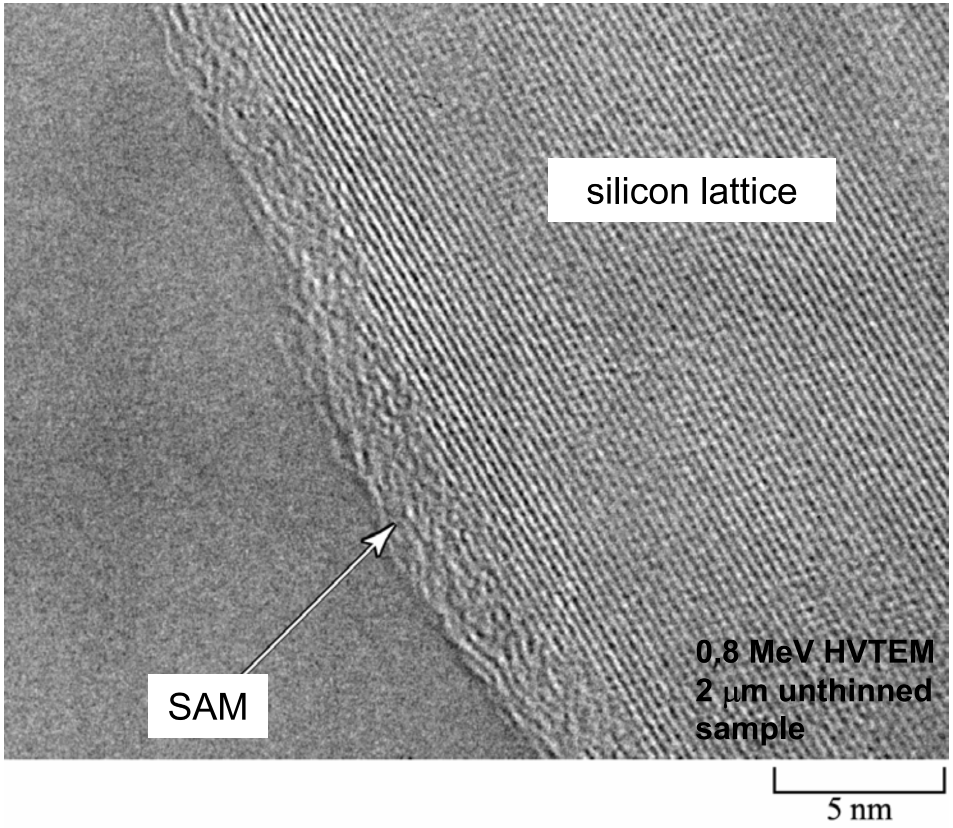
- *Reaction-layer fatigue* provides a mechanism for delayed failure in thin films of materials that are ostensibly immune to stress corrosion and fatigue in their bulk form

Muhlstein and Ritchie, *Int. J. Fract.*, 2003

Alkene-Based Self-Assembled Monolayer Coatings

- fatigue testing in the absence of oxide formation achieved through the application of aklene-based monolayer coatings

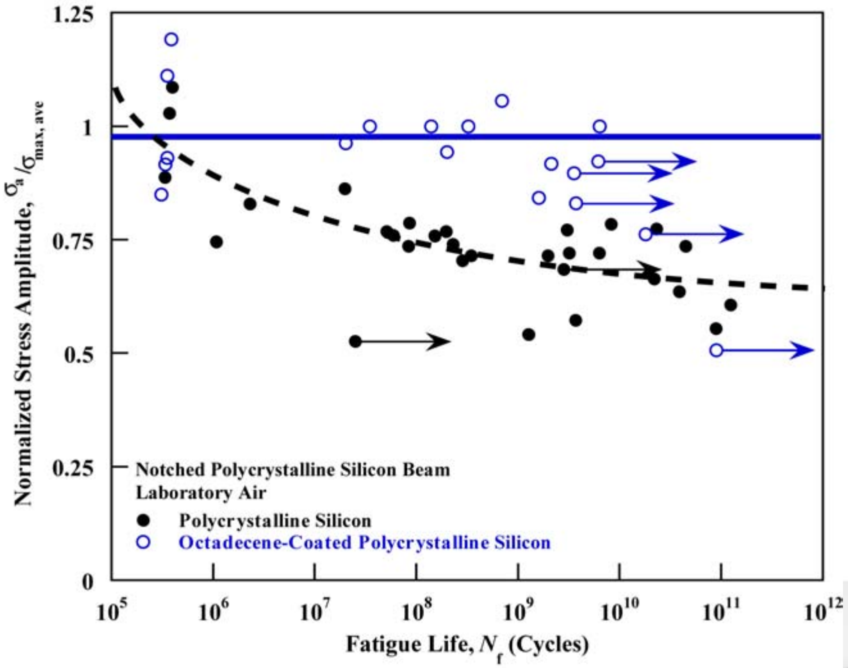




- Si chip is dipped in HF and then coated with alkene-based monolayer coating – *1-octadecene*
- alkene-based coating bonds directly to the H-terminated silicon surface
- coating is a few nm thick, hydrophobic, and stable up to 400°C; *providing a surface barrier to moisture and oxygen*

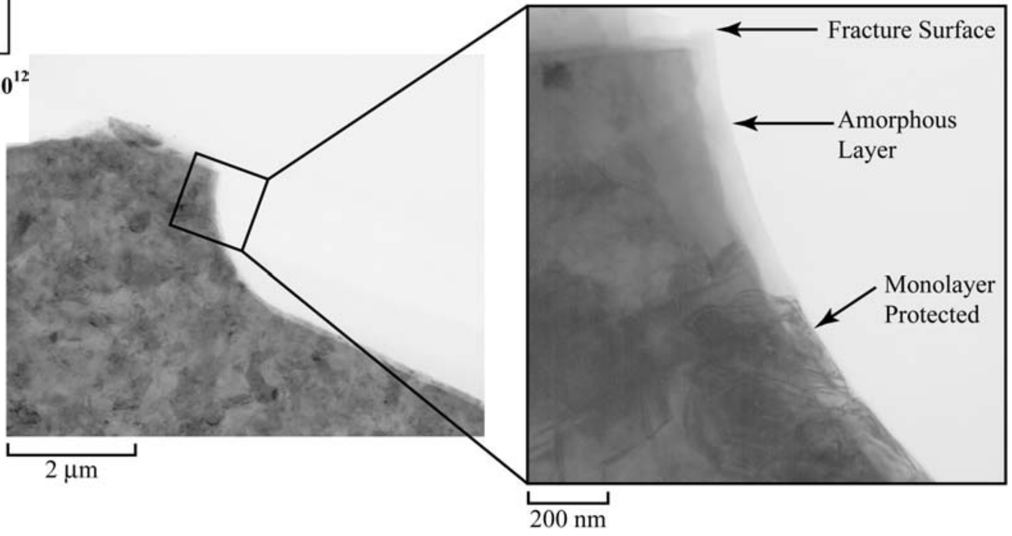
Muhlstein, Ashurst, Maboudian, Ritchie, 2001

Suppression of Reaction-Layer Fatigue



- SAM-coated Si samples display far reduced susceptibility to cyclic fatigue
- absence of oxide formation acts to prevent premature fatigue in Si-films

- alkene-based SAM coatings, however, do lower the fracture strength
- oxidation during release smooths out surface; with coatings, sharp surface features remain



Muhlstein, Stach, Ritchie, *Acta Mat.*, 2002

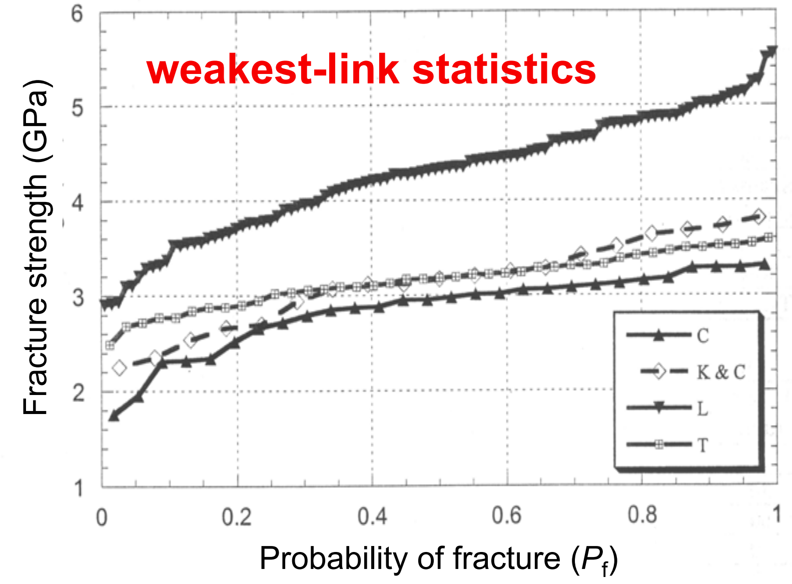
Conclusions

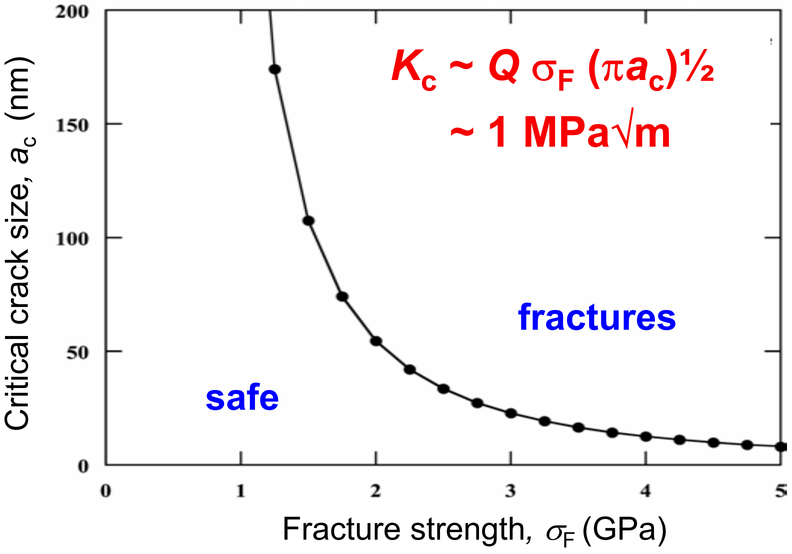
- Below a ductile-brittle transition temperature of ~500°C, Si displays a high fracture strength (1 - 20 GPa in mono- and 3 - 5 GPa in poly-crystalline Si)
- However, Si is intrinsically brittle with a fracture toughness of ~1 MPa$\sqrt{\text{m}}$ (approximately twice that of window pane glass!). This value is independent of microstructure and dopant type
- Evaluation of probability of fracture can be made using weakest-link statistics and/or nanoscale crack detection
- Thin film (micron-scale) Si is susceptible to delayed fracture under sustained and particularly high-cycle fatigue loading - prematurely failure can occur in room air at ~50% of the fracture strength
- Mechanism of cyclic fatigue is associated with mechanically-induced thickening and moisture-induced cracking of the native oxide (SiO_2) layer
- Mechanism significant in thin-film (<u>and not bulk</u>) Si as the critical crack sizes for device failure are less than native oxide thickness, *i.e.*, $a_c < h_{oxide}$
- Suppression of oxide formation at the notch root, using alkene-based SAM coatings, markedly reduces the susceptibility of thin-film silicon to fatigue.

Bottom line: What affects fracture in silicon?

- Brittle Fracture
  - Si-Si bond rupture
  - defect (crack) population
  - residual stresses

  Probability of fracture depends on defect (crack) population
  - smooth surfaces, round-off edges, etch out cracks
  - use weakest-link statistics
  - detect microcracks on the scale of tens of nanometers
- Delayed Fracture
  - cracking in native oxide layer (thin film silicon)


weakest-link statistics


$K_c \sim Q\, \sigma_F\, (\pi a_c)^{1/2}$

$\sim 1\ \mathrm{MPa}\sqrt{\mathrm{m}}$

fractures

safe