**Indentation Unloading Phase Transformations in Silicon: A New Perspective**

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**Introduction**

The load-displacement curve shows abnormalities during the unloading of indentations in silicon. These abnormalities are linked to phase transformations [1]. Applying dynamic nanoindentation to the unloading segment should, in theory, allow the evaluation of the contact pressures at which such transformations occur. However, these methods are typically designed to only measure mechanical properties during the loading process [2]. The nanoindentation protocol presented in this work aims to make the transformation pressures directly accessible [3]. Furthermore, constant-load holding segments were added during unloading. The impact of such segments on the phase transformations was assessed with Raman spectroscopy.

**Symbols/Abbreviations**

\[ P \] load
\[ \varepsilon \] reduced elastic modulus
\[ H \] contact depth
\[ S \] dynamic contact stiffness
\[ A \] contact area
\[ E \] area function fitting constants
\[ H \] hardness
\[ p \] mean contact pressure

**Methodology**

\[ A(h_0) = C_0 h_0^2 + C_1 h_0 + C_2 h_0^2 + \ldots \]

\[ A = \left( \frac{\sqrt{\pi} \varepsilon}{2} \right)^2 = \frac{\pi \varepsilon^2}{4E_r} \]

\[ H = \frac{p}{A} \]

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Schematic of the usage of the reduced elastic modulus in the nanoindentation protocol used to measure the transformation pressures [3]. The area function of the tip holds during loading, and together with the CSM signal, the mechanical properties can be calculated with the Oliver-Pharr formulas [4]. However, during unloading, the area function loses its validity [2]. The approach is now to determine an average reduced elastic modulus during loading. This value is then used to calculate a contact area during unloading. Subsequently, an "unloading hardness" (the mean contact pressure) can be calculated [3].

**Summary**

- Under the assumption of a constant reduced modulus, CSM can be used to calculate the contact pressure during unloading uninterrupted.
- Continuous unloading experiments show that the transformation pressures are lowered for faster unloading rates.
- Transformations also happen purely time-dependent if the contact pressure (and thus the driving force) is kept constant.
- During this holding process, a continuous amorphous transformation occurs.
- High transformation pressures favor the formation of metastable, crystalline silicon, whereas low transformation pressures lead to amorphous silicon.

**Interrupting Unloading by Constant Load Holds + Raman Analysis**

Pressure traces while holding: jumps of the contact pressure to the "upper band" indicate a constant load pop-out. Especially for the 15 mN hold, a continuous increase in pressure can be seen for samples that have not exhibited a pop-out yet.

**Continuous Unloading**

The burst-like pop-out is associated with the generation of metastable, crystalline silicon phases, whereas the continuous elbow leads to amorphous silicon. Transformations to a mix of crystalline and amorphous silicon also lead to a mixed load-displacement response [1].

The lower line shows representative contact pressure profiles acquired with the new protocol.

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