Appl. Phys. A (2016)122:607
DOI 10.1007/s00339-016-0142-4

Applied Physics A
Materials Science & Processing

Volumetric and timescale analysis of phase transformation in single-crystal silicon during nanoindentation

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Received: 15 March 2016 / Accepted: 17 May 2016

Abstract Clarifying the phase transformation process and mechanism of single-crystal silicon induced by high pressure is essential for preparation of new silicon phases. Although many previous researches have focused in this area, the volume of high-pressure phases and the duration of phase transformation are still unclear. In this paper, the volume change and the duration of phase transformation from Si-II phase into Si-XII/Si-III phases were investigated quantitatively by introducing a holding process in the unloading stage of a nanoindentation test. Experimental results indicate that the high-pressure phase volume is dependent strongly on the maximum indentation load and independent of the loading/unloading rate and the holding time at the maximum indentation load, while phase transformation duration is independent of the aforementioned experimental parameters. By analyzing the results, a critical volume of Si-XII/Si-III phases was identified which determines the occurrence of sudden phase transformation, and a modified nucleation and growth mechanism of high-pressure phases was proposed. These results provide new insights into high-pressure phase transformations in single-crystal silicon.

1 Introduction

As an important semiconductor material both in industrial applications and scientific research, single-crystal silicon has attracted continuous interests from multidisciplinary researchers. Pressure-induced phase transformations in single-crystal silicon have been intensively reported during diamond anvil cell [1, 2] and nanoindentation tests [3–9]. Recently, phase transformations are also observed during short-pulsed laser-induced confined micro-explosions in silicon [10–13]. By these high-pressure techniques, some new phases with attracting mechanical, chemical, optical and electrical properties have been revealed, which may open up new applications of silicon. For example, Si-II phase has better plasticity than diamond cubic Si-I phase, providing the opportunity for ductile machining of silicon [14]. Si-XII phase exhibits a narrow bandgap with greater overlap with the solar spectrum than other phases [15, 16], and Si-III phase takes a feature of semimetal [17]. These features make them promising applications in future microelectronic and photovoltaics [15, 16, 18].

To explore their potential applications, phase transformation processes and mechanisms between these intermediate phases have been widely investigated by nanoindentation combined with cross-sectional transmission electron microscopy (XTEM) [19–22], Raman microspectroscopy [4, 7, 23, 24] and in situ electrical characterization [20, 25–27]. When the applied pressure increases to ~11 GPa during loading, Si-I phase will transform into Si-II phase. However, phase transformations during unloading strongly depend on the maximum indentation load and loading/unloading rate [3, 28, 29]. Commonly, a large indentation load and low loading/unloading rate will promote the transformation from Si-II into a mixture of high-pressure Si-XII/Si-III phases, leading to discontinuous displacement burst in the unloading curve (namely pop-out) because of the density difference between these phases [9]. Now, pop-out in the unloading curve has been widely used as an indicator that denotes phase transformation from Si-II into Si-XII/Si-III. When the loading/unloading rate is very fast or

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the indentation load is small, Si-II phase readily transforms into amorphous phase, resulting in appearance of the elbow phenomenon. Recent research indicates that the holding time at the maximum load also affects phase transformations in single-crystal silicon [30].

Although these results enhance the understanding of phase transformations in single-crystal silicon, some unclear issues still exist and need clarification. For example, the volume of high-pressure phases and the duration of the transformation (for convenience, hereafter simply named as phase transformation volume and duration, respectively) from Si-II into Si-XII/Si-III remain unclear, and key factors controlling this phase transformation need to be explored. According to the nucleation and growth mechanism [19], fast unloading suppresses the nucleation and subsequent growth of Si-XII/Si-III phases. However, does fast unloading lead to smaller phase transformation volume and longer duration compared to slow unloading? A large maximum indentation load will induce larger pressure-affecting region beneath the indenter and increase the possibility for the nucleation of Si-XII/Si-III phases. Does a larger indentation load shorten the phase transformation duration because of more Si-XII/Si-III seeds formed beneath the indenter? A long holding time at the maximum indentation load may increase the nucleation of new phases, so does a long holding time increase the phase transformation volume and shorten the duration?

These questions about phase transformation volume and duration from Si-II phase into Si-XII/Si-III phases have rarely been investigated before, but they are very important because they are closely related to the understanding of phase transformation mechanisms and strategies for controlling the phase transformation process. The main reasons that these questions have not been discussed in previous research may be the wide load range in unloading for occurrence of pop-out [31] and the occurrence of kink pop-out [3], which bring difficulties to carry out comparative analysis of phase transformation volume and duration in common nanoindentation tests. In this study, to answer these questions, we introduce a modified nanoindentation protocol with a holding process in unloading (simply named as HPU). This protocol can effectively stimulate the pop-out to occur during the HPU; thus, effects of various experimental parameters on phase transformation volume and duration from Si-II phase into Si-XII/Si-III phases can be comparatively investigated.

2 Materials and experimental

A *p*-type single-crystal silicon (100) sample was prepared from a wafer, which possesses a resistivity of 1.00 ~ 2.00 Ω cm. Nanoindentation tests were performed on an ENT-1100 nanoindentation instrument (Elionix Inc., Japan) equipped with a Berkovich indenter. Before nanoindentation on silicon, area function of the indenter was carefully calibrated by the standard materials-fused quartz.

Firstly, ten nanoindentation tests were carried out to obtain the load range in unloading for occurrence of pop-out. Under the experimental conditions (the maximum indentation load of 50 mN, loading/unloading rate of 5 mN/s and holding time of 1 s at the maximum indentation load), pop-outs occurred in the load range of ~9 to ~20 mN in unloading. This agrees well with our previous results that under the same condition, the load in unloading for occurrence of pop-out fluctuates in a relatively large range [3, 31], which makes it difficult for comparative analysis of phase transformation volume and duration under various experimental parameters.

On the other hand, our previous research [32] suggests that a HPU can effectively stimulate the occurrence of pop-out. Hence, the experimental protocol with a HPU as shown in Fig. 1a will be adopted to study effects of various experimental parameters on phase transformation volume and duration of silicon in unloading, because it will bring the following three advantages. First, if the holding load in unloading is the same, pop-out can be induced at the same load. Thus, the single-variable principle is achieved, and comparative analysis can be performed for various experimental parameters. Second, because the load is kept the same during the HPU, ideal pop-out (indentation displacement horizontally bursts) can be induced rather than kink pop-out (indentation displacement bursts accompanying with the decrease in indentation load) [3], which is benefit for subsequent analysis of phase transformation volume and duration. Third, by using this testing protocol, pop-out can be effectively stimulated even under fast unloading [32] which usually induces the elbow during common nanoindentation testing with complete unloading. Thus, phase transformation volume and duration under fast unloading can also be investigated.

As mentioned above, pop-out occurred in the load range of ~9 to ~20 mN in unloading, so an intermediate holding load ($\Delta P = 15$ mN) as shown in Fig. 1a was selected to stimulate the occurrence of phase transformation. A holding time of 20 s with a sampling interval of 0.1 s was given during the HPU. Under this protocol, nanoindentation experiments under various loading/unloading rates, maximum indentation loads and holding time at the maximum indentation load $P_{\max}$ were performed to study their effects. The detailed experimental parameters for each variable are listed in Tables 1, 2 and 3, respectively. After these nanoindentation tests, residual phases in the indents were detected using a laser micro-Raman spectrometer NRS-3000 (JASCO, Tokyo, Japan) with a 532-nm wavelength laser focused to a ~1-μm spot size.

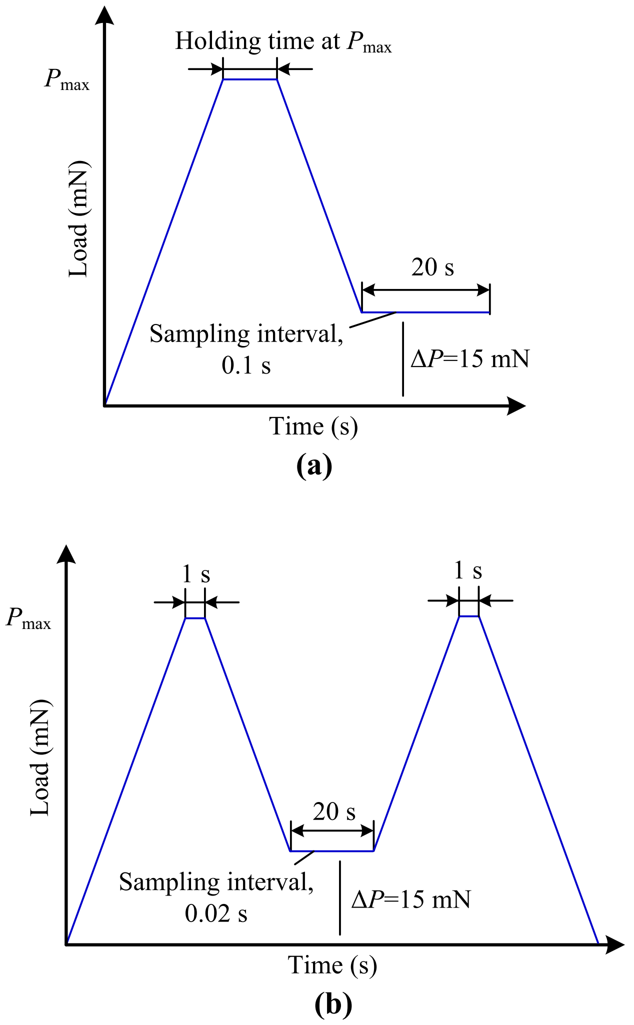

Fig. 1 Experimental protocol with a holding process in unloading (HPU) at $\Delta P = 15$ mN: **a** one cycle and **b** two cycles. In **a**, the sampling interval at ΔP is 0.1 s, and it is 0.02 s in **b**

Table 1 Experimental parameters for studying effects of the loading/unloading rate

Loading/unloading rate (mN/s)	1, 2, 5, 10, 25
Maximum indentation load, P_{max} (mN)	50
Holding time at P_{max} (s)	1
Load at the HPU, ΔP (mN)	15
Sampling interval at ΔP (s)	0.1

Table 2 Experimental parameters for studying effects of the maximum indentation load

Loading/unloading rate (mN/s)	10
Maximum indentation load, P_{max} (mN)	30, 40, 50, 60, 70
Holding time at P_{max} (s)	1
Load at the HPU, ΔP (mN)	15
Sampling interval at ΔP (s)	0.1

Table 3 Experimental parameters for studying effects of the holding time at the maximum indentation load

Loading/unloading rate (mN/s)	10
Maximum indentation load, P_{max} (mN)	50
Holding time at P_{max} (s)	1, 5, 10, 15, 20, 25, 30
Load at the HPU, ΔP (mN)	15
Sampling interval at ΔP (s)	0.1

Table 4 Experimental parameters for studying effects of the sampling interval during the HPU

Loading/unloading rate (mN/s)	1, 2, 5, 10, 25
Maximum indentation load, P_{max} (mN)	50
Holding time at P_{max} (s)	1
Load at the HPU, ΔP (mN)	15
Sampling interval at ΔP (s)	0.02

Because the sampling interval during the HPU in the experimental protocol shown in Fig. 1a is fixed by the nanoindentation testing software, another similar experimental protocol with an additional nanoindentation cycle was used to study the effect of sampling interval. Considering that only the pop-out occurring during the HPU will be compared and discussed, the first nanoindentation cycle in Fig. 1b is actually the same to that in Fig. 1a except the sampling interval. The experimental parameters for studying effects of the sampling interval during the HPU are listed in Table 4.

For each experimental condition mentioned above, ten nanoindentation tests were carried out to obtain reliable results.

3 Results and discussion

3.1 Three cases occurring in unloading

Although previous research indicates that occurrence of pop-out depends on experimental parameters [3], especially the maximum indentation load and unloading rate, it is still a random event. This means that even experimental conditions are the same, various phenomena will appear in unloading, such as pop-out, kink pop-out and elbow in common nanoindentation testing. For nanoindentation

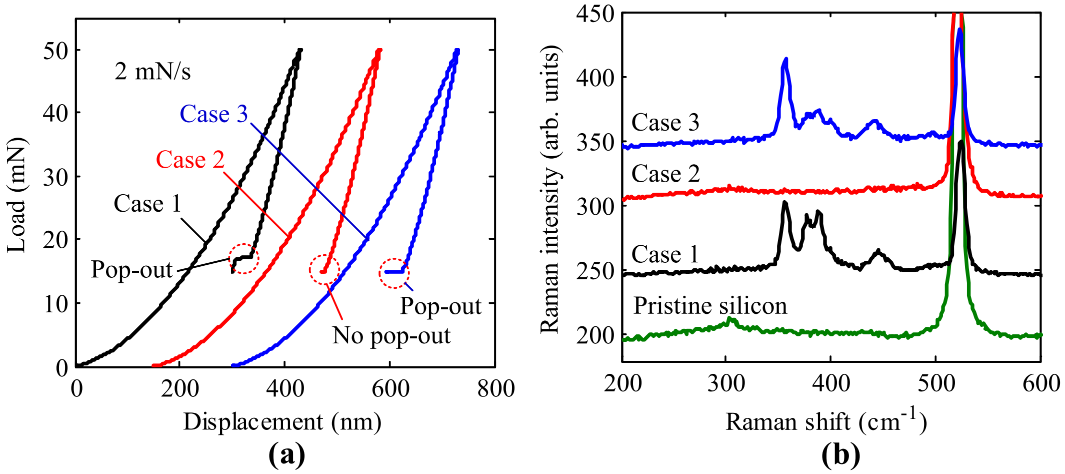

Fig. 2 **a** Three cases occurring in unloading: case 1—pop-out occurring before the HPU, case 2—no pop-out occurring during the HPU and case 3—pop-out occurring during the HPU. **b** Raman spectra corresponding to three cases in **a**. For comparison, Raman spectrum of the pristine silicon is also presented

testing using the experimental protocol with a HPU, three cases were also induced in unloading as shown in Fig. 2a. In case 1, pop-out occurred before the HPU. In case 2, no pop-out occurred during the HPU. In case 3, pop-out occurred during the HPU. Corresponding to these three cases, different residual phases were also detected in indents as shown in Fig. 2b. For comparison, Raman spectrum of the pristine silicon is also presented. Because no pop-out appeared in case 2, its Raman spectrum is similar to that of the pristine silicon. However, for cases 1 and 3, new peaks with similar Raman shift are observed in their Raman spectra. According to Refs. [33–36], peaks at ~356, 378, 399, 440 and 445 cm^{-1} denote Si-XII, and the peak at ~386 cm^{-1} denotes Si-III. The slight difference in Raman intensity in case 1 and case 3 may result from slight difference in the measuring point, because it is very difficult to position exactly the same measuring position on the residual indents by the optical system of micro-Raman spectrometer. Results in Fig. 2 confirm that the same residual phases, a mixture of high-pressure Si-XII/Si-III phases, were formed in cases 1 and 3, independent of the position for occurrence of pop-out in unloading. With consideration of those advantages mentioned in Sect. 2 for the pop-out occurring during the HPU, case 3 will be used in the following sections to quantitatively analyze effects of experimental parameters on phase transformation volume and duration from Si-II into Si-XII/Si-III.

3.2 Quantitative method for analyzing phase transformation volume and duration

To quantitatively analyze phase transformation volume and duration from Si-II transforming into Si-XII/Si-III, the evaluation method and criteria should be defined first. Before this, the ideal pop-out should be confirmed that has occurred during the HPU. For this purpose, Fig. 3a and b presents the load–time and displacement–time curves corresponding to case 3 in Fig. 2a. In Fig. 3a, the indentation load linearly increases and then holds 1 s at the maximum indentation load of 50 mN. After that, it linearly decreases to the holding load of 15 mN and then holds 20 s. In Fig. 3b, a sudden displacement decrease appears during the HPU, suggesting that pop-out has occurred. Figure 3c gives the local enlarged view of Fig. 3b, showing the displacement–time relationship during the pop-out in detail. Figure 3a and b shows that during the pop-out, the indentation load keeps constant and the displacement bursts. Thus, an ideal pop-out has been stimulated during the HPU. Considering that the holding load in unloading is the same for all nanoindentation tests, the phase transformation displacement (decreased displacement) during the pop-out as illustrated in Fig. 3c can be used to evaluate the phase transformation volume, simply named as pop-out displacement. The last stable point before pop-out and first stable point after pop-out are regarded as the starting and ending points of phase transformation. The corresponding time difference is the phase transformation duration, simply named as pop-out duration.

3.3 Effects of experimental parameters

According to the evaluation method proposed in Sect. 3.2, pop-out displacement and duration under various experimental parameters are calculated and summarized in Figs. 4, 5 and 6 and Tables 5, 6 and 7.

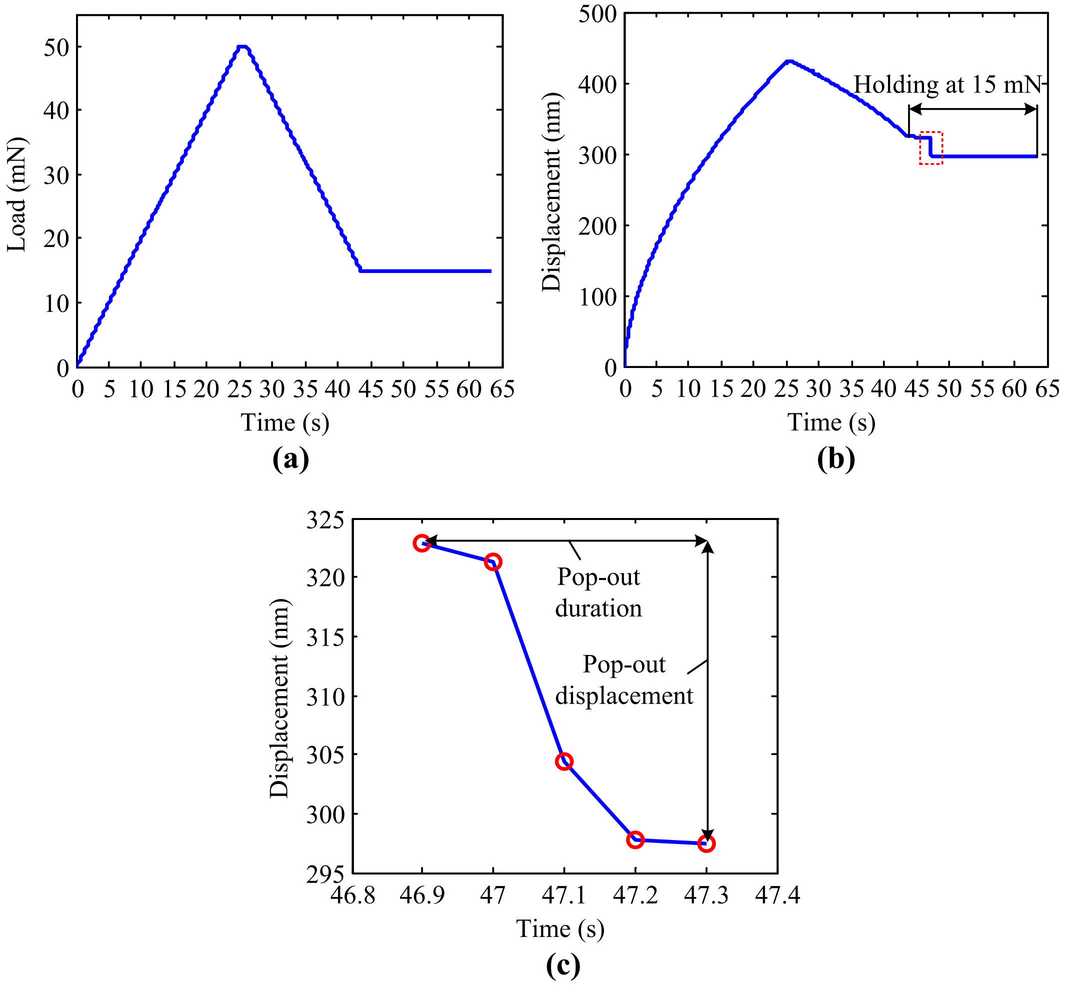

Fig. 3 **a** Load–time curve and **b** displacement–time curve corresponding to case 3 in Fig. 2. **c** Local enlarged view of **b** showing the displacement–time relationship during the pop-out in detail

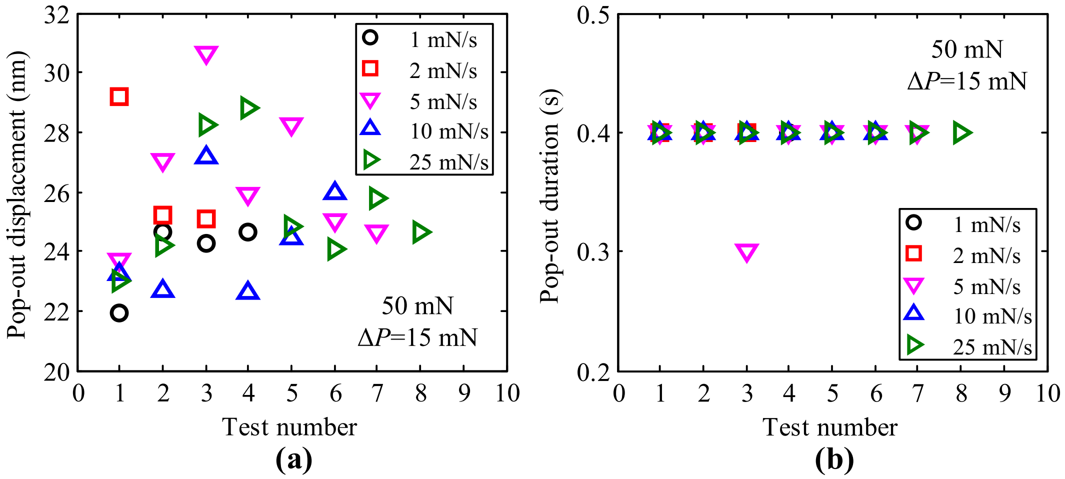

Fig. 4 Pop-out displacement and duration under various loading/unloading rates

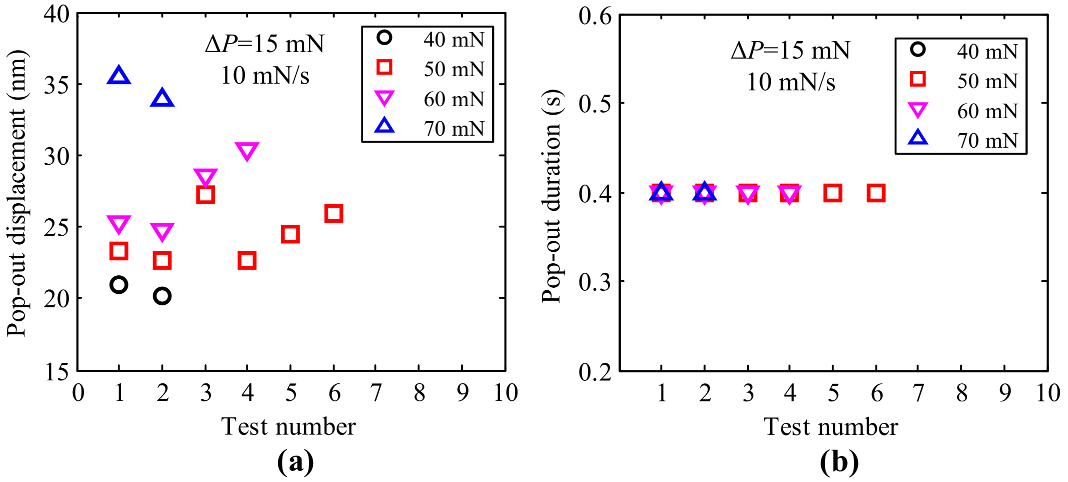

Fig. 5 Pop-out displacement and duration under various maximum indentation loads

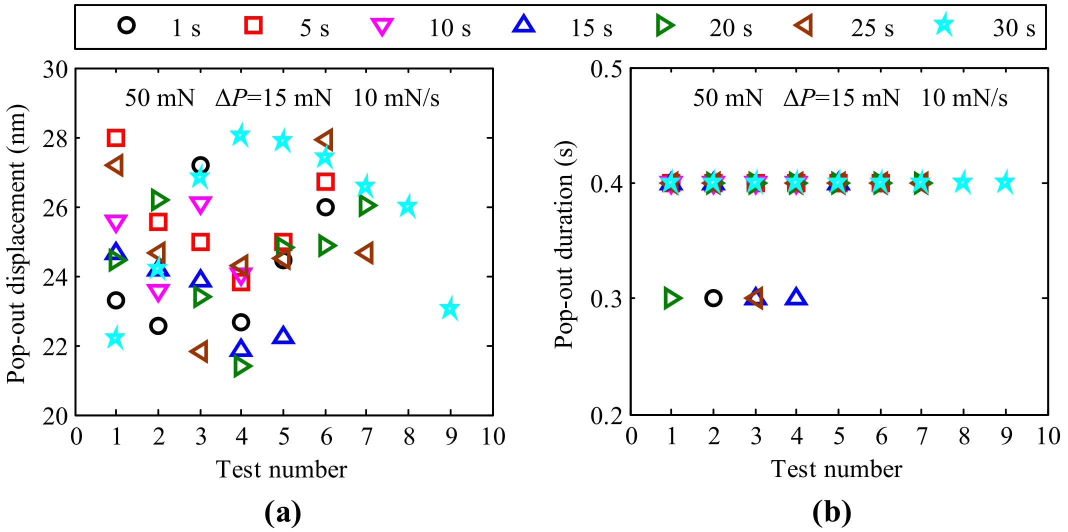

Fig. 6 Pop-out displacement and duration under various holding time at the maximum indentation load

Table 5 Rate of case 3 and average pop-out displacement under various loading/unloading rates

Loading/unloading rate (mN/s)	Rate of case 3	Average pop-out displacement (nm)	Rate of case 1
1	4/10	23.88	4/10
2	3/10	26.50	5/10
5	7/10	26.44	1/10
10	6/10	24.37	1/10
25	8/10	25.45	1/10

Table 6 Rate of case 3 and average pop-out displacement under various maximum indentation loads

Maximum indentation load (mN)	Rate of case 3	Average pop-out displacement (nm)	Rate of case 1
30	0/10	–	0/10
40	2/10	20.55	0/10
50	6/10	24.37	1/10
60	4/10	27.22	6/10
70	2/10	34.74	8/10

In Fig. 4 and Table 5, compared to the low loading/unloading rates (1 and 2 mN/s), more pop-outs occurred during the HPU under fast loading/unloading rates (5–25 mN/s). The reason is that when the unloading rate is low, more pop-outs readily occurred before the HPU as shown in Table 5. For fast unloading, nucleation and growth of high-pressure phases may be hindered [19], and

Table 7 Rate of case 3 and average pop-out displacement under various holding time at the maximum indentation load

Holding time at maximum load (s)	Rate of case 3	Average pop-out displacement (nm)	Rate of case 1
1	6/10	24.37	1/10
5	6/10	25.67	1/10
10	4/10	24.80	3/10
15	5/10	23.37	2/10
20	7/10	24.44	1/10
25	7/10	25.01	2/10
30	9/10	25.77	0/10

the HPU may provide additional chance for further growth of high-pressure phases. Thus, more pop-outs were stimulated during the HPU. Figure 4a and Table 5 show that although pop-out displacement is not a constant value for the same experimental conditions, the loading/unloading rate varying from 1 to 25 mN/s has small impact on the average pop-out displacement. For various loading/unloading rates, the average pop-out displacement is in the range of ~23–26 nm, which results from the same maximum indentation load that induces the same pressure-affecting region beneath the indenter.

In Fig. 5a and Table 6, no pop-out occurred during the HPU for the maximum indentation load of 30 mN, and all the load–displacement curves (not given here) show the case 2 in Fig. 2a. For the maximum indentation loads of 40, 60 and 70 mN, few pop-outs occurred during the HPU compared to that for 50 mN. The reason is that with the increase in the maximum indentation load, the load at which pop-out occurs trends to increase [31]. The holding load of 15 mN is experimentally selected for the maximum indentation load of 50 mN, and it is suitable to effectively stimulate the occurrence of pop-out during the HPU for this indentation load. However, for the maximum indentation loads of 60 and 70 mN, more pop-outs preferably occurred before the holding load of 15 mN (Table 6), because increased maximum indentation load induces the increased load at which pop-out occurs. Similarly, for the indentation loads <50 mN, the load at which pop-out occurs decreases. Thus, no pop-out or few pop-outs were stimulated during the holding process at 15 mN in unloading. Table 6 shows that with the increase in the maximum indentation load, the average pop-out displacement tends to increase because of larger pressure-affecting region induced by the increased indentation load.

In Fig. 6 and Table 7, similar conclusion to the effect of loading/unloading rate can be derived that although the holding time at the maximum indentation load may affect the rate of case 3, it has small impact on the average pop-out displacement because of the same maximum indentation load of 50 mN. The average pop-out displacement under various holding time at the maximum indentation load is also in the range of ~23–26 nm.

Aforementioned analysis focuses on effects of experimental parameters on pop-out displacement. Next, their effects on pop-out duration will be discussed. Figures 4b, 5b and 6b show that pop-out duration under various experimental parameters is relatively stable. With the sampling interval of 0.1 s during the HPU, pop-out duration is 0.4 s for most of nanoindentation tests. For some tests in Figs. 4b and 6b, 0.3 s is also obtained. The reason may be that the starting or ending points of phase transformation are not just at the sampling points, i.e., phase transformation may start or end between two adjacent sampling points in some tests because the sampling interval in the experimental protocol shown in Fig. 1a is 0.1 s (maybe a little big). As shown in Fig. 3c, the decreased displacement for each sampling interval is not the same. Thus, if phase transformation starts at different time between two adjacent sampling points, a small difference in measured pop-out duration may be induced.

According to aforementioned analysis, it can be concluded that pop-out duration is not sensitive to nanoindentation experimental parameters, and it keeps stable at 0.4 s for various experimental parameters. Considering that the sampling interval of 0.1 s may be a little big to distinguish the difference in pop-out duration under various experimental parameters, more experiments using the protocol with a smaller sampling interval of 0.02 s shown in Fig. 1b were performed to further confirm this conclusion. Previous research indicates that occurrence of pop-out strongly depends on the loading/unloading rate [3, 7, 28]; thus, the variable, loading/unloading rate was selected for example. Results are presented in Fig. 7 and Table 8. The same result to Table 5 is observed that more pop-outs were stimulated during the HPU under fast loading/unloading, and the average pop-out displacement for various loading/unloading rates still keeps stable. Furthermore, pop-out duration is confirmed to be not sensitive to the loading/unloading rate, and it is stable at 0.16–0.18 s under the sampling interval of 0.02 s during the HPU. The fluctuation between 0.16 and 0.18 s results from the sampling resolution (0.02 s). Compared to the pop-out duration of 0.3–0.4 s obtained with the sampling interval of 0.1 s, this difference also results from the difference in sampling resolution. However, all the results in Figs. 4b, 5b, 6b and 7b indicate a same fact that pop-out duration is not sensitive to nanoindentation experimental parameters.

3.4 Discussion

Although previous researchers have widely reported that nanoindentation experimental parameters [3, 28–30], especially the loading/unloading rate, strongly affect phase

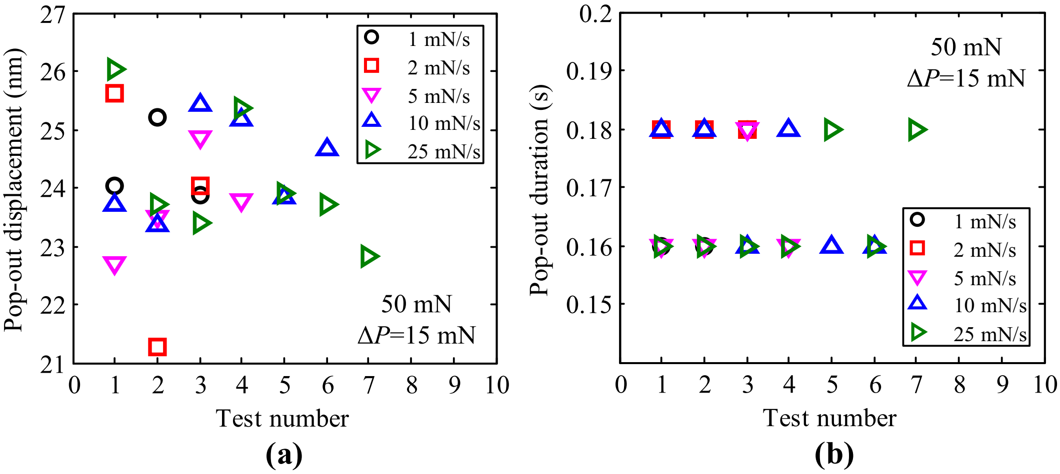

Fig. 7 Pop-out displacement and duration under various loading/unloading rates with the sampling interval of 0.02 s during the HPU

Table 8 Rate of case 3 and average pop-out displacement under various loading/unloading rates with the sampling interval of 0.02 s during the HPU

Loading/unloading rate (mN/s)	Rate of case 3	Average pop-out displacement (nm)
1	3/10	24.37
2	3/10	23.64
5	4/10	23.71
10	6/10	24.37
25	7/10	24.14

transformation from Si-II phase into high-pressure Si-XII/Si-III phases, i.e., occurrence of pop-out, results in this study show that the loading/unloading rate and the holding time at the maximum indentation load have small impact on pop-out displacement and duration. Although the increased maximum indentation load induces the increase in the average pop-out displacement, pop-out duration still keeps stable. The non-sensitivity of pop-out displacement and duration to the loading/unloading rate and the sensitivity of occurrence of pop-out to the loading/unloading rate imply that new mechanisms or processes may exist during phase transformation from Si-II into Si-XII/Si-III.

By fast unloading at different points, Ruffell et al. [19] proposed a nucleation and growth mechanism to explain phase transformations in nanoindentation unloading of single-crystal silicon. It is a two-step process. First, Si-XII/Si-III phases randomly nucleate within Si-II at the early stage of unloading, and they work as seeds for subsequent growth. Second, Si-II becomes more unstable with pressure release after these high-pressure phase seeds have formed, and it undergoes further transformation into Si-XII/Si-III by rapid growth from these seeds when a critical pressure is reached. Accompanying with the formation of substantial volume of Si-XII/Si-III, indentation displacement decreases because of decreased density of Si-XII/Si-III compared to Si-II, and thus, pop-out appears in the unloading curve.

This two-step mechanism can give reasonable explanation for the phenomenon that fast unloading reduces the possibility for occurrence of pop-out, because it hinders the nucleation and growth of Si-XII/Si-III phases. However, it is difficult to explain why pop-out duration is the same for various experimental parameters by this two-step mechanism. Furthermore, it is also difficult to explain why pop-out occurs suddenly not gradually. A critical pressure may be an argumentative reason to explain the sudden occurrence of pop-out. However, the facts that the load at which pop-out occurs in unloading under the same maximum indentation load varies in a large range and also pop-out can be effectively stimulated during the holding process at various loads in unloading, exclude the reason of critical pressure.

Combining the facts that fast unloading reduces the possibility for occurrence of pop-out but has no impact on pop-out duration as well as pop-out is a burst phenomenon with a constant phase transformation duration, a critical stage is derived to exist after the nucleation of Si-XII/Si-III seeds, i.e., the critical volume of Si-XII/Si-III as shown in Fig. 8, which may determine the occurrence of sudden phase transformation. This means that only when the volume of Si-XII/Si-III phases reaches a critical value, substantial volume of Si-II phase could suddenly transform into Si-XII/Si-III phases, yielding the pop-out. Experimental parameters only affect the possibility from step 1 to 2, but they do not affect the transformation process from step 2 to 3. Once a critical volume of Si-XII/Si-III phases has reached, subsequent sudden transformation from Si-II into Si-XII/Si-III experiences a same process. Phase transformation volume during this sudden transformation

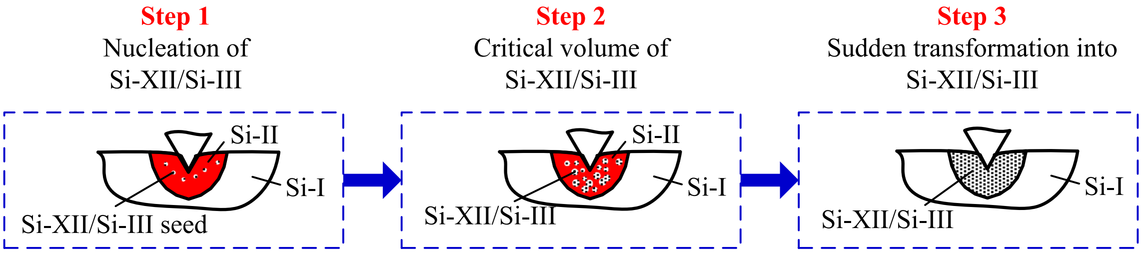

Fig. 8 Possible phase transformation processes from Si-II into Si-XII/Si-III. Step 2, critical volume of Si-XII/Si-III, may determine whether the sudden phase transformation occurs or not

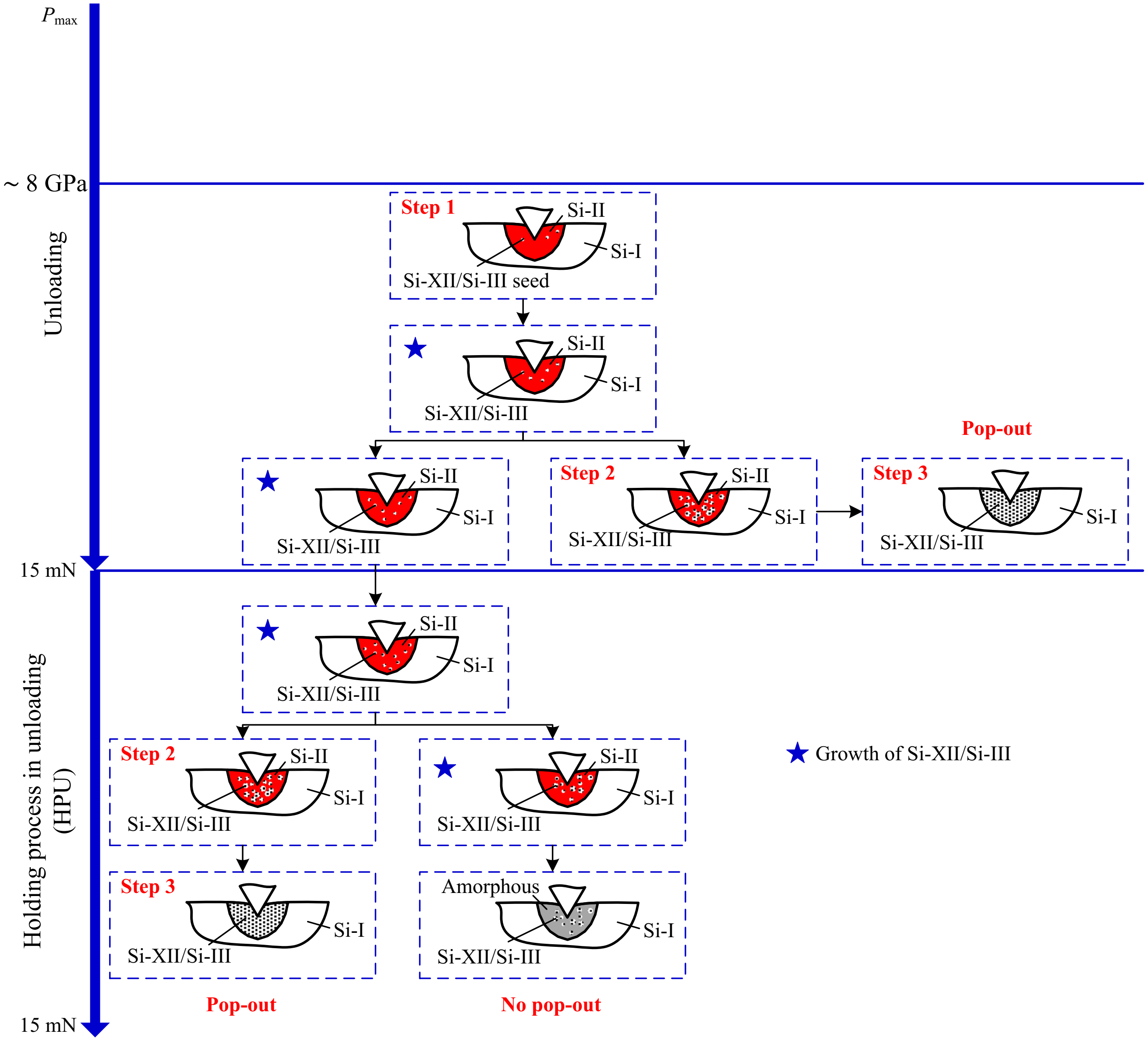

Fig. 9 Diagram to explain occurrence or no occurrence of pop-out in unloading

mainly depends on the maximum indentation load, but phase transformation duration is independent of experimental parameters.

According to the added step shown in Fig. 8, Fig. 9 illustrates different phase transformation paths in nanoindentation unloading of single-crystal silicon to further explain different phenomena observed under various experimental parameters. Our recent research [37] by investigating the creep displacement during the HPU indicated that initial nucleation of Si-XII/Si-III within Si-II is pressure dependent. When a critical pressure of ~8 GPa is achieved, small volumes of Si-XII/Si-III seed within Si-II even under a fast unloading [37]. After that, they grow with pressure release, and this process depends on the unloading rate and maximum indentation load. Slow unloading and large indentation load will promote the growth of Si-XII/Si-III, increasing the possibility to reach the critical volume of Si-XII/Si-III. Thus, more pop-outs occurred before the HPU under slow unloading rates (for example, 1 and 2 mN/s in Table 5) and large indentation loads (for example, 60 and 70 mN in Table 6). For those tests under fast unloading and small indentation load, subsequent growth of Si-XII/Si-III is hindered. Thus, before the HPU, the critical volume of Si-XII/Si-III is hard to be reached. Hence, few pop-outs occurred before the HPU under these experimental parameters (for example, 5–25 mN/s in Table 5 and 30 and 40 mN in Table 6). However, Si-XII/Si-III could further grow during the HPU and reach the critical volume for sudden phase transformation. Thus, many pop-outs were effectively stimulated during the HPU. However, for some tests, although the volume of Si-XII/Si-III increased during the HPU, it still did not reach the critical value, and thus, no pop-out occurred for these tests. The reason for that the holding time at the maximum indentation load has small impact on the occurrence of pop-out is that the phase beneath the indenter is all Si-II phase at the maximum indentation load, and the random nucleation of Si-XII/Si-III has not happened.

4 Conclusions

A new experimental protocol with a holding process in unloading (HPU) was introduced into nanoindentation tests, by which ideal pop-outs (the indentation load keeps constant and the displacement suddenly decreases) were effectively stimulated during the HPU. Nanoindentation tests under various loading/unloading rates, maximum indentation loads and holding time at the maximum indentation load were performed to study their effects on phase transformation volume and duration from Si-II phase into Si-XII/Si-III phases. By quantitatively analyzing the pop-out occurring during the HPU, the following conclusions were drawn.

The high-pressure phase volume is dependent strongly on the maximum indentation load, but independent of the loading/unloading rate and the holding time at the maximum indentation load. Although experimental parameters, especially the loading/unloading rate and the maximum indentation load, affect the possibility for occurrence of pop-out before and during the HPU, they do not affect phase transformation duration, which keeps stable under various experimental parameters.

According to these results and analysis, the critical volume of Si-XII/Si-III was identified between the nucleation of Si-XII/Si-III seeds and the sudden transformation from Si-II into Si-XII/Si-III. Experimental parameters affect the random nucleation and subsequent growth of Si-XII/Si-III and thus affect the possibility to reach the critical volume (i.e., the possibility for occurrence of pop-out). However, once the critical volume of Si-XII/Si-III has reached, the sudden transformation of substantial volume of Si-II into Si-XII/Si-III experiences a same process, independently of experimental parameters. Phase transformation volume during this sudden transformation mainly depends on the maximum indentation load, but phase transformation duration is independent of experimental parameters. These results enhance our understanding of phase transformations in single-crystal silicon, which is important for preparation of new silicon phases and exploring new applications.

Acknowledgments H. Huang is an International Research Fellow of the Japan Society for the Promotion of Science (JSPS). This study has been financially supported by Grant-in-Aid for JSPS Fellows (Grant No. 26-04048) and Grant-in-Aid for Exploratory Research (Grant No. 15K13838).

References

1. J. Crain, G.J. Ackland, J.R. Maclean, R.O. Piltz, P.D. Hatton, G.S. Pawley, Phys. Rev. B **50**(17), 13043 (1994)
2. Z.D. Zeng, Q.S. Zeng, W.L. Mao, S.X. Qu, J. Appl. Phys. **115**(10), 103514 (2014)
3. T. Juliano, Y. Gogotsi, V. Domnich, J. Mater. Res. **18**(5), 1192 (2003)
4. Y.B. Gerbig, C.A. Michaels, R.F. Cook, J. Mater. Res. **30**(3), 390 (2015)
5. N. Fujisawa, J.S. Williams, M.V. Swain, J. Mater. Res. **22**(11), 2992 (2007)
6. L. Chang, L.C. Zhang, Acta Mater. **57**(7), 2148 (2009)
7. V. Domnich, Y. Gogotsi, S. Dub, Appl. Phys. Lett. **76**(16), 2214 (2000)
8. H. Huang, J.W. Yan, Scr. Mater. **102**, 35 (2015)
9. V. Domnich, Y. Gogotsi, Rev. Adv. Mater. Sci. **3**(1), 1 (2002)
10. L. Rapp, B. Haberl, J.E. Bradby, E.G. Gamaly, J.S. Williams, A.V. Rode, Appl. Phys. A Mater. **114**(1), 33 (2014)
11. L. Rapp, B. Haberl, C.J. Pickard, J.E. Bradby, E.G. Gamaly, J.S. Williams, A.V. Rode, Nat. Commun. **6**, 7555 (2015)
12. S. Zhao, E.N. Hahn, B. Kad, B.A. Remington, C.E. Wehrenberg, E.M. Bringa, M.A. Meyers, Acta Mater. **103**, 519 (2016)
13. P.C. Verburg, L.A. Smillie, G.R.B.E. Romer, B. Haberl, J.E. Bradby, J.S. Williams, A.J.H. in't Veld, Appl. Phys. A Mater. **120**(2), 683 (2015)
14. J.W. Yan, K. Syoji, T. Kuriyagawa, H. Suzuki, J. Mater. Process. Tech. **121**(2–3), 363 (2002)

15. B.D. Malone, J.D. Sau, M.L. Cohen, Phys. Rev. B **78**(16), 161202 (2008)
16. B.D. Malone, J.D. Sau, M.L. Cohen, Phys. Rev. B **78**(3), 035210 (2008)
17. J.M. Besson, E.H. Mokhtari, J. Gonzalez, G. Weill, Phys. Rev. Lett. **59**(4), 473 (1987)
18. S. Wippermann, M. Voros, D. Rocca, A. Gali, G. Zimanyi, G. Galli, Phys. Rev. Lett. **110**(4), 046804 (2013)
19. S. Ruffell, J.E. Bradby, J.S. Williams, P. Munroe, J. Appl. Phys. **102**(6), 063521 (2007)
20. N. Fujisawa, S. Ruffell, J.E. Bradby, J.S. Williams, B. Haberl, O.L. Warren, J. Appl. Phys. **105**(10), 106111 (2009)
21. J.W. Yan, H. Takahashi, J. Tamaki, X. Gai, T. Kuriyagawa, Appl. Phys. Lett. **87**(21), 211901 (2005)
22. D.B. Ge, V. Domnich, Y. Gogotsi, J. Appl. Phys. **93**(5), 2418 (2003)
23. Y.B. Gerbig, C.A. Michaels, A.M. Forster, R.F. Cook, Phys. Rev. B **85**(10), 104102 (2012)
24. H. Huang, J.W. Yan, J. Mater. Res. **30**(11), 1861 (2015)
25. S. Ruffell, J.E. Bradby, J.S. Williams, O.L. Warren, J. Mater. Res. **22**(3), 578 (2007)
26. S. Ruffell, J.E. Bradby, N. Fujisawa, J.S. Williams, J. Appl. Phys. **101**(8), 083531 (2007)
27. D.J. Sprouster, S. Ruffell, J.E. Bradby, D.D. Stauffer, R.C. Major, O.L. Warren, J.S. Williams, Acta Mater. **71**, 153 (2014)
28. J.I. Jang, M.J. Lance, S.Q. Wen, T.Y. Tsui, G.M. Pharr, Acta Mater. **53**(6), 1759 (2005)
29. J.W. Yan, H. Takahashi, X.H. Gai, H. Harada, J. Tamaki, T. Kuriyagawa, Mater. Sci. Eng. A Struct. **423**(1–2), 19 (2006)
30. S. Wong, B. Haberl, J.S. Williams, J.E. Bradby, J. Appl. Phys. **118**, 245904 (2015)
31. H. Huang, H.W. Zhao, C.L. Shi, L. Zhang, S.G. Wan, C.Y. Geng, Materials **6**(4), 1496 (2013)
32. H. Huang, J.W. Yan, Semicond. Sci. Tech. **30**(11), 115001 (2015)
33. P.S. Pizani, R.G. Jasinevicius, A.R. Zanatta, Appl. Phys. Lett. **89**(3), 031917 (2006)
34. R.G. Jasinevicius, J.G. Duducha, P.S. Pizani, Mater. Lett. **62**(6–7), 812 (2008)
35. R.G. Jasinevicius, J.G. Duduch, P.S. Pizani, Semicond. Sci. Tech. **22**(5), 561 (2007)
36. Y. Gogotsi, C. Baek, F. Kirscht, Semicond. Sci. Tech. **14**(11), 936 (1999)
37. H. Huang, J.W. Yan, Appl. Phys. A Mater. Sci. Process. **122**(4), 409 (2016). doi:10.1007/s00339-016-9973-2