



Understanding phase-transformation-induced pop-out behaviour in Si under cyclic loading and elevated temperature indentation conditions

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Abstract – Phase transformations can occur in silicon under indentation. On unloading, a ‘pop-out’ usually occurs when the crystalline phases Si-III and Si-XII are formed but no ‘pop-out’ occurs when the end phase is amorphous silicon. Cyclic loading studies have shown that even when no ‘pop-out’ is observed, there is a gradual formation of a small volume of Si-III/Si-XII phases within amorphous silicon with increasing cycle, leading eventually to a catastrophic formation of Si-III/Si-XII, and a pop-out event, during a subsequent cycle. As indentation temperature increases, the entire volume under the indent can transform to these phases without a ‘pop-out’.

Under indentation both crystalline silicon (Si-I) and amorphous silicon (a-Si) can undergo phase transformation to a denser metallic phase, so-called Si-II. On unloading, Si-II further transforms to either a mixture of additional high pressure phases (Si-III and Si-XII) or to a-Si, depending on the unloading conditions [1]. These phase transformations can cause discontinuities in the load versus penetration depth curves, including marked ‘pop-in’ and ‘pop-out’ behaviour. The occurrence of a clear ‘pop-out’ is usually indicative of the nucleation of mixed Si-III/Si-XII phases during unloading. In this study we investigate the ‘pop-out’ behaviour in some detail during cyclic loading conditions, and also as a function of indentation temperature (up to about 150°C), to provide further insight into the transformation behaviour on unloading. In addition, the effect of a significant oxygen content within silicon on the ‘pop-out’ and transformation behaviour is examined. We correlate cyclic loading (load versus penetration curves) with in-situ electrical measurements made using a conducting diamond indenter tip. Atomic force microscopy (AFM), Raman microspectroscopy and transmission electron microscopy (TEM) are used to characterize the indent morphology, phase composition and microstructure following indentation.

Cyclic loading carried out under conditions where the a-Si end phase is more likely to occur shows interesting hysteretic behaviour, whereby the a-Si undergoes further transformation on subsequent loading and transformation back to a-Si again on unloading. When a ‘pop-out’ occurs, indicating that Si-III/Si-XII formation has occurred, the behaviour during subsequent cycles rapidly becomes elastic, indicating that the latter crystalline phases do not re-transform to Si-II on re-loading. We introduce the concept of an effective indenter shape on re-indentation to show that Si-XII/Si-III has a greater critical hydrostatic pressure for re-transformation to Si-II than that of the diamond cubic Si-I. The electrical measurements are particularly sensitive to very small volumes of Si-III/Si-XII formation during unloading, even before pop-out has occurred. Cyclic loading causes an increasing but small volume of these mixed crystalline phases until pop-out occurs. Following ‘pop-out’, when Si-III/Si-XII dominates the indent volume, subsequent cycles quickly convert the remaining a-Si to Si-III/Si-XII.

For both crystalline Si-I and a-Si substrates, the probability of pop-out is initially enhanced with increasing indentation temperature but drops to zero for temperatures above 100°C. For indentation in crystalline Si-I, Raman measurements of the residual indents show that Si-III and Si-XII are only present when a pop-out occurs. Interestingly, for a-Si, these crystalline phases are always formed for temperatures greater than 75 °C, even in the absence of a pop-out event. These data indicate that elevated indentation temperatures can enhance nucleation of the Si-III/Si-XII phases to such an extent that a sudden pop-out does not occur. In the case of oxygen present in the starting Si substrates, a pop-out and the formation of crystalline Si-III/Si-XII phases are substantially suppressed. These results are discussed in terms of the probability of nucleating crystalline phases from Si-II during pressure release.

Reference

[1] J. E. Bradby, J. S. Williams, J. Wong-Leung, M. V. Swain and P. Munroe, *J. Materials Research*, **16**, 1500 (2001).