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Deformation mechanisms at pop-out in monocrystalline silicon under nanoindentation

L. Chang, L.C. Zhang *

School of Aerospace, Mechanical and Mechatronic Engineering, The University of Sydney, Sydney, NSW 2006, Australia

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Abstract

This paper clarifies a common misunderstanding of the phase transformation in monocrystalline silicon under nanoindentation, namely that a pop-out represents the onset of a phase transition. Through a detailed investigation into the indentation-induced deformation of monocrystalline silicon using a Berkovich indenter, it was found that a pop-out does not correspond to the onset of the transformation. The critical contact pressure for initiating phase transformation during unloading is independent of the maximum indentation load or of the unloading rate. The size of a pop-out depends on the time it takes place (earlier and later), and its location alters the proportion of the transferred phases (amorphous and crystalline phases) after complete unloading. A lower unloading rate or a higher maximum indentation load promotes the occurrence of a pop-out.

Keywords: Silicon; Nanoindentation; Pop-out; Phase transformation

1. Introduction

Over the past decade, phase transformations in monocrystalline silicon induced by micro/nanoindentation have been extensively studied both experimentally and theoretically [1–5]. A characteristic event, known as a pop-out, observed in the load–displacement curve of an indentation during unloading has attracted considerable interest [6–10]. It has been commonly supposed that the pop-out signals the onset of the phase transformation from Si-II to Si-III and/or Si-XII [7–10]. This belief was mainly due to the deduction from an experiment that silicon in a diamond anvil cell experienced a phase transformation from Si-II to less dense phases, Si-III and/or Si-XII [11], and that the pop-out phenomenon could simply be attributed to a sudden volume expansion of the material beneath the indentation zone during unloading. In making such a deduction, unfortunately, the difference in stresses that the silicon experiences in the diamond anvil cell (under a hydrostatic stress) and in an indentation (under a combination of hydrostatic and deviatoric stresses) has been entirely overlooked.

On the other hand, some studies reported that the average contact pressure at a pop-out ranged from 3.5 to 12 GPa [5,9], which then led to the conclusion that during the unloading of an indentation cycle the Si-II phase must have remained stable within this pressure range. Nevertheless, some others argued that because the location of the pop-outs in the unloading curves was relatively stable, the critical contact pressure for the phase transformation from Si-II to Si-III/Si-XII should be a constant [10]. These controversial conclusions have generated confusions in understanding the pop-out mechanism.

It was reported experimentally that the occurrence of a pop-out was highly dependent on the maximum indentation load and the loading/unloading rate [5,7,9,10]. This seems to imply that the phase changes involved in a pop-out are determined by the loading/unloading history, rather than isolated events during the unloading process.

* Corresponding author. Tel.: +61 2 9351 2835; fax: +61 2 9351 3760.
E-mail address: l.zhang@usyd.edu.au (L.C. Zhang).

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However, a scientific understanding of the indentation-induced deformation behavior of silicon is unavailable. Little work has been done to systematically analyze the evolution process of phase changes in silicon.

This paper will investigate in detail the deformation behavior of silicon under nanoindentation to try to clarify the confusion and misunderstanding in relation to the pop-out phenomenon.

2. Materials and methods

The nanoindentation tests were conducted on (1 0 0) silicon surfaces with a diamond Berkovich indenter. A nano-triboindenter (Hysitron Inc., USA) was used in an engineered enclosure which isolated the instrument from a wide range of noise frequencies and allowed it to operate in a stable environment. Before a test, the surface of the silicon specimen was precisely polished to guarantee that the specimen surface was sufficiently smooth (Ra < 2 nm), and that the subsurface structure of the specimen was damage-free (examined by cross-sectional transmission electron microscopy).

To characterize the deformation behaviour of silicon under different loading conditions, the nanoindentation tests were conducted with two different peak loads $F_{max} = 10$ and 30 mN in combination with various loading/unloading rates of 0.5, 1 and 5 mN s^{-1}. For all the tests, the holding time at the F_{max} was 30 s to minimize the time-dependent plastic effect. For each testing condition, at least 16 tests were repeated.

3. Results and discussion

3.1. Variation of the unloading curves

Figs. 1 and 2 show the load–displacement (indentation depth) curves under various loading conditions. For comparison, each figure contains the curves of at least 10 repeated tests under nominally the same loading condition. It is clear that the deformation behavior of silicon is purely elastic at the initial unloading, because the unloading curve in this stage perfectly follows the power-law relation [12–14]:

$$F = \alpha(h - h_r)^m \tag{1}$$

where P is the load, h is the depth, h_r is the residual depth after the complete unloading, and α and m are material constants. Such deformation characteristics mean that the higher-pressure phases developed in the loading process remain stable at the initial unloading when the indentation pressure is high [6,7], leading to an overall elastic response of the material governed by the mechanical property of the Si-I phase.

After the elastic unloading stage, the displacement curve shows elastic/plastic behavior, indicated by a bifurcation from the elastic unloading (Figs. 1 and 2). A pop-out can sometimes happen after the bifurcation. It has been well established that inelastic deformation in silicon under nanoindentations is mainly caused by phase transformations and that the contributions from other deformation mechanisms, e.g. dislocations, are minimal even when F_{max} is much greater than the values we used in this study [4]. Thus the bifurcation from the elastic curve shown in Figs. 1 and 2 indicates that a phase transformation takes place. It is clear from the repeated tests under nominally the same indentation condition that pop-outs do not appear at the same location of the unloading curve, but the bifurcation from the elastic curve, and hence the onset of the phase transition, takes place at the same location.

3.2. Evolution process of the phase transformation

3.2.1. Contact pressure at the onset of the phase transformation

According to the observation and analysis above, the onset of the phase transition takes place approximately at the bifurcation point from the elastic to plastic. Since this point is still on the elastic curve, the average contact pressure at the point, p_a, can be calculated using the elastic theory of contact mechanics, i.e.:

$$p_a = \frac{F}{A(h_c)} \tag{2}$$

in which $A(h_c)$ is the area function at contact depth h_c determined by:

$$A(h_c) = 24h_c^2 + 1412h_c \tag{3}$$

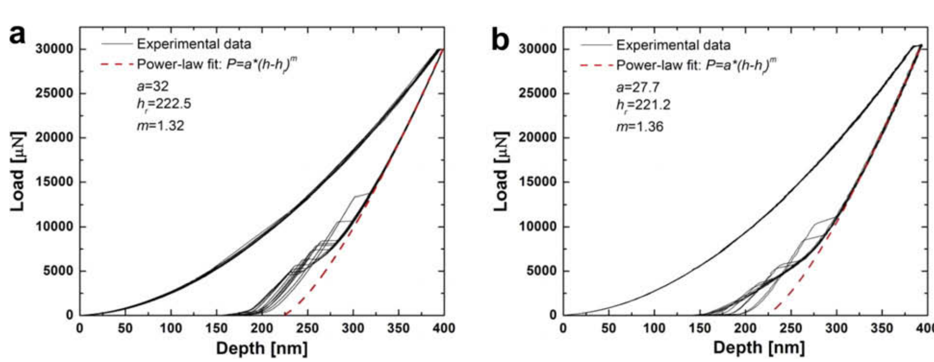

Fig. 1. Variations in load–depth curves with different loading/unloading rates: (a) 0.5 mN s^{-1} and (b) 5 mN s^{-1}. The maximum load $F_{max} = 30$ mN.

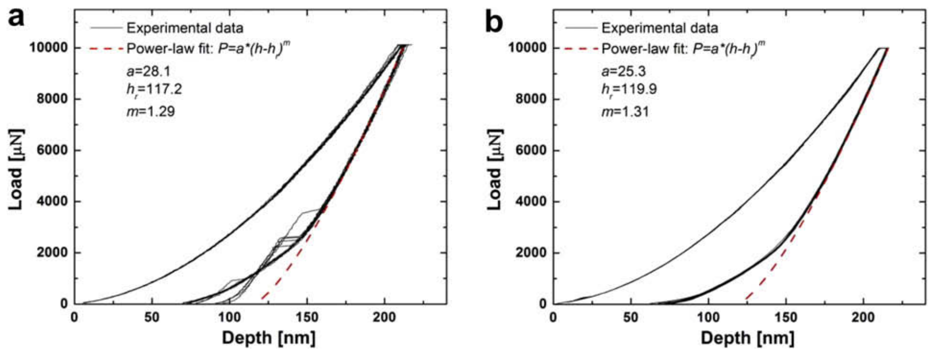

Fig. 2. Variations in load–depth curves with different loading/unloading rates: (a) 0.5 mN s^{-1} and (b) 5 mN s^{-1}. The maximum load $F_{max} = 10$ mN.

according to Chang and Zhang [15], and the contact depth can be determined by:

$$h_c = h_f - h_s \tag{4}$$

in which h_f is the full indentation depth and h_s is the elastic deflection of the material at the perimeter of the indentation area specified by [12,16]:

$$h_s = h_{s\_max}\sqrt{\frac{F}{F_{max}}} \tag{5}$$

where h_{s_max} is the elastic deflection at the maximum load F_{max} [13], i.e.:

$$h_{s\_max} = \varepsilon\frac{F_{max}}{S} \tag{6}$$

in which ε is a geometrical constant (=0.75 for the indenter used in the present study) and S is the stiffness of the sample at the maximum load F_{max}. Then, with Eqs. (2)–(6), the average contact pressures at the onset of the phase transformation (i.e. at the bifurcation point mentioned previously), p_a, can be obtained as 7.6, 7.8 and 7.7 GPa at the unloading rates of 0.5, 1 and 5 mN s^{-1}, respectively, when $F_{max} = 30$ mN (Fig. 1). Similarly, when $F_{max} = 10$ mN, we found that the p_a values corresponding to the unloading rates of 0.5, 1 and 5 mN s^{-1} are 7.7, 7.7 and 7.6 GPa, respectively (Fig. 2). These results show clearly that the average contact pressure at the onset of the phase transformation remains mostly a constant, and its value is consistent with the critical pressure for the phase transition from Si-II to Si-III/Si-XII and/or to amorphous phases (7.4 to 8.5 GPa [4,11,17]). Hence, it is reasonable to conclude that the onset of the phase transformation during unloading occurs once the contact pressure reaches the critical value, and that this is independent of the peak indentation load, F_{max}, or of the loading/unloading rate. These clarify the confusion in the literatures as outlined in Section 1.

3.2.2. Subsequent phase changes

After the onset of the phase transformation, the material's elastic/plastic response reflected by the variation of an unloading curve could be either an elbow or a pop-out (Figs. 1 and 2). We noticed that the curves with elbows produced by nominally the same indentation condition overlap extremely well. However, the process becomes more complicated when pop-outs appear. As shown in Fig. 3, after the onset of plasticity but before the pop-out, the unloading curves bend like elbows and overlap nicely. After the pop-outs, the unloading curves no longer overlap, but vary in parallel to each other (Figs. 1 and 2). Nevertheless, it is interesting to note that they can be described precisely again by the power-law relation in Eq. (1). In other words, the unloading process after a pop-out becomes purely elastic once again (Fig. 3).

Based on the above observations, we can construct a deformation diagram as illustrated in Fig. 4, where Fig. 4a shows a typical unloading curve with a pop-out and Fig. 4b–e demonstrate the changes in microstructures/phases of silicon in the deformation zone corresponding to the various stages denoted in Fig. 4a. As shown in the figures, the silicon behaves purely elastically from (b) to (c) with an unchanged phase structure. With the continuous release of the load to a critical value, F_{cri} (Fig. 4a), and hence a critical contact pressure, a phase transformation commences, initiating at the interface between Si-II and Si-I at which the critical pressure is first reached. The transformation then expands gradually towards the centre

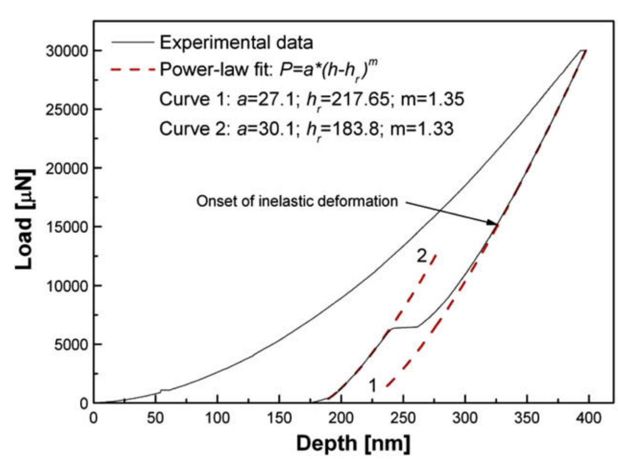

Fig. 3. The power-law fit with the unloading curves for a typical indentation cycle with a pop-out under the maximum load of 30 mN and a loading/unloading rate of 1 mN s^{-1}.

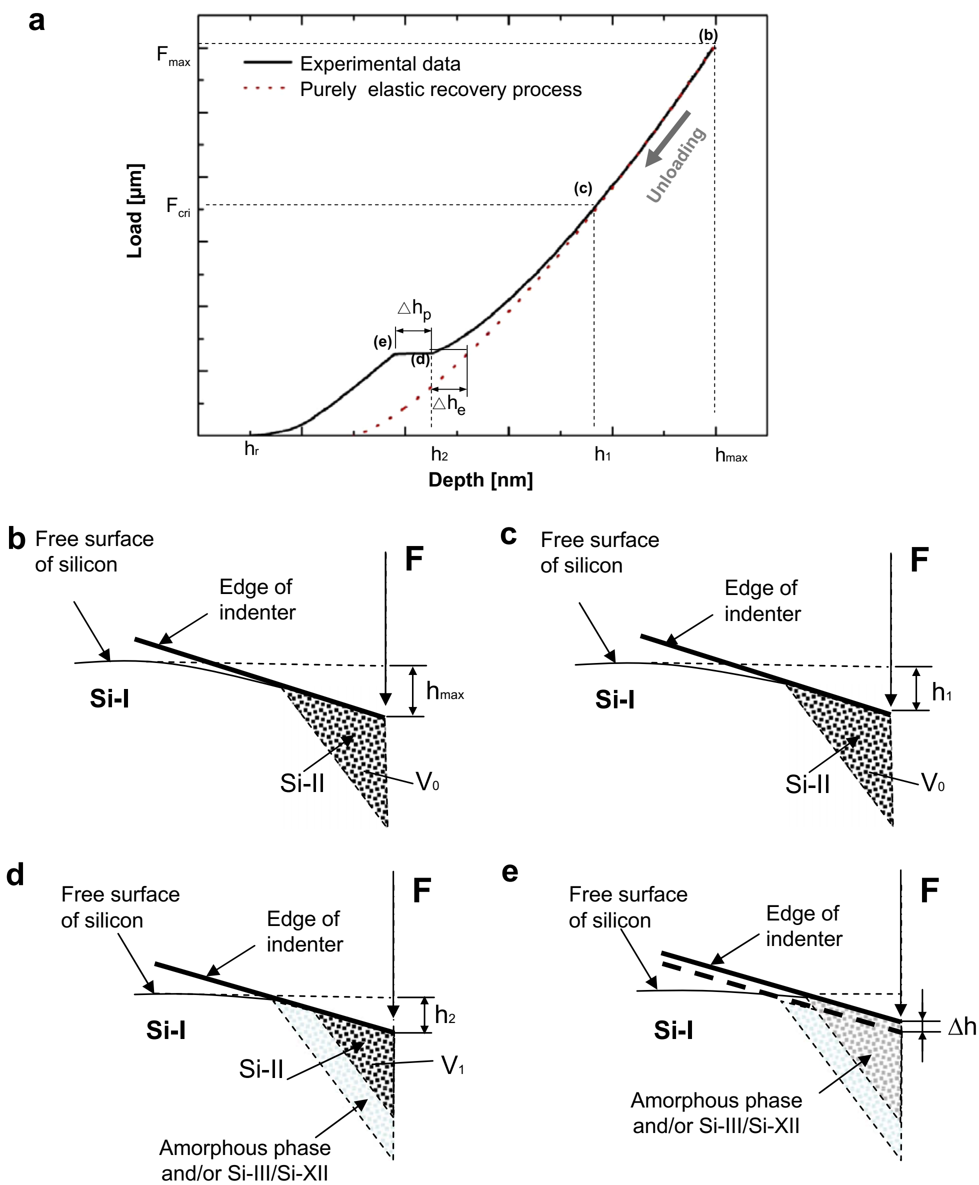

Fig. 4. (a) A typical unloading curve for silicon, and the microstructures in the deformation zone at the different unloading stages; (b) the deformation zone is fully filled with Si-II with a volume of V_0 at the beginning of unloading stage; (c) the Si-II zone remains stable when the contact pressure is higher than the critical pressure of p_{cri}; (d) the phase transition commences with further unloading and the volume of the residual Si-II zone reduces to V_1; (e) a sudden phase transformation occurs within the Si-II region and thus a pop-out appears on the unloading curve.

of the deformation zone (Fig. 4d). In response, the unloading curve bifurcates from the purely elastic process. During the initial stage, the phase transformation process is relatively slow due to the absence of preference nucleation sites. Accordingly, the volume change caused by the phase transformation within the deformation zone is limited. With further phase transformation upon the subsequent unloading, more phase-seeds nucleate and grow, leading to an acceleration of the transformation and hence a faster volume expansion. As a result, a bend (an elbow) appears, representing the gradual evolution of the phase transformation. This process can continue until the end of the entire unloading.

Along with the gradual phase transformation process described above, a rapid growth of the high-pressure phases can take place in the deformation zone, which will cause a sudden volume expansion (Fig. 4a and e). Consequently, a distinct displacement discontinuity, a pop-out, appears. After that, no more phase transformation takes place in the deformation zone and the unloading process returns to an elastic state.

Therefore, the different shapes of unloading curves with an elbow or a pop-out are the results of different evolution processes of the phase transformations in silicon. Clearly, an elbow or a pop-out cannot be viewed as the signal of the onset of the formation of specific phases. Cross-sectional transmission electron microscopy [18] has shown that the microstructures in the transformation zones corresponding to different shapes of load–displacement curves are very similar to each other, all composed of a mixture of amorphous and crystalline phases although their quantities and spatial distributions vary.

3.3. Deformation mechanism at a pop-out

In this section, we aim to understand the underlying mechanism at a pop-out by a detailed examination of the pop-out characteristics under different loading conditions.

3.3.1. Pop-outs under a holding load

We noticed that a pop-out could occur even when we held the load unchanged for a period of time during an unloading process. As shown in Fig. 5, during the unloading process, the load was held at a certain value, e.g. 10 mN, for 60 s. The tests were repeated at least 10 times. The pop-out was found to occur randomly during the holding stage (Fig. 6). Since the tests were carried out in an enclosure with a stable environment, the result seems to show the non-equilibrium characteristics of the sudden growth of high-pressure phases. This is reflected by the random emergence of the pop-outs under the same loading condition (Figs. 1 and 2). It is worthwhile pointing out that when the holding load was above the critical load for the commencement of the phase transition, e.g. 20 mN, the pop-out never occurred during the holding time. This again confirms that the pop-out occurs after the onset of the phase transition.

As shown in Fig. 5, the duration of the pop-out event is very short, about 0.12–0.15 s. When we carried out indentations with different holding loads at various unloading rates, we found that the size of the pop-outs, i.e. the distance of the displacement jump (Δh_p in Fig. 4a), is related to the holding load applied, but almost independent of the unloading rate (Fig. 5). Fig. 6 summarizes the size of the pop-outs, Δh_p, as a function of the holding load applied. It is clear that the pop-out size decreases with decreasing holding load. Such pop-out size variation is controlled by the event mechanism and can be easily understood if our deformation diagram, Fig. 4a–e, is recalled. According to the diagram, a pop-out is the consequence of a sudden volume expansion due to the rapid phase transition in the Si-II zone underneath the indenter. Hence, the size of a pop-out, Δh_p, is determined by the volume of the transferred phases (V_1 in Fig. 4c) in the short duration of the pop-out emergence. When a pop-out happens at a higher load level, its size must be larger because the distance from the pop-out to the bifurcation point is short and less material has experienced phase transformation before the emergence of the pop-out. Fig. 6a shows exactly the variation of Δh_p in this way.

To further understand the relationship between the pop-out size, Δh_p, and the volume of material subjected to phase transformation, let us investigate more completely the indentation process. Let Δh_e be the deviation of the start of a pop-out from the elasticity (Fig. 4a). Because the unloading process after the pop-out is elastic as shown previously, then the summation of Δh_e and Δh_p, i.e. $H = \Delta h_e + \Delta h_p$, can be considered as a measure of the total plastic deformation caused by the transformed materials. Fig. 6a and b compare the sizes of Δh_p, Δh_e and H. Since Δh_e is determined by the volume of the transferred phases before the pop-out (i.e. $V_0 - V_1$ in Fig. 4), whereas Δh_p is determined by V_1, Δh_p should increase as Δh_e decreases as shown in Fig. 6a. We can see that $H = \Delta h_e + \Delta h_p$ is not a constant under nominally the same unloading condition (Fig. 6b). This means that H is influenced by the time a pop-out emerges (earlier or later). Since the total volume of the transformed materials, V_0, is a constant under a certain peak load (Fig. 4), the different H values due to the time difference in pop-out occurrence suggest that the locations of pop-outs in the unloading curves alter the proportion of the transformed phases (amorphous and crystalline phases) after the complete unloading.

3.3.2. Effect of unloading conditions on pop-outs

As shown in Figs. 1 and 2, the probability for the occurrence of a pop-out was greatly dependent on the value of the maximum indentation load F_{max} and of the unloading rate. In the case of $F_{max} = 30$ mN, when the unloading rate was 0.5 mN s^{-1}, pop-outs always occurred. However, when the unloading rate was 1 mN s^{-1}, 15 of the 16 tests gave pop-outs. When the unloading rate was increased to

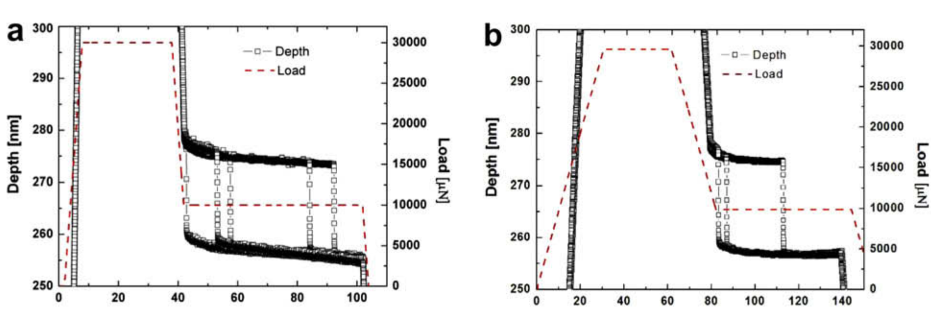

Fig. 5. Pop-out events take place under a holding load of 10 mN on the unloading segment at different loading/unloading rates: (a) 5 mN s^{-1} and (b) 1 mN s^{-1}.

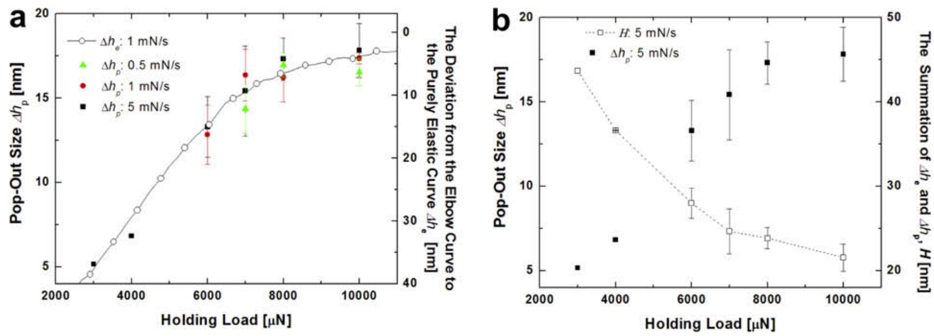

Fig. 6. The size of pop-out, Δh_p, as a function of the holding load applied: (a) compared with the deviation of the elbow curve from the power-law fitting curve, Δh_e; (b) compared with the summation of Δh_p and Δh_e, H. The maximum load $F_{max} = 30$ mN.

5 mN s^{-1}, only 6 of the 16 tests produced pop-outs. In the case of $F_{max} = 10$ mN, pop-out occurred for 8, 6 and 0 times out of the 16 tests when the unloading rate was 0.5, 1 and 5 mN s^{-1}, respectively. These observations mean that a lower unloading rate or a higher peak load favors the occurrence of pop-out.

The dependence of the pop-out on the unloading rate can be explained by the crystalline nucleation and growth mechanism. Since a pop-out is the result of a rapid phase growth, the process requires time to generate sufficient nucleation sites and to allow the crystalline to grow to certain volume. It is therefore reasonable that a lower unloading rate promotes a pop-out. Under a given unloading rate, the chance of a pop-out occurring is higher if F_{max} is greater because in this case the deformation zone will be larger, which will increase the probability of nucleation events.

4. Conclusions

Our investigation leads to the following conclusions:

(1) A pop-out in silicon does not represent the onset of a phase transition.
(2) The onset of a phase transformation during unloading occurs once the contact pressure reaches the critical value (about 8 GPa). This critical pressure is independent of the maximum indentation load, F_{max}, or of the unloading rate.
(3) The size of a pop-out depends on the time it takes to appear during unloading. When a pop-out happens at a higher load level, its size is greater, and vice versa. The location of a pop-out in an unloading curve alters the proportion of the transformed phases (amorphous and crystalline phases) after complete unloading.
(4) A lower unloading rate or a higher maximum indentation load F_{max} promotes the occurrence of a pop-out.

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