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A reaction-layer mechanism for the delayed failure of micron-scale polycrystalline silicon structural films subjected to high-cycle fatigue loading

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Abstract

A study has been made to discern the mechanisms for the delayed failure of 2-μm thick structural films of n^+-type, polycrystalline silicon under high-cycle fatigue loading conditions. Such polycrystalline silicon films are used in small-scale structural applications including microelectromechanical systems (MEMS) and are known to display 'metal-like' stress-life (*S/N*) fatigue behavior in room temperature air environments. Previously, fatigue lives in excess of 10^{11} cycles have been observed at high frequency (~40 kHz), fully-reversed stress amplitudes as low as half the fracture strength using a surface micromachined, resonant-loaded, fatigue characterization structure. In this work the accumulation of fatigue-induced oxidation and cracking of the native SiO_2 of the polycrystalline silicon was established using transmission electron and infrared microscopy and correlated with experimentally observed changes in specimen compliance using numerical models. These results were used to establish that the mechanism of the apparent fatigue failure of thin-film silicon involves sequential oxidation and environmentally-assisted crack growth solely within the native SiO_2 layer. This 'reaction-layer fatigue' mechanism is only significant in thin films where the critical crack size for catastrophic failure can be reached by a crack growing within the oxide layer. It is shown that the susceptibility of thin-film silicon to such failures can be suppressed by the use of alkene-based monolayer coatings that prevent the formation of the native oxide.

Keywords: Silicon; Fatigue; Thin films; MEMS; Self-assembled monolayer coatings

1. Introduction

The promise of revolutionary commercial products at small dimensions has fueled the rapid development of microelectromechanical systems (MEMS) and the enabling technologies of surface micromachining. Silicon-based structural films have emerged as the dominant material system for MEMS because the micromachining technologies for silicon are readily adapted from the microelectronics industry, and are compatible with fabrication strategies for the integrated circuits necessary for actuation and control of the systems.

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However, the long-term durability of these microsystems may be compromised by the susceptibility of thin-film silicon to delayed failure during cyclic loading conditions in ambient air [1–8].

Cyclic fatigue is the most commonly encountered mode of failure in structural materials, occurring in both ductile (metallic) and brittle (ceramic) solids (although the mechanisms are quite different) [9]. The mechanistic understanding of fatigue together with the use of damage/fracture mechanics to describe its effect at continuum dimensions has allowed for the reliable design and operation of innumerable macro-scale structures, such as aircraft airframes and engines. At the micro-scale, the fatigue of ductile materials is attributed to cyclic plasticity involving dislocation motion that causes alternating blunting and resharpening of a pre-existing crack tip as it advances [10]. In contrast, brittle materials invariably lack dislocation mobility at ambient temperatures, such that fatigue occurs by cycle-dependent degradation of the (extrinsic) toughness of the material in the wake of the crack tip that developed from preexisting material inhomogeneities [11]. Prior to this work, the relevance of these fatigue mechanisms to silicon films had yet to be established.

Silicon is generally regarded as a prototypical brittle material; dislocation activity is generally not observed at low homologous temperatures (below ~500 °C) and there is little evidence of extrinsic toughening, such as grain bridging or microcracking [12]. Moreover, silicon is not susceptible to environmentally-induced cracking (i.e., stress-corrosion cracking) in moist air or water [13–15] at growth rates measurable in bulk specimens. *These observations strongly suggest that silicon should not fatigue at room temperature.* Indeed, there has been no evidence to date that bulk silicon is susceptible to fatigue failure. However, there is substantial evidence that cyclically-stressed, micron-scale, silicon films can fail prematurely under high-cycle fatigue loading [1–8,16].

The observation that silicon thin films can fail under cyclic loading was first reported by Connally and Brown a decade ago [1]. Since then, the present authors and others [2–7] have confirmed that 2 to 20 μm thick single crystal and polycrystalline silicon films can fail in fatigue at stresses as low as half their (single-cycle) fracture strength after more than ~10^{11} cycles. Despite such results, the mechanistic origins of why thin-film silicon should apparently suffer fatigue failure have remained elusive. Early studies highlighted the importance of water vapor and speculated that the mechanism may be associated with static fatigue of the native silica layer [1,7]. Other proposed explanations have involved dislocation activity in compression-loaded silicon (e.g., [17]), stress-induced phase transformations [4], and impurity effects [4], although in no instance has conclusive experimental evidence been presented to support any of these mechanisms. Moreover, until now there has never been any direct observation of fatigue damage in micron-scale silicon, nor indications on how it accumulates.

A recent study by the authors [18], however, provided the initial experimental evidence that the crack initiation and growth processes involved in the apparent fatigue of silicon are confined to the amorphous SiO_2 reaction layer that forms on surfaces upon their exposure to air. In this paper, we present a mechanism for the apparent fatigue of silicon, termed reaction-layer fatigue, on the basis of prior stress-life fatigue data, a compliance technique for monitoring the damage accumulation, and microstructural analysis using high-voltage transmission electron microscopy. Additionally, we suggest a method for suppressing the cyclic fatigue of silicon films through the use of alkene-based monolayer coatings that is validated with stress-life fatigue data.

2. Experimental procedures

The 2-μm thick silicon films were fabricated from the first structural polycrystalline silicon layer on run 18 of the MCNC/Cronos MUMPs™ process. This surface micromachining process utilizes low-pressure chemical vapor deposition (LPCVD) to manufacture n^+-type (resistivity, ρ=1.9 × 10^{-3} Ω·cm) polycrystalline silicon [19]. Wafer curvature measurements showed the film to have a compressive residual stress of about 9 MPa [19]; out-of-plane deformation due to a through-thickness

residual stress gradient could not be detected using white-light interferometry. Secondary ion mass spectroscopy (SIMS), referenced to known standards, was used to quantify the concentration of hydrogen, carbon, oxygen, and phosphorous present.

The elastic properties of polycrystalline silicon thin films approach the average behavior of idealized polycrystalline materials. An average of the Voigt and Reuss bounds for a random, polycrystalline aggregate (Young's modulus, E=163 GPa, Poisson's ratio, ν=0.23 [20]) were used to estimate the elastic behavior of the material. The fracture strength of polycrystalline silicon typically ranges from 3 to 5 GPa depending on loading condition, specimen size, and test technique. The fracture toughness, K_c, is ~1 MPa$\sqrt{m}$ [12,21].

The microstructure of the films was characterized using transmission electron microscopy (TEM). Cross-sectional TEM specimens were prepared from the patterned films using standard laboratory practices [22]. Pairs of patterned chips containing the surface micromachined structures were glued together face-to-face, mechanically thinned, dimpled, and ion milled to the desired electron transparency. Diffraction contrast and high-resolution microscopy of the these specimens was performed using the Berkeley JEOL Atomic Resolution Microscope (ARM) at an operating voltage of 800 kV and a JEOL 3010 TEM operating at 300 kV. Analytical characterization was accomplished using a Philips CM200 Field Emission microscope equipped with a Link Energy Dispersive Spectrometer (EDS) and a Gatan Image Filter for electron energy loss spectroscopy (EELS) and energy filtered imaging (EFTEM). Plan view observations of the grain morphology and oxide structure were accomplished using both the ARM and the Kratos High Voltage Electron Microscope (HVTEM) operating at 0.8–1.0 MeV. Plan view samples were prepared by simply lifting the micromachined structures off of the substrate using a tungsten probe tip and placing them onto 100 mesh clam shell grids. For HVTEM studies, no additional thinning was necessary to image through the entire 2 μm thick samples.

The stress-life (S/N) fatigue behavior of the polycrystalline silicon films was determined using a ~300-μm square, ~2-μm thick, surface micromachined fatigue characterization structure, as described in ref. [5] (Fig. 1). Briefly, the notched cantilever beam specimen (~40-μm long, 19.5-μm wide, with a 13-μm deep, ~1 μm root radius notch) is attached to a large, perforated, plate-shaped mass and is electrostatically forced to resonate. On opposite sides of the resonant mass are interdigitated 'fingers' commonly known as 'comb drives'; one side is for electrostatic actuation, the other provides capacitive sensing of motion. The specimen is attached to an electrical ground, and a sinusoidal voltage (with no direct-current (DC) offset) at half the natural frequency is applied to one comb drive, thereby inducing a resonant response in the plane of the figure. These conditions generate fully reversed, constant amplitude, sinusoidal stresses at the notch, i.e., a load ratio (ratio of minimum to maximum load) of R=−1, that are controlled to better than 1% precision with a resolution of ~5%. Specimens were cycled to failure at resonance (~40 kHz) in ambient air (~25 °C, 30–50% relative humidity) at stress amplitudes ranging from ~2 to 4 GPa using the control scheme described in refs. [4,5].

Specimens were prepared by removing the sacrificial oxide layer in 49% aqueous hydrofluoric acid (HF) for $2^1/_2$ or 3 min, drying at 110 °C in air, and subsequently mounting in ceramic electronic packages for testing [5]. In an attempt to suppress formation of the native oxide and access of moisture to the silicon surface, specific specimens were coated with an alkene-based monolayer of 1-octadecene, $C_{16}H_{33}CH{=}CH_2$, after removal of the sacrificial oxide. The monolayer was then applied to the surface of the silicon in a reactor containing a solution of one part 1-octadecene in nine parts hexadecane [23]. This hydrophobic monolayer bonds directly to the hydrogen-terminated surface atoms of the silicon film created by the exposure to hydrofluoric acid such that no oxide can form; it acts as an effective barrier to both oxygen and water [23].

The experimentally-measured motion of the resonating fatigue characterization structure was used to determine the applied stress amplitude, natural frequency, and to monitor the accumulation of fatigue damage prior to failure. The magnitude

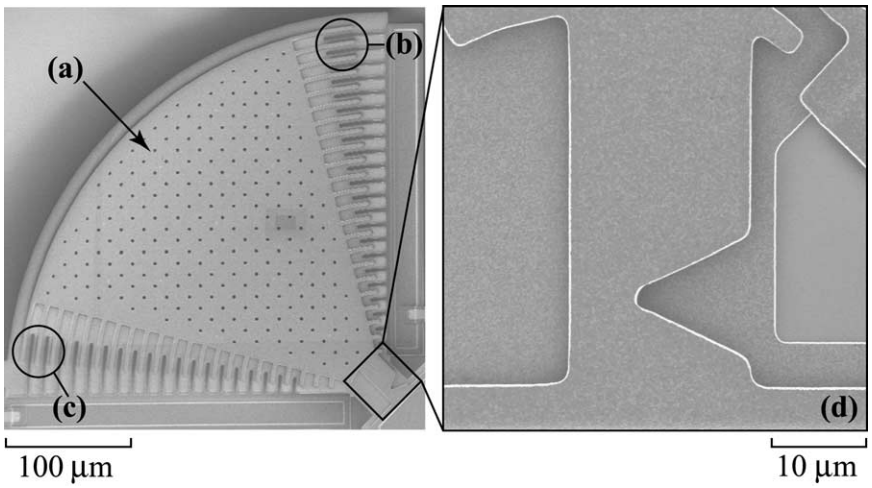

Fig. 1. Scanning electron micrograph of the fatigue life characterization structure and notched cantilever beam specimen used in this investigation. The (a) mass, (b) comb drive actuator, (c) capacitive displacement sensor, and (d) notched cantilever beam specimen (inset) are shown.

of the displacements was carefully calibrated, as detailed in ref. [5]. Finite element models were used to establish the relationship between the displacements and the maximum principal stress at the notch. It was previously demonstrated that measured changes in natural frequency may be attributed to damage accumulation in the specimen [7,24]. Thus, additional numerical models of structures containing cracks were used to determine the relationship between crack length and natural frequency (i.e., compliance) and the stress-intensity factor, K. The models were constructed using a commercial software package (ANSYS v. 5.7); full details are reported in ref. [25]. In the present paper, such methods were used to measure in situ the propagation of nanometer-scale cracks by monitoring the change in natural frequency of the sample. Crack-growth rates were determined using a modified secant method applied over ranges of crack extension of 2 nm with a 50% overlap with the previous calculation window; the average crack-growth rate was calculated based on a linear fit of the experimental data. The maximum stress intensity immediately prior to failure was taken as an estimate of the fracture toughness of the material.

After testing, the crack path and fracture surfaces of the specimens were characterized using scanning electron microscopy (SEM) and HVTEM. To avoid corrupting any microstructural or fractographic features, neither SEM conductive coatings nor TEM thinning processes were used.

To evaluate the possibility of specimen heating due to the large amplitude, high frequency stresses and the induced electrical current used to measure motion of the structure, high-resolution infrared (IR) imaging of the fatigue characterization structure was performed in order to map temperature changes during testing. Thermal images were generated by plotting the difference between IR images (12-bit resolution) collected while the structure was resonated at a constant stress amplitude, and at rest. Individual IR images were collected by averaging over 2 sec at an acquisition rate of 50 Hz. Temperature changes as small as 20 mK could be detected with a spatial resolution of better than 8 μm.

3. Results

3.1. Microstructural analysis

The microstructural analysis of the 2-μm thick polycrystalline silicon film, shown in the cross-sectional TEM image of Fig. 2a, revealed an equiaxed

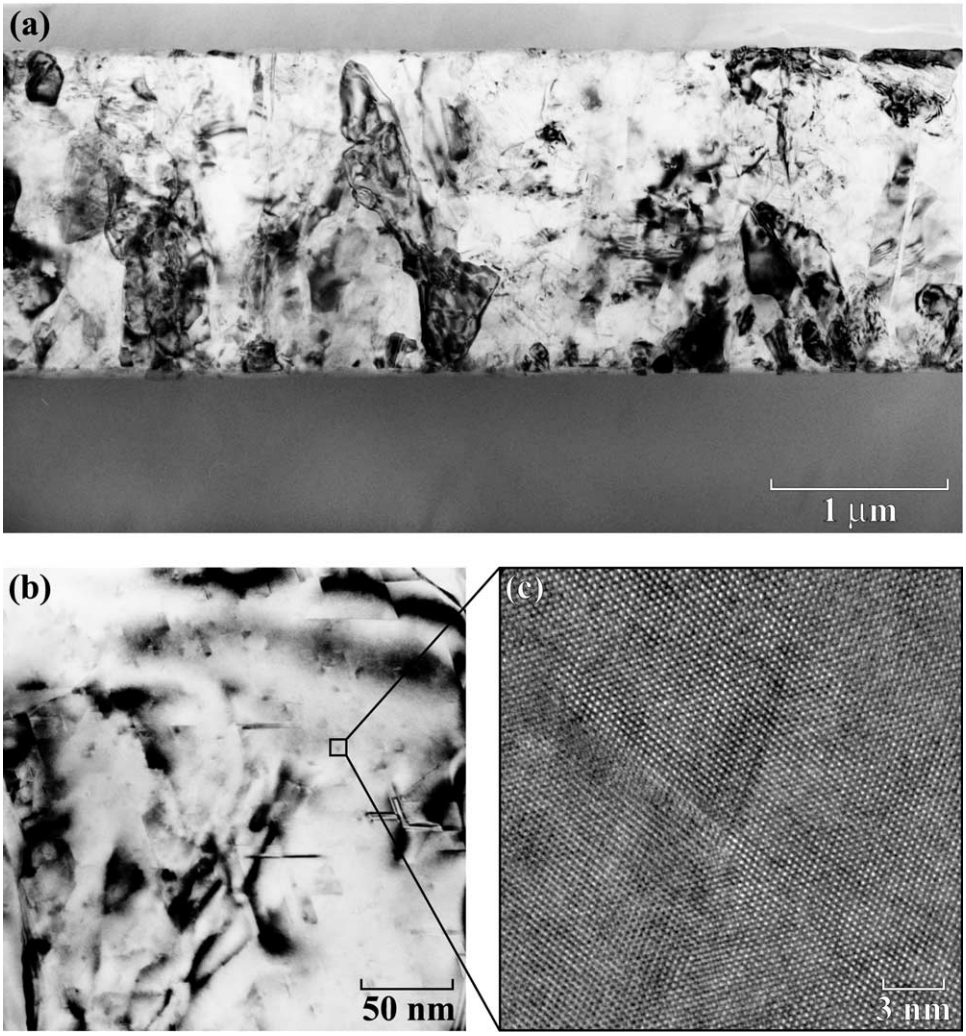

Fig. 2. (a) Microstructure of the polycrystalline silicon structural film showing a typical cross-sectional TEM image of the through-thickness grain morphology. TEM images of defect types, showing: (b) 220 bright field image of the interior of the grain to highlight microtwins, stacking faults, and Lomer–Cottrell dislocation locks, (c) high resolution image of a Lomer–Cottrell lock (inset).

grain morphology (grain size of ~100 nm), with no evidence of strong texture (from corresponding selected-area diffraction). No variations in microstructure were apparent near features such as the root of the notch, as expected given the deposition and etching strategy used in the surface micromachining process. The lack of a textured columnar structure, which is routinely observed in thin-film silicon [26], may be a result of the 900°C annealing used to dope the silicon with phosphorous and relax the residual stresses associated with growth of the film.

SIMS analysis of the contaminants present revealed the interior of the film to contain $\sim 2 \times 10^{18}$ atoms/cm^3 hydrogen, 1×10^{18} atoms/cm^3 oxygen, and 6×10^{17} atoms/cm^3 carbon [5], levels which are consistent with the processing history of the film. In addition, 1×10^{19} atoms/cm^3 of phosphorous were detected from the phosphosilicate glass used to dope the film. The films were found

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