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Citation: Journal of Applied Physics **115**, 103514 (2014); doi: 10.1063/1.4868156
View online: http://dx.doi.org/10.1063/1.4868156
View Table of Contents: http://scitation.aip.org/content/aip/journal/jap/115/10?ver=pdfcov
Published by the AIP Publishing

JOURNAL OF APPLIED PHYSICS **115**, 103514 (2014)

Phase transitions in metastable phases of silicon

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(Received 4 December 2013; accepted 27 February 2014; published online 13 March 2014)

Phase transitions in indentation induced Si-III/XII phases were investigated using a diamond anvil cell and nanoindentation combined with micro-Raman spectroscopy. The *in situ* high pressure Raman results demonstrate that the Si-III and Si-XII phases have very similar Raman spectra, indicating their relative amount cannot be determined if they are both present in a sample. The Si-III and Si-XII phases coexist in the indentations produced by a nanoindenter on a single crystalline silicon wafer as a result of the local residual compressive stresses near 1 GPa. High power laser annealing on the indentations can initiate a rapid Si-III/XII → Si-I phase transition. The newly formed polycrystalline Si-I phase initially has very small grain size, and the grains grow when the annealing time is extended. Si-IV phase was not observed in our experiment. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4868156]

I. INTRODUCTION

Silicon (Si) is a key material for technological applications and fundamental condensed matter physics study, and its complex phase diagram under compression has attracted intense research interest.[1–3] By using high pressure X-ray diffraction (XRD) and resistivity measurements in a diamond anvil cell (DAC), it is found that Si undergoes a series of phase transitions during compression, from the diamond cubic structure (Si-I) at ambient conditions to the metallic β-Sn phase (Si-II) at ~12 GPa, to Imma (Si-XI) at ~13 GPa, and to a primitive hexagonal structure (Si-V) at ~16 GPa.[4,5] The Si-II → Si-XI → Si-V transitions are reversible upon decompression, however, instead of a reversible transition to the original Si-I phase, the Si-II phase transforms to a semimetallic R8 (Si-XII) phase at approximately 9.3 GPa, and further to a metastable body-centered BC8 (Si-III) phase when pressure is completely released.[6]

In addition to the numerous investigations using a DAC, pressure-induced phase transitions in Si are also observed in indentation experiments with precisely controlled strain rates. Combined with micro-Raman spectroscopy, structure analysis in the micron sized indentations can be easily performed. Indentation has drawn significant attention as it can serve as an efficient method to simulate the mechanical deformation and structure evolution in Si during machining and other contact loading in practical industrial processes.[7–10] Si-I transforms to ductile Si-II during loading, and this is critical for the ultra-high precision machining of Si which is a brittle material at ambient conditions.[7] The onset pressure for this phase transition during indentation is lower than in DAC experiments, which is attributed to the presence of considerable shear stresses during indentation. During unloading, Si-II transforms into Si-III and Si-XII, or amorphous Si (a-Si), depending on the maximum loading and strain rate in the indentation experiment.[11,12] There is argument that the metastable phase upon complete unloading is Si-III,[13] as only Si-III can be preserved at ambient pressure according to *in situ* high pressure XRD studies using DACs, and the Raman spectra taken in indentations can be attributed to Si-III alone.[13] However, most indentation studies claim that the indentation induced metastable Si phases are a mixture of Si-III and Si-XII phases with quite different electrical, chemical properties from Si-I.[2,14] Knowledge of the phase transition and stability of these metastable phases are therefore critical for developing practical applications.

Si-III and Si-XII are usually characterized by Raman peaks located at ~430 cm^{-1} and ~350 cm^{-1}, which are believed to be associated with Si-III and Si-XII, respectively.[7] The Si-III/Si-XII ratio was found to increase during annealing by monitoring the intensity change of those two Raman peaks, implying Si-XII either transforms to Si-III, or transforms to Si-I at a faster rate than Si-III transforms into Si-I.[7,15] In contrast, another study showed the opposite result with the Si-III/Si-XII ratio decreasing during annealing.[16] Various phase transitions from Si-III/XII to Si-I, Si-IV, Si-XIII, or even a-Si were reported when the indentations were annealed between 175 and 450 °C for different durations.[15–18] These conflicting results call for further study, and we will present evidence below showing that the relative intensities of the 350 cm^{-1} and 430 cm^{-1} peak are not sensitive to the Si-XII and Si-III fractions.

In this study, we combine both DAC and nanoindentation experiments with micro-Raman spectroscopy to systematically investigate the phase transitions and metastability of Si-III and Si-XII. The results help to clarify the intense debate surrounding the metastable Si-III and Si-XII phases and improve our understanding of behavior of Si.

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II. EXPERIMENTS

A. *In situ* high pressure Raman experiments

A single crystalline Si sample was loaded into a symmetric DAC together with a tiny ruby ball as a pressure calibrant. Pressure was measured by monitoring the shift in the R1 fluorescence line of ruby.[19] The sample chamber was a 120 μm diameter hole drilled in a T301 stainless steel gasket. Silicone oil was used as the pressure transmitting medium. *In situ* high pressure Raman spectra were collected through one transparent diamond anvil of the DAC using a Renishaw inVia Raman microscope with a 532 nm laser.

B. Nanoindentation experiments

Nanoindentation experiments were carried out using an Agilent Nano Indenter G200 system on a single crystalline (100)-oriented Si wafer. The maximum loading force was set to 80 mN, with loading and unloading rates at 4 mN/s. These experimental parameters favor transition from Si-II $\rightarrow$ Si-III/XII upon unloading. The force-depth (P-h) curves showed pop-outs in the unloading segment, implying the occurrence of the Si-II $\rightarrow$ Si-III/XII phase transition. A 5×5 indentation array was produced on the Si wafer, with 50 micron intervals between the two nearest indentations.

C. *In situ* laser annealing Raman experiments

In situ laser annealing Raman experiments were performed using the Renishaw inVia Raman microscope as well. An objective lens with magnification of 100 was used to focus the laser beam down to $\sim$1 μm diameter. The laser power was manipulated from 1.2 mW to 24 mW in different experiments, corresponding to a power density range 150–3000 kW/cm^2. The sample was annealed by the laser while the Raman spectra were simultaneously collected. The thermal effect of laser exposure became significant when higher laser power was used. Both continuous and pulse laser modes were employed in the experiments by controlling the laser shutter.

III. RESULTS AND DISCUSSION

A. *In situ* high pressure Raman spectroscopy of Si

Figure 1 shows the Raman spectra of the Si sample at different pressures during compression and decompression. The first-order band (Raman peak at 520.9 cm^{-1} at 0 GPa) shifts towards higher wavenumber due to lattice contraction during compression.[20] The Si-I $\rightarrow$ Si-II phase transition occurs when the pressure reaches $\sim$12 GPa.[3] The strongest $\sim$520 cm^{-1} band of Si-I disappears at 16.2 GPa, indicating the transformation has completed. As a metallic phase, Si-II has a very weak Raman signal.[21] No obvious Raman bands were observed in the spectrum taken at 16.2 GPa under our experimental conditions.

During decompression, previous XRD studies suggest the Si-II phase starts to transform to Si-XII at 9.3 GPa.[6] This is quite consistent with our observation that several Raman peaks ($\sim$162, 180, 366 cm^{-1}, etc.) appear at 8.6 GPa (see Fig. 1). The intensity of these Raman peaks increases upon

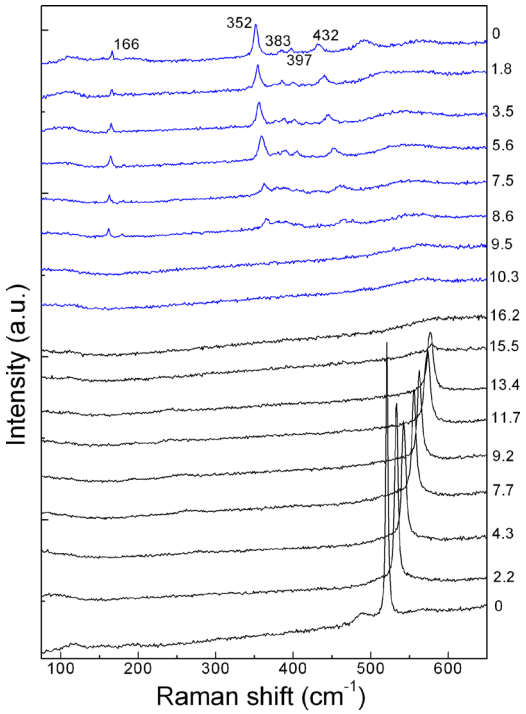

FIG. 1. Raman spectra of a single crystalline silicon sample during compression to 16.2 GPa (black) and decompression to 0 GPa (blue), with pressures labeled besides each spectrum in GPa. A low power of 2.4 mW was used with a collection time of 10 s for each spectrum in order to minimize the thermal effect of the laser. The broad peaks at 110, 490, and 567 cm^{-1} come from the silicone oil pressure transmitting medium. These peaks get weaker during compression and recover upon decompression.

further decompression, implying the continuous phase transition from Si-II to Si-XII. Previous XRD studies showed Si-XII transforms to Si-III when pressure drops below 2.7 GPa, and almost fully converts to Si-III at ambient pressure,[6,13] while our Raman spectra collected at 3.5 GPa, 1.8 GPa, and 0 GPa look very similar to each other. This suggests the Si-XII $\rightarrow$ Si-III phase transition does not have visible effect on Raman spectrum of silicon, and relative intensities of the 350 cm^{-1} and 430 cm^{-1} peak are not sensitive to the Si-XII and Si-III fractions.

In order to identify the Raman bands of Si-III and Si-XII, the frequencies for the three strongest peaks in the Raman spectra as functions of pressure upon decompression were investigated (Fig. 2). No abrupt change in the frequencies is observed around 2.7 GPa for any of the peaks, where the Si-XII $\rightarrow$ Si-III phase transition is expected to occur,[6] consistent with the previous high pressure Raman study.[22] This result indicates that the peak positions for Si-III and Si-XII phases are actually indistinguishable, so it is not practical to resolve them using Raman spectroscopy. This agrees with the results of *ab initio* phonon calculations, which suggest the calculated phonon frequencies of all Raman active BC8 (Si-III) modes have frequencies within $\pm$10% of a Raman active R8 (Si-XII) mode, as a result of the closely related structures of these two phases.[6] Therefore, it is not feasible to determine the relative amounts of coexisting Si-III and Si-XII by their Raman spectra, e.g., using the intensity ratio of Raman peaks at $\sim$350 cm^{-1} and $\sim$430 cm^{-1} which has been extensively employed.[13,23]

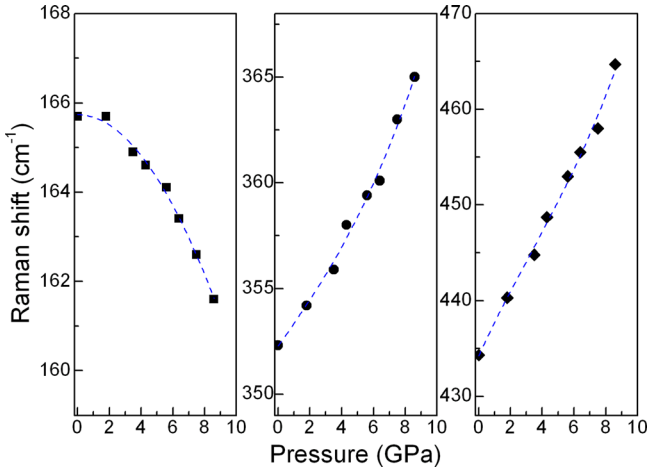

FIG. 2. Raman peaks frequencies for the Si sample as functions of pressure during decompression. The blue dashed curves are guides for the eye.

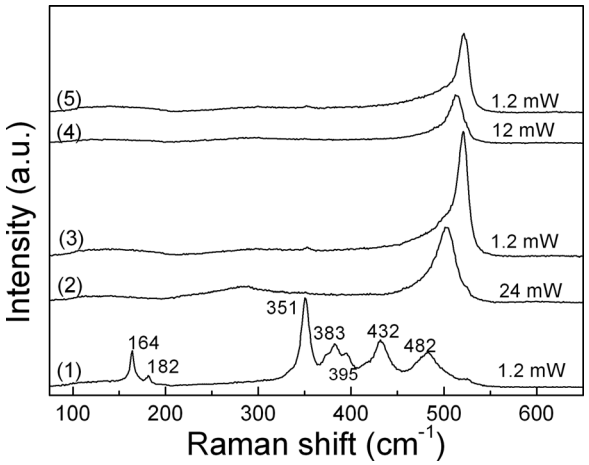

FIG. 3. A series of Raman spectra collected at 1 atm in an indentation using different laser powers: 1.2 mW (1), 24 mW (2), 1.2 mW (3), 12 mW (4), and 1.2 mW (5). The collection time was set to 1 s for the 24 mW and 12 mW measurements, and 20 s for the 1.2 mW measurements.

Although the Si-XII → Si-III phase transition was widely observed in DAC experiments upon decompression to ambient pressure,[6] Si-XII was believed to be partially preserved upon fully unloading in nanoindentation experiments due to the presence of residual stresses in the indentation.[17] The stress conditions close to the indentation are very complicated and deviate from the ideal in-plane stress, but the residual stress can still be estimated from the shift of the first-order Raman band for Si-I surrounding the indentation, using the equation below[24]

$$\Delta\omega(\mathrm{cm}^{-1}) = -4.0\sigma(\mathrm{GPa}),$$

where $\Delta\omega$ is the Raman band shift from the 520.5 cm^{-1}, and σ is the in−plane stress. The band frequency in our experiment is ∼524 cm^{-1}, giving a compressive stress of ∼0.9 GPa. As this residual stress corresponds to an order of magnitude of GPa, it is reasonable that some Si-XII maintains in the residual indentation as other nanoindentation experiments suggested.[17] Thus, it is doubtful one can use Raman spectroscopy alone to determine the Si-III/Si-XII ratio in indentations.

B. Si-III/Si-XII phase transition under laser heating

Although the Raman spectrum is not sensitive for distinguishing the amount of Si-III and Si-XII when they are both present due to their very similar spectra, it is still a sensitive micro-probe to study the transitions of Si-III/Si-XII into other phases. The *in situ* laser annealing Raman measurements were conducted on indentation induced Si-III/Si-XII to study their thermal stability and phase transitions. The initial Raman spectrum of an indentation was measured with a very low laser power of 1.2 mW before the annealing experiments (see curve 1 in Fig. 3). The typical Raman bands for Si-III/XII phase agree well with other studies.[16,17] In addition, we can also find a broad peak at ∼480 cm^{-1}. This peak was designated to Si-XIII phase according to Ge *et al.*'s study.[17] We found that the intensity of the 480 cm^{-1} peak was very sensitive to the test position in the indentation, implying it should be a minor phase in the indentation. We cannot rule out the possible presence of amorphous Si (*a*-Si) in the indention, which has a broad band at 400–500 cm^{-1}.[25] However, the amount of *a*-Si (if present) should be very limited since the very low unloading rate used in our experiment does not favor the formation of *a*-Si,[11,12] as well as the absence of obvious broad band at 80–200 cm^{-1} (TA mode for a-Si).[25] The weak peak at ∼524 cm^{-1} comes from the surrounding Si-I.

The indentation was then annealed for 1 s using a 24 mW laser (power density ∼3000 kW/cm^2), and the Raman spectrum was collected simultaneously within 1 s (see curve 2 in Fig. 3). Surprisingly, the Raman peaks for the Si-III/XII phase almost disappear. Instead, a strong asymmetrical broad peak at ∼505 cm^{-1} emerges along with a weak peak at ∼284 cm^{-1}. Obviously a very rapid phase transition occurred during laser annealing, forming a "new phase" as a consumer of the original Si-III/XII phase. The intense peak at 505 cm^{-1} is very similar to the characteristic peak of the Si-IV phase, which was discovered by TEM and XRD and has its strongest Raman peak located between 503 and 510 cm^{-1}.[17,25–27] In addition, Si-IV was found to be formed in the nanoindentation region after 5–10 min annealing at 200 °C, showing strongest Raman peak at 510 cm^{-1}.[17] Si-III synthesized using a DAC was reported to transform to Si-IV after annealing at 200 °C for 2 h.[2] These previous results suggest that the Si-III/XII → Si-IV phase transition may occur during laser annealing in our experiment.

However, further Raman measurement using a very low excitation power (1.2 mW) at the same position after laser annealing shows an obviously different spectrum (spectrum 3 in Fig. 3). The strongest peak shifts to 521 cm^{-1}, which coincides with the well-known characteristic peak of Si-I, and shows a large shift from the 505 cm^{-1} peak observed in spectrum 2. An interesting question is then raised: Is there a Si-III/XII → Si-IV phase transition during laser heating followed by another transition Si-IV → Si-I during cooling down? Actually, our knowledge about the Si-IV phase is quite limited. An *in situ* laser annealing experiment suggests that laser induced Si-IV in an indentation is not stable at

ambient temperature and transforms to *a*-Si upon cooling down.[25] In contrast, several studies declare that Si-IV are observed at ambient conditions.[2,26,27]

To clarify the phase transition during laser annealing and cooling down, we further performed a diagnostic experiment. An indentation was annealed at 1 atm for 1 s using a 24 mW laser with a Raman spectrum collected simultaneously, then the laser shutter was closed to cool it down. This process was repeated 10 times, and the representative spectra are shown in Fig. 4. If the transitions from Si-III/XII → Si-IV (heating) and Si-IV → Si-I (cooling) indeed occur during the first measurement, we should only have the Si-I phase in the following nine measurements, because once the stable Si-I (very stable up to its melting point ~1400 °C) is formed it will be retained during any subsequent annealing. Thus, the first spectrum ("Si-IV") should be obviously different from the other nine spectra (Si-I). However, in Fig. 4, we can see that all the Raman spectra are very similar.

Therefore, the only interpretation for the above observation is that there is no Si-IV but only Si-I, and the large deviation of the peak position from 520.5 cm^{-1} is just a thermal shift.[28] This means the Si-III/XII → Si-I phase transition occurs during the heating. To further confirm this thermal effect, another Raman spectrum collected using a 12 mW laser is shown in Fig. 3 (curve 4). The strongest Raman peak shifts to 514 cm^{-1} in this spectrum, which is consistent with the expectation that the peak position highly depends on the laser power (with a slope of ~−0.7 cm^{-1}/mW). The accurate local temperature during annealing is unknown as the anti-Stokes line is not available in the Raman system used in this study, although the temperature can be estimated according to the Raman frequency (ω)-temperature (T) dependence in Si-I below[28]

$$d\omega/dT = -0.022\,\mathrm{cm}^{-1}/\mathrm{K}.$$

The temperature corresponding to the 24 mW and 12 mW laser is approximately 730 °C and 320 °C, respectively, given the frequency at room temperature (25 °C) is 520.5 cm^{-1}. It has been shown that the lifetime of the Si-III/XII is temperature dependent, and it is over 1 min at 320 °C and ambient pressure.[15] Therefore, it is very interesting that the laser annealing at a similar temperature can initiate a rapid Si-III/XII → Si-I phase transition within 1 s.

The local temperature increase caused by laser radiation in single crystalline Si (Si-I) is usually negligible as a result of its good thermal conductivity (no Raman peak shift can be observed when laser power increases from 1.2 to 24 mW). However, for polycrystalline Si-I formed during laser annealing in the indentation, the high power laser (12 mW, 24 mW) results in a temperature increase of several hundred degrees. This implies that the grain size of the Si-I in this case is very small, as the thermal conductivity of a material generally decreases with decreasing domain size due to the increasing phonon scattering at grain boundaries. For instance, the thermal conductivity of polycrystalline Si-I with 10 nm grain size (~4 $Wm^{-1}K^{-1}$) is nearly two orders of magnitude lower than that of single crystalline Si (~148 $Wm^{-1}K^{-1}$).[29] In addition, the laser annealing duration is only 1 s each time in our experiments, so the Si-I nucleation does not have enough time to grow, leading to a polycrystalline Si-I with a very limited grain size. Besides the reduction in thermal conductivity, the ultra small grain size may also result in a downshift of the first order Raman peak due to phonon confinement.[30] However, the Raman

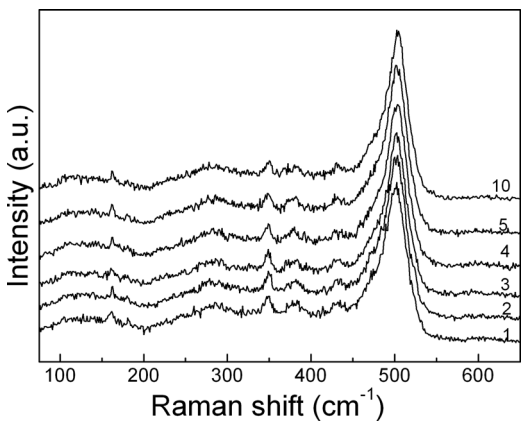

FIG. 4. A series of Raman spectra collected at 1 atm in an indentation with a collection time of 1 s for each spectrum using a 24 mW laser. The testing region was not exposed to the laser between each collection. The number labeled above each spectrum is the sequence of the spectrum.

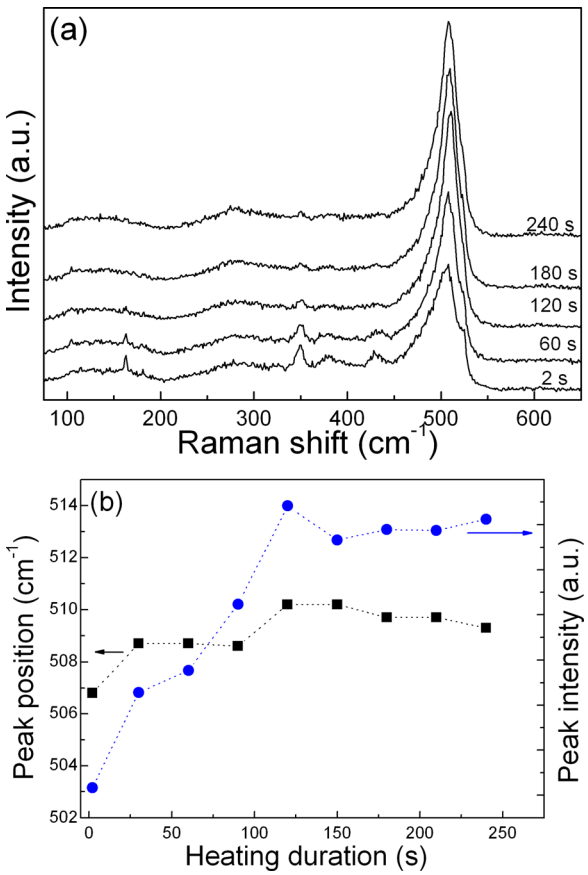

FIG. 5. (a) A series of Raman spectra collected at 1 atm in an indentation with a collection time of 2 s during continuous laser annealing at 24 mW. The number above each spectrum is the annealing duration when the spectrum was collected. (b) The peak position (black squares) and peak intensity (blue dots) as functions of the annealing time. The peaks are fit with Voigt functions after linear background subtraction.

peak of Si-I yielded using a 1.2 mW laser (521 cm^{-1}) does not show any downshift, which sets a lower limit of 20 nm for the grain size for the Si-I formed in our annealing experiment.[30] Therefore, the redshift of the Raman peak from ~521 cm^{-1} (1.2 mW laser) to ~505 cm^{-1} (24 mW laser) is a purely thermal effect.

The timescale of the laser annealing is very short, so what happens if the indentation is annealed for a longer period? Figure 5(a) shows the Raman spectra of a new indentation during continuous annealing using a 24 mW laser. The intensity of Si-III/XII Raman peaks (351 cm^{-1}, 383 cm^{-1}, 432 cm^{-1}) decreases dramatically after 2 s annealing. The main Raman band shifts to higher wavenumber when the annealing time is extended from 2 s to 120 s, then saturates during further annealing (see Fig. 5(b)). This can be explained by the thermal effect being controlled by the grain size change. Fine Si-I grains formed at the very beginning grow larger during further annealing, resulting in an increasing thermal conductivity and thus decreasing temperature. Meanwhile, the peak intensity increases along with the annealing time, suggesting the continuous transition from Si-III/XII → Si-I and growing grain size.

Compared with other annealing investigations of the metastable Si-III/XII phases where other metastable phases like Si-IV, Si-XIII, or *a*-Si are reported, we only observed the Si-III/XII → Si-I phase transition in this study. This may be attributed to the relatively higher temperature in our study (320 or 730 °C versus 175–200 °C). We repeated the above experiments on several indentations and found no significant differences in the results.

IV. SUMMARY

Using a DAC and nanoindentation combined with micro-Raman spectroscopy, the phase transition and metastability of Si-III/XII phases were systematically investigated. The *in situ* high pressure Raman results show that Si-XII and Si-III have very similar Raman spectra; therefore, it is very challenging to distinguish them or determine their relative amount when they are both present. For the indentations in our study, Si-III and Si-XII probably coexist as a result of the high residual compressive stress (~0.9 GPa). High power laser irradiation of the indentations can initiate a rapid Si-III/XII → Si-I phase transition within 1 s. The newly formed polycrystalline Si-I has a very small grain size, and grain growth was observed when the annealing time was extended. Si-IV or other metastable phases were not observed during the annealing of the Si-III/XII phases in our experiment. Our results indicate that one needs to be very cautious when using Raman spectroscopy to study phase transitions in Si. For instance, the Si-I yielded in our study may be easily mistaken for Si-IV. The effects of temperature, grain size, etc., on the Raman spectrum need to be considered carefully.

ACKNOWLEDGMENTS

This work was supported as part of the EFree, an Energy Frontier Research Center funded by the US Department of Energy, Office of Science, Office of Basic Energy Sciences under Award No. DE-SG0001057. Zhejiang University participants are supported by the National Natural Science Foundation of China (Nos. 11222218, 11321202), the Science and Technology Innovative Research Team of Zhejiang Province (2009R50010), and the China Postdoctoral Science Foundation.

[1]J. C. Jamieson, Science **139**, 762–764 (1963).
[2]J. M. Besson, E. H. Mokhtari, J. Gonzalez, and G. Weill, Phys. Rev. Lett. **59**, 473–476 (1987).
[3]J. Z. Hu, L. D. Merkle, C. S. Menoni, and I. L. Spain, Phys. Rev. B **34**, 4679–4684 (1986).
[4]G. A. Voronin, C. Pantea, T. W. Zerda, L. Wang, and Y. Zhao, Phys. Rev. B **68**, 020102 (2003).
[5]M. I. McMahon and R. J. Nelmes, Phys. Rev. B **47**, 8337–8340 (1993).
[6]R. O. Piltz, J. R. Maclean, S. J. Clark, G. J. Ackland, P. D. Hatton, and J. Crain, Phys. Rev. B **52**, 4072–4085 (1995).
[7]A. Kailer, Y. G. Gogotsi, and K. G. Nickel, J. Appl. Phys. **81**, 3057–3063 (1997).
[8]B. V. Tanikella, A. H. Somasekhar, A. T. Sowers, R. J. Nemanich, and R. O. Scattergood, Appl. Phys. Lett. **69**, 2870–2872 (1996).
[9]R. F. Cook, J. Mater. Sci. **41**, 841–872 (2006).
[10]Z. D. Zeng, L. Wang, X. Y. Ma, S. X. Qu, J. H. Chen, Y. G. Liu, and D. R. Yang, Scr. Mater. **64**, 832–835 (2011).
[11]V. Domnich, Y. Gogotsi, and S. Dub, Appl. Phys. Lett. **76**, 2214–2216 (2000).
[12]J. I. Jang, M. J. Lance, S. Q. Wen, T. Y. Tsui, and G. M. Pharr, Acta Mater. **53**, 1759–1770 (2005).
[13]M. M. Chaudhri, Phys. Rev. B **84**, 237301 (2011).
[14]R. Rao, J. E. Bradby, and J. S. Williams, Appl. Phys. Lett. **91**, 123113 (2007).
[15]S. Ruffell, J. E. Bradby, and J. S. Williams, Appl. Phys. Lett. **90**, 131901 (2007).
[16]S. Ruffell, B. Haberl, S. Koenig, J. E. Bradby, and J. S. Williams, J. Appl. Phys. **105**, 093513 (2009).
[17]D. B. Ge, V. Domnich, and Y. Gogotsi, J. Appl. Phys. **95**, 2725–2731 (2004).
[18]R. J. Kobliska, S. A. Solin, M. Selders, R. K. Chang, R. Alben, M. F. Thorpe, and D. Weaire, Phys. Rev. Lett. **29**, 725–728 (1972).
[19]H. K. Mao, P. M. Bell, J. W. Shaner, and D. J. Steinberg, J. Appl. Phys. **49**, 3276–3283 (1978).
[20]B. A. Weinstein and G. J. Piermarini, Phys. Rev. B **12**, 1172–1186 (1975).
[21]H. Olijnyk, Phys. Rev. Lett. **68**, 2232–2234 (1992).
[22]H. Olijnyk and A. P. Jephcoat, Phys. Status Solidi B **211**, 413–420 (1999).
[23]S. Ruffell, K. Sears, A. P. Knights, J. E. Bradby, and J. S. Williams, Phys. Rev. B **83**, 075316 (2011).
[24]I. DeWolf, Semicond. Sci. Technol. **11**, 139–154 (1996).
[25]K. H. Wu, X. Q. Yan, and M. W. Chen, Appl. Phys. Lett. **91**, 101903 (2007).
[26]A. Fontcuberta i Morral, J. Arbiol, J. D. Prades, A. Cirera, and J. R. Morante, Adv. Mater. **19**, 1347–1351 (2007).
[27]G. Weill, J. L. Mansot, G. Sagon, C. Carlone, and J. M. Besson, Semicond. Sci. Technol. **4**, 280–282 (1989).
[28]J. Menendez and M. Cardona, Phys. Rev. B **29**, 2051–2059 (1984).
[29]Z. J. Wang, J. E. Alaniz, W. Y. Jang, J. E. Garay, and C. Dames, Nano Lett. **11**, 2206–2213 (2011).
[30]I. H. Campbell and P. M. Fauchet, Solid State Commun. **58**, 739–741 (1986).