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Methyl monolayers improve the fracture strength and durability of silicon nanobeams

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Monolayer-thick coatings have a significant effect on the fracture strength and durability of 210-nm-thick, smooth (~ 0.4 nm rms roughness), single crystal silicon nanobeams. The initial Weibull fracture strength of beams terminated with a methyl (CH_3) monolayer was 18.2 GPa. This strength did not degrade after a 23-day exposure to air. In contrast, beams terminated with a monolayer of hydrogen atoms were initially weaker than methyl-terminated beams, and their strength degraded rapidly in air. After a 23-day air exposure, the strength of H-terminated beams was reduced by at least 30%. Since strength durability is correlated with the oxidation resistance of the monolayers, the degradation of H-terminated beams is attributed to the formation of oxide nuclei that act as local stress concentrators. © 2006 American Institute of Physics. [DOI: 10.1063/1.2400180]

Due to their small sizes and correspondingly low number of defects, nanoscale materials are expected to have significantly higher strengths than their macroscopic counterparts, potentially enabling the production of nanomechanical devices that withstand very high stress operation with low probability of failure. This expectation, along with the increasing importance of commercial and research-grade microelectromechanical systems, has stimulated a growing interest in the mechanical strength of nanoscale materials, particularly silicon.¹⁻⁵

In a previous study,⁶ we showed that small changes in surface roughness can significantly degrade the fracture strength of single crystal silicon nanobeams. Devices with relatively smooth surfaces (0.4 nm rms) displayed fracture strengths comparable to theoretical predictions for defect-free beams, whereas similar devices with slightly rougher surfaces (1.5 nm rms) had 20% lower fracture strengths. These small changes in roughness can be caused by minor changes in fabrication (e.g., changes in etchant concentration or composition), which suggest that careful attention to processing conditions will be necessary for the production of high strength devices.

For practical applications, the maintenance of strength throughout the structure's service life is often as important as the high initial strength. Can nanoscale materials maintain their anticipated high initial strengths? Or does their small size make nanoscale materials more susceptible to corrosion and other environmental effects? The answers to these questions are poorly understood and likely material dependent. For the case of polysilicon, previous experiments have concluded that nanoscale polysilicon does not undergo stress corrosion cracking.⁷ In contrast, polysilicon devices subject to high stresses during cyclic loading do show evidence of fatigue; this effect is attributed to the effects of alternating tensile and compressive stresses on the native oxide layer (i.e., amorphous SiO_2) that forms in air.⁷⁻⁹

In this letter, we show that the fracture strength of nanoscale silicon beams is surprisingly sensitive to the chemical state of the surface. Devices terminated with a single monolayer of hydrogen atoms degraded rapidly with air exposure—a 23-day exposure to air resulted in a 30% decrease in fracture strength. In contrast, methyl(CH_3) terminated beams were initially stronger than hydrogen-terminated beams and showed no evidence of degradation during the three-week test period.

To characterize the effects of surface chemistry on the fracture reliability of nanoscale silicon, 210-nm-thick, 500-nm-wide, 12-micron-long doubly clamped suspended beams were fabricated from 0.1° miscut, $>1000 \Omega \text{ cm}$, floating zone single crystal Si(111) wafers as described previously.⁶ In brief, the lateral shape and thickness of the beams were defined using photolithography and reactive ion etching (RIE); the long axis of the beams was aligned with the $[\bar{1}10]$ direction. A 100-nm-thick protective oxide layer was then grown on all exposed silicon surfaces, including the top and sides of the beams. Using a second stage of photolithography and RIE, deep triangular trenches were formed around, but not under, the protected structures. After a modified RCA clean,¹⁰ the beams were released from the substrate using a 3 min potassium hydroxide etch (50% w/v aq., Lab Chem, 72 °C) followed by a 2 min tetramethylammonium hydroxide etch (25% w/w aq., Transene, 72 °C). This etch sequence produced beams with relatively smooth (0.4 nm rms) surfaces for fracture initiation, as verified by atomic force microscopy (AFM) analysis. Finally, the protective oxide layer was removed (without etching the underlying silicon surface) with a 2 min immersion in room-temperature buffered oxide etch, a 5:1 mixture of $\text{NH}_4\text{F}:\text{HF}$ (aq., J. T. Baker), followed by copious rinsing in ultrapure water (Millipore). After this step, all exposed silicon surfaces were terminated by a single monolayer of hydrogen atoms, as verified by infrared spectroscopy on similarly prepared samples.

Since H-terminated Si(111) surfaces are known to slowly oxidize in air over the course of days,¹¹ methyl-terminated nanobeams were also tested. The methyl groups form a

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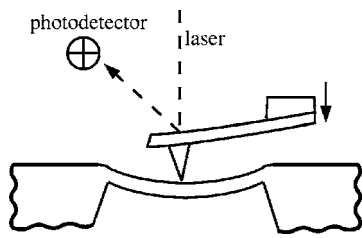


FIG. 1. Schematic of AFM cantilever loading a supported nanobeam.

monolayer-thick “waxy” coating on the surface which significantly impedes the oxidation of the underlying substrate.¹² In contrast to long chain alkyl monolayers [$-C_nH_{2n+1}, n \geq 2$], which are limited to half-monolayer coverage by steric effects, methyl groups can terminate every site on a Si(111) surface.¹³ To prepare the methyl-terminated beams,¹⁴ H-terminated beams were first exposed to 3 Torr of Cl_2 (g), then illuminated with a 254 nm pen lamp for 3 min to produce Cl radicals. This procedure produced fully Cl-terminated resonators. The samples were then refluxed in methyl Grignard reagent (3M CH_3MgCl in THF, Aldrich) under a constant flow of argon for 2.5 h. After reaction, the samples were rinsed twice in anhydrous methanol and once in ultrapure water.

The mechanical strength of the functionalized nanobeams was characterized with an AFM. An uncoated, stiff, single crystal Si AFM cantilever (Veeco TAP525) was used to load the beams up to the point of fracture, as sketched in Fig. 1. The applied force and the deflection of the beam were monitored during loading, and the fracture strength (maximum stresses corresponding to failure load) was determined with the aid of a finite element analysis. At least seven replicate tests were performed for each set of experimental con-

TABLE I. Weibull fit parameters for data in Fig. 2.

Termination	Time in air (days)	σ_0 (GPa)	ρ
H	3	16.2	7.8
	13	13.8	11.1
	23	11.1	6.9
CH_3	3	18.2	10.6
	13	18.0	12.3
	23	18.7	13.6

ditions. The inset to Fig. 2 shows a scanning electron microscope (SEM) image of a test beam before and after fracture. Importantly, the beam design ensured that the point of maximum stress was at the beam center. As a result, all samples fractured along the primary cleavage planes, $\{111\}$, near the beam center. This controlled fracture process explains the triangular shape of the fractured beam (inset of Fig. 2), which reflects the orientation of $\{111\}$ planes. Further details of the experimental and analysis procedures can be found elsewhere.⁶

The failure of brittle materials is commonly described by a Weibull probability distribution.⁴ Accordingly, the probability of failure P_f at a given stress σ is given by $P_f(\sigma) = 1 - e^{-(\sigma/\sigma_0)^\rho}$, where σ_0 is the characteristic Weibull strength and ρ is the Weibull shape parameter which characterizes the spread in the strengths.

The probabilities of failure of the initially H-terminated beams after 3-, 13-, and 23-day exposures to office air are shown in Fig. 2(a). These data are well fitted by a Weibull probability distribution, as indicated by the (best fit) solid lines. The fit parameters are reported in Table I. Clearly, the H-terminated beams degrade rapidly in air. After 3 weeks, the fracture strength was less than 70% of its initial value. This result is concerning, as all “HF-last” cleans, which are common in industrial processing,¹⁵ produce an initially H-terminated surface.

Methyl-terminated nanobeams display remarkably different behaviors. As shown by the data in Fig. 2(b) and Table I, methyl-terminated beams were 10% stronger than H-terminated beams after 3 days in air. Over the 3-week monitoring period, no systematic decrease in the strength of methyl-terminated beams was observed. This trend is evident in Fig. 3, which shows that H-terminated beams displayed a nearly linear decrease in fracture strength with air exposure. Interestingly, the best-fit lines suggest that the H- and

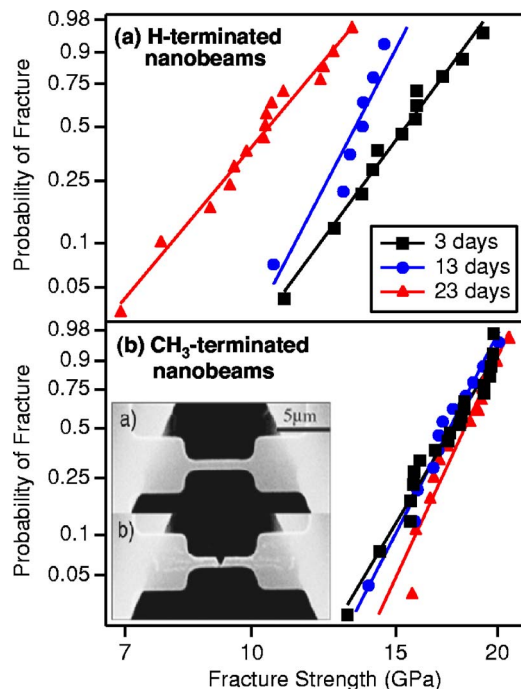


FIG. 2. Weibull fracture probability plots of functionalized Si nanobeams after exposure to air for 3, 13, and 23 days. The lines represent best fits to the Weibull distribution. (a) The strength of H-terminated beams degrades rapidly in air. (b) CH_3 -terminated beams maintain their strength over the course of the experiment. Inset: SEM image of a test beam (a) before and (b) after fracture.

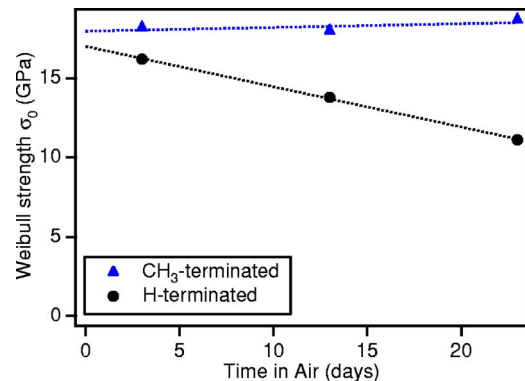


FIG. 3. Change of Weibull fracture strength of H- and CH_3 -terminated nanobeams with exposure to air. The dotted lines represent the best fits.

methyl-terminated surfaces may have similar initial strengths.

Why does 1 ML (monolayer) of molecules have such a dramatic effect on the strength of approximately 1000-atom-thick beams? We hypothesize that this difference is not due to the strength of the monolayer, but rather its ability to protect the silicon from oxidation, as H- and CH₃-terminated Si(111) surfaces differ dramatically in their oxidation resistance. As shown by Neuwald *et al.*,¹¹ H-terminated Si(111) surfaces slowly oxidize in air in a highly heterogeneous process. After a few hours of air exposure, 1–2 nm diameter oxide nuclei develop randomly across the surface. With increasing air exposure, the number, but not the size, of the nuclei increases, and the formation of a full monolayer of oxide requires 8–33 days of air exposure (as measured by scanning tunneling microscopy and x-ray photoemission spectroscopy,^{12,11} respectively). In contrast, methyl-terminated surfaces are much more resistant to oxidation.¹² Additionally, the oxide formed on methyl-terminated surfaces may be qualitatively different from that formed on H-terminated surfaces in terms of both its electronic defect density¹² and its chemical structure.¹⁶

We hypothesize that the silicon oxide nuclei formed on the H-terminated beams act as stress concentrators in much the same way that surface roughness does.⁶ Additionally, silicon oxidation is accompanied by a large volume change, as one atom of oxygen is effectively inserted into every Si–Si bond. As a result, oxides formed at room temperature are highly stressed. For the specific case of room-temperature Si(111) oxidation, a compressive stress of 7180 dyn/cm/ML (7.18 μN/μm/ML) has been measured.¹⁷

Our proposed mechanism is significantly different from that observed on polycrystalline silicon devices during cyclic loading.⁹ In the latter case, failure was attributed to the formation and stress-corrosion-assisted propagation of cracks in the 30-nm-thick oxide layer on the fabricated devices. These cracks were directly imaged using transmission electron microscopy. Even after extended exposures, single crystal sili-

con does not form a thick oxide layer. Instead, oxidation is kinetically limited to a few monolayers.¹⁸

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