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Understanding pressure-induced phase-transformation behavior in silicon through \textit{in situ} electrical probing under cyclic loading conditions

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Cyclic indentation of crystalline silicon exhibits interesting pressure-induced phase-transformation behavior whereby sequential changes in the phase composition ultimately lead to a catastrophic (“pop-out”) event during subsequent cycles and complete transformation to high pressure Si-III and Si-XII phases. This study combines \textit{in situ} electrical measurements with cyclic loading to monitor such phase-transformation behavior. We find that, if a pop-out is not observed on the unloading curve, the end phase is predominantly amorphous but a small and increasing volume of Si-III/Si-XII results with each cycle. At a critical Si-III/Si-XII volume, pop-out can occur on a subsequent cycle, whereafter Si-III/Si-XII dominates the indent volume. © 2009 American Institute of Physics.

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I. INTRODUCTION

Indentation-induced phase transformations in crystalline silicon (c-Si) have attracted considerable technological interest. During indentation loading, the diamond cubic Si-I undergoes a transformation to a metallic $\beta$-Sn phase (Si-II) at a pressure of $\sim11$ GPa.\textsuperscript{1–3} This Si-II phase is unstable at pressures below $\sim8$ GPa and undergoes further phase transformations during unloading. For slow unloading a phase transformation to a mixture of the polycrystalline high pressure Si-XII (R8) and Si-III (BC8) phases\textsuperscript{4,5} is favored, whereas for fast unloading an amorphous phase (a-Si) can result as the dominant end phase.\textsuperscript{6–10} A correlation has been confirmed between the occurrence of a sudden depth decrease or “pop-out” during unloading and the formation of Si-III/Si-XII material.\textsuperscript{6,8} If no pop-out event occurs during unloading, the final structure of the unloaded material has been found to be predominantly amorphous.\textsuperscript{6–8,10} However, a recent study indicated that trace volumes of these high pressure phases within a-Si could be found following rapid unloading for which no pop-out events occurred.\textsuperscript{11} Indeed, it has been suggested that the Si-II to Si-XII/Si-III transformation is a probabilistic event\textsuperscript{6,8} that proceeds by a nucleation and growth process during the unloading cycle. Nevertheless, the reason for the sudden transformation of a large volume of Si-II to Si-III/Si-XII, as characterized by the observed pop-out event, is not clear.

Some previous efforts to further understand the phase-transformation behavior have employed cyclic loading experiments.\textsuperscript{12–14} The load-displacement response during each cycle showed a similar hysteresis (presumably a similar pressure-induced transformation sequence) until a pop-out event occurs, after which the hysteresis disappears and the deformation becomes completely elastic.\textsuperscript{12–14} The current authors have previously shown that \textit{in situ} electrical measurements provide high sensitivity for monitoring the nanoindentation-induced phase transformations in Si.\textsuperscript{15,16} In this study, we combine \textit{in situ} electrical measurements with cyclic loading to monitor the formation and subsequent evolution of Si-III/Si-XII. Cross-sectional transmission electron microscopy (XTEM) of the residual indents is used to help understand the complex phase-transformation behavior in silicon under cyclic loading conditions.

II. MATERIALS AND METHODS

A crystalline silicon sample was cleaved from a Czochralski-grown Si(100) wafer (boron-doped to a resistivity of 10 to 20 $\Omega$ cm) for cyclic loading experiments using a Triboindenter® (Hysitron, Inc., Minneapolis, MN, USA) fitted with an electrically conductive diamond Berkovich tip. Immediately before mounting in the indenter, the cleaved sample was cleaned in organic solvents and placed in dilute hydrofluoric acid ($10.1$ H$_2$O to $48\%$ HF) for $\sim30$ s to strip the native oxide. The load on the sample was cyclically varied in a saw-tooth pattern between $0.1$ mN and $10$ mN (9 cycles) using constant load and unload rates of $10$ mN/s and $5$ mN/s, respectively. This load history results in a finite probability of less than one for the occurrence of a pop-out event. A constant voltage of $+1$ V was applied to the stage to which the sample was electrically connected, and the resulting current flow through the sample/indenter tip was monitored during the cyclic indentation. Fifty indentation experiments were performed on the sample. The detailed description of the \textit{in situ} electrical measurements can be found elsewhere.\textsuperscript{15}

III. RESULTS AND DISCUSSION

The load-displacement curves of a typical cyclic indentation experiment, denoted here by experiment A, are shown in Fig. 1(i). Upon indentation loading by the diamond Berkovich tip in the first cycle, the Si-I beneath the indenter transforms to Si-II.\textsuperscript{3} During this process, a small fraction of the Si-II may flow out from under the indenter to the free surface

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to instantaneously transform to \(a\)-Si at the contact edge due to the rapid pressure drop experienced in the extruded material.\(^3\) On unloading, the Si-II beneath the indenter further transforms to an amorphous phase in the absence of pop-out.\(^6\)–\(^8\),\(^10\) The metallic-to-amorphous transition is thought to commence when the rate of the depth recovery becomes notably faster during unloading (in this case, at about 1/4 of the peak load)\(^6\) and comes to completion at full unloading. After the first load/unload cycle, reload/unload hysteresis\(^5\) is seen repeatedly during the subsequent four reload/unload cycles. In these cases, the residual \(a\)-Si end phase is transformed to Si-II on loading and predominantly back to \(a\)-Si again on fast unloading.

A pop-out is observed in cycle 6. After the pop-out event, the load-displacement hysteresis decreases dramatically and progressively with increasing cycle number until the response becomes fully elastic. This is because the mixed Si-III/Si-XII phases, once formed in the indent volume, do not retransform to Si-II up to the maximum load due to its high mechanical stability or hardness, as established in a separate study.\(^11\) This behavior was observed for all tests for which a pop-out event occurred during the cyclic loading sequence. After pop-out, the majority of the phase-transformed zone is composed of Si-III/Si-XII but there has been some evidence (from TEM studies) that residual amounts of \(a\)-Si (<5%) are still present within the zone.\(^10\) Thus the small amount of hysteresis observed for 1–2 cycles after the pop-out event is most likely residual \(a\)-Si within the zone retransforming to Si-II during reloading until this has been fully transformed to Si-III/Si-XII on unloading. The load-displacement area is thus an indicator of the amount of \(a\)-Si remaining in the indent volume at the start of a particular cycle.

Figure 1(ii) shows the area of the load-displacement hysteresis of each reload/unload cycle plotted against the cycle number. The progressive area decrease with increasing cycle number after the pop-out event is clearly evident. More interestingly, the hysteresis area has decreased with increasing cycle number prior to pop-out, thus suggesting a gradual decrease in the \(a\)-Si end phase volume during these pre pop-out cycles. We suggest that small amounts of the \(a\)-Si in the indent volume, through transformation to Si-II in the fully reloaded condition, are being sequentially replaced by small volumes of the mechanically stable Si-III/Si-XII phases during the unloading of each cycle before the occurrence of the pop-out event. This hypothesis will be tested with respect to other observations made below.

Figure 2 shows the indenter displacements at minimum loads as a function of cycle number for experiment A and another experiment without pop-out, denoted here by experiment B. From the figure, the indenter displacement at the minimum load increased gradually with increasing cycle number until the occurrence of pop-out, after which it jumped to a much greater value (see experiment A) before converging to a higher value with increasing cycle number (not shown). This finding is consistent with our hypothesis since the increased volume ratio of the mixed Si-III/Si-XII phases to the less dense \(a\)-Si would be expected to cause the residual indent volume to become denser, hence increasing the indent depth at the minimum load.

Figure 3 shows the through-tip current versus time measurements. It is clear that the peak current (at the maximum load) decreases with increasing cycle number even before the pop-out event. This trend could be attributed to two effects: (1) the electrical contact area between the tip and sample decreases with each cycle; and/or (2) the material in contact with the tip decreases in conductivity with increasing cycle. On the basis that the upper portion of the unloading curve path remained basically unchanged during the sequential cycles until the occurrence of pop-out (Fig. 1), the contact

![Figure 1](image1.png)

**FIG. 1.** (i) Load-displacement curves of a typical cyclic indentation experiment (exp. A) with the reload/unload curves of the \(n\)th cycle shifted rightward by 50 \((n-1)\) nm to enable detailed inspection of individual cycles. The open circle indicates the onset of pop-out. (ii) Load-displacement hysteresis area vs cycle number of exp. A with the dashed vertical line indicating the onset of pop-out.

![Figure 2](image2.png)

**FIG. 2.** Indenter displacements at the minimum load of the \(n\)th cycle relative to those of the first cycle plotted as a function of cycle number for exp. A and exp. B.

![Figure 3](image3.png)

**FIG. 3.** Electrical current vs time of exp. A, where the dashed vertical line indicates the onset of pop-out and the closed circles show the data points corresponding to the respective load peaks \((F=F_{\text{max}})\).
stiffness and hence the sample/tip contact area at the peak load would have been essentially constant during these cycles without pop-out. Therefore, any changes in contact area would be minimal and would not account for the 25% (4–3 μA) decrease in peak current from the first cycle to the one immediately before pop-out. Thus, the mean electrical conductivity of the indent volume (i.e., the current at the maximum load divided by the same sample/tip contact area) in the fully reloaded condition must have decreased with increasing cycle number. The mixed Si-III/Si-XII phases are expected to be electrically more insulating than the metallic Si-II phase, as it has been reported that Si-III is a semimetal and Si-XII is a semimetal or semiconductor with a small, indirect band gap. The increased volume ratio of the Si-III/Si-XII to the electrically more conductive Si-II, as per our hypothesis, would cause the overall conductivity of the indent volume in the reloaded condition to decrease, and hence the observed conductivity trend is also consistent with our hypothesis. After pop-out, as expected, the conductivity drops further to a value that presumably reflects the conductivity of the mixed Si-III/Si-XII phases.

Figure 4 shows the bright-field XTEM of a residual indent that had undergone no pop-out throughout the cyclic loading. In fact, discrete dark regions can be clearly identified in the amorphous indent with the local diffraction pattern (see the inset of Fig. 4) indicating the presence of Si-III or/and Si-XII.

We have shown that substantial changes in the mechanical response of the silicon to cyclic loading are observed after a pop-out event where the phase-transformed zone is composed mostly of mixed Si-III/XII phases. Although only slight changes in the mechanical response are observed sequentially prior to the pop-out event, electrical measurements show substantial changes in conductivity of the silicon that can be correlated with these small changes in the load/unload curves. Furthermore, the XTEM study has shown the presence of Si-III or/and Si-XII in the cyclically loaded indent prior to pop-out. These data thus support the nucleation and growth model for the formation of Si-III/XII during unloading. Small volumes of Si-II appear to be transforming to Si-XII and Si-III without any pop-out and the seed volume of Si-III/Si-XII phases increases during each subsequent load/unload cycle, thus enhancing the probability for pop-out. Indeed, it would appear that, when the seed volume reaches a critical value, a pop-out (sudden transformation of the remaining a-Si to Si-III/Si-XII) has a high probability of occurring during unloading on the next cycle.

IV. CONCLUSIONS

In summary, we have shown that both the mechanical behavior (load-displacement hysteresis) and the electrical conductivity change during cyclic loading prior to pop-out (i.e., in cases where the residual end phase is predominantly a-Si). This suggests a gradual decrease in the a-Si volume during the initial cycles prior to pop-out and a small increasing transformation to Si-III/Si-XII. TEM data supports this proposal and has identified such small volumes of Si-III/Si-XII prior to pop-out. As the volume of Si-III/Si-XII phases increases with increasing cycle number, the probability of sudden transformation of remaining a-Si to Si-III/Si-XII during subsequent cycles increases leading to a pop-out. Following pop-out, when the Si-III and Si-XII phases dominate the residual indent volume, subsequent cycles quickly convert any remaining a-Si to these high pressure crystalline phases leading to a totally elastic load-unload response.

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