Annealing of nanoindentation-induced high pressure crystalline phases created in crystalline and amorphous silicon

S. Ruffell,[a)] B. Haberl, S. Koenig,[b)] J. E. Bradby, and J. S. Williams
Department of Electronic Materials Engineering, Research School of Physics and Engineering, Australian National University, Canberra, 0200, Australia

Thermally induced phase transformation of Si-III/Si-XII zones formed by nanoindentation has been studied during low temperature ($200 < T < 300$ °C) thermal annealing by Raman microspectroscopy and transmission electron microscopy. Two sizes of spherical indenter tips have been used to create substantially different volumes of phase transformed zones in both crystalline (c-Si) and amorphous silicon (a-Si) to study the zone size and starting matrix effects. The overall transformation is from Si-III/XII to poly- or nanocrystalline Si-I through intermediate phases of Si-XIII and Si-IV. Attempts have been made to determine the exact transformation pathways. Two scenarios are possible: either Si-XII first transforms to Si-III before transforming to Si-I through the intermediate phases or that Si-XII goes through the intermediate phases while Si-III transforms directly to Si-I. Finally, the phase transformations are slower in the larger indents and the starting matrix (crystalline or amorphous) has a substantial effect on the transformation kinetics of the small indents compared to the larger ones. We attribute this increased stability to both matrix effects (nucleation) and a difference in overall residual stress in indents made in a-Si compared to c-Si. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3124366]

I. INTRODUCTION

Significant interest in nanoindentation-induced phase transformations of silicon over recent years resulted in a substantial increase in the understanding of the transformation pathways.[1–10] These pressure-induced transformations are of great interest, but the exact mechanisms behind the phenomena are still not well understood. It has also been shown that relaxed ion-implanted amorphous silicon (a-Si) undergoes similar phase transformations to high pressure crystalline phases during nanoindentation.[7,11,12] In addition, the formation of the high pressure crystalline phases occurs much more readily for the case of a-Si.[7,12] For both starting matrices, a transformation to a conducting metallic phase (Si-II) occurs at a critical pressure of ~12 GPa during loading. Upon unloading, the metallic phase further transforms to either a-Si or a mixture of high pressure polycrystalline phases (Si-III and Si-XII); the formation of the latter being favored for slow unloading and is usually accompanied by a pop-out event in load versus penetration curves.[2,8,13–16]

Despite many reports of studies on the phase transformations, relatively little attention has been paid to the properties of the end phases including their evolution during low temperature annealing.[5,14,17,18] A recent study by the present authors investigated the annealing kinetics of high pressure phases (Si-III and Si-XII) created in crystalline silicon (c-Si) by nanoindentation with a ~4.3 μm spherical tip over the temperature range from 130 to 300 °C.[18] The overall transformation during annealing was Si-III/XII to fine grained polycrystalline Si-I. In addition, it was observed that Si-XII annealed out at a greater rate than Si-III suggesting that ei-

ther Si-XII first transforms to Si-III before converting to Si-I or that Si-XII and Si-III both transform to Si-I with Si-XII doing so more quickly. Unfortunately it was not possible to extract any further detail from this previous nanoindentation data, but the former scenario seems more likely since an early annealing study of Si-III/Si-XII created in a diamond anvil cell also observed this transformation sequence.[19,20] However, zones of Si-III/Si-XII formed by nanoindentation contain high residual stresses, which may alter the phase transformations during annealing when compared with those formed by a high pressure cell. In a more recent study, Ge *et al.*[17] suggested that during heating of transmission electron microscopy (TEM) samples of indented c-Si at 200 °C the phase transformation sequence is as follows: Si-XII → Si-III → Si-XIII → a-Si or Si-IV → Si-I. However, it might be expected that the phase transformations during heating of these thin (electron transparent) TEM specimens may differ from those in bulk samples. Finally, no annealing studies of high pressure phases formed in an a-Si matrix have been previously reported nor has the effect of indentation conditions prior to annealing on the phase transformations been studied. It is of interest, therefore, to investigate the annealing kinetics of these phases formed in an a-Si matrix for comparison to the c-Si case. Raman microspectroscopy is a convenient means to track the evolution of the high pressure phases. An advantage of studying these thermally driven transformations in a-Si is that the large signal from a surrounding c-Si matrix is eliminated from the Raman measurements, thus enhancing identification of additional intermediate phases which may form during annealing. The current study investigates these thermally driven phase transformations as a function of temperature, indentation conditions (loading, tip size), and starting matrix.

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a)Author to whom correspondence should be addressed. Electronic mail: simon.ruffell@anu.edu.au.
b)Visiting student from Universität Augsburg.

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II. EXPERIMENT

Czochralski grown Si(100) wafers, *p*-doped with boron to a resistivity of $8-12$ Ω cm, were used for nanoindentation and some of the material was ion implanted with Si at -170 °C at energies up to 2 MeV to form a surface amorphous layer of 2 μm thickness. This layer was relaxed by furnace annealing in a nitrogen atmosphere at 450 °C for 30 min. Approximately 1×1 cm^2 samples were then cleaved from this wafer for nanoindentation and annealing.

Indentation was performed at room temperature using an Ultra-Micro-Indentation-System 2000 with a $\sim$4.3 μm spherical indenter tip (same conditions as the previous annealing study[21]) and a $\sim$17.7 μm spherical indenter tip. For the remainder of this paper the 4.3 μm indents will be referred to as "small" and the 17.7 μm indents will be referred to as "large." For the smaller tip a maximum load of 80 mN was used with unloading performed in 40 increments (average unload rate $\sim$0.9 mN/s). For the bigger tip a maximum load of 750 mN was used with the unloading performed in 200 increments (average unload rate $\sim$1.3 mN/s). In both cases, these conditions ensured that a so-called pop-out event occurred on unloading of all indentations, indicating that the phase transformed zone contained high pressure crystalline phases (Si-III and Si-XII). However, a pop-out event does not guarantee that the entire volume is composed of high pressure (Si-III/XII) phases. Many indents will contain a mixture of Si-III and Si-XII and some a-Si, although the fraction of a-Si under our indentation conditions is expected to be small (less than about 5% as estimated from cross-sectional TEM measurements). Five indents were made on each sample for each of the annealing times and temperatures studied. Since the nucleation and growth of the high pressure phases during unloading are driven by random nucleation events, the final microstructure differs from one indent to another even when formed under identical conditions. By sampling five indents per sample, an overall measurement can be obtained that averages over any small differences between indents made under identical conditions.

Each sample was furnace annealed in flowing nitrogen. A 1 min push-in and pull-out was used. Annealing was performed over the temperature range from 200 to 300 °C. Temperatures outside this range caused the high pressure phases to anneal out in a time much less than 1 min or in a prohibitively long time.

Thereafter, the indentations were measured using a Renishaw 2000 Raman microscope fitted with a 632.8 nm laser focused to $\sim$1 μm spot diameter. The volume of high pressure phases (Si-III/XII) remaining in the indents was tracked by monitoring the intensity of the peaks at $\sim$353 and $\sim$438 cm^{-1} corresponding to Si-XII and Si-III, respectively.[17] In addition, formation of any intermediate phases during annealing could be observed. The laser spot is similar in size to the small residual indents created by the 4.3 μm spherical tip using the loading conditions here. The spectra, therefore, contain contributions from the phase transformed material, the silicon below the phase transformed zone, and from the surrounding a-Si or c-Si matrix. For the case of the larger indent zones with a residual diam-
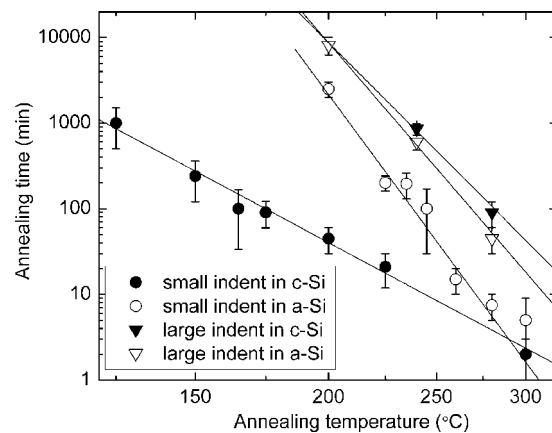

FIG. 1. Arrhenius plot of annealing time as a function of annealing temperature for indents made in c-Si and a-Si using the $\sim$4.3 μm spherical indenter applying a maximum load of 80 mN and indents made in c-Si and a-Si using the $\sim$17.7 μm spherical indenter applying a maximum load of 750 mN.

eter of $\sim$9 μm and a depth of $\sim$400 nm of the transformed zone, the contributions from the substrate surrounding the transformed zones are small. However, in those indents the whole phase transformed zone cannot be sampled in one measurement so the Raman measurements will be sensitive to local variations in the microstructure within the transformed zone. To keep the spectra of the different indents comparable, care was taken to obtain all the spectra from the middle of the residual indent.

Selected samples were examined by TEM to measure possible differences in the microstructure of the phase transformed zones both before and after annealing. Samples were made by a focused ion-beam milling and "lift-out" method for cross-sectional TEM (XTEM). The process is described in detail elsewhere.[22] Samples were examined using a Philips CM 300 transmission electron microscope operating at an accelerating voltage of 300 kV.

III. RESULTS

The time for the overall transformation from Si-III/Si-XII to Si-I was estimated from Raman measurements by taking the annealing time for which no Si-III/Si-XII was detected and the only crystalline phase was Si-I. Further annealing from this point did not result in further changes to the spectra. Figure 1 shows an Arrhenius plot of this annealing time as a function of annealing temperature. Data from the small indents in a-Si and the large indents in both the a-Si

TABLE I. Comparison of the ratio of the Si-XII peak at 355 cm^{-1} and the Si-III peak at 438 cm^{-1} for small indents made in a-Si and c-Si and large indents made in a-Si and c-Si (20 indents of each type were measured to extract these data). No significant differences in the volume ratio of these phases can be extracted from the Raman measurements.

Indent	Ratio of Si-III to Si-XII
Small in c-Si	0.21 ± 0.08
Small in a-Si	0.17 ± 0.04
Large in c-Si	0.18 ± 0.05
Large in a-Si	0.21 ± 0.09

TABLE II. Table showing the average peak positions for the Si-III and Si-XII phases in the Raman spectra extracted from large and small indents made in a-Si and c-Si. Data were extracted by sampling 20 indents of each type.

	Small indents		Large indents	
	c-Si	a-Si	c-Si	a-Si
Position of Si-III/XII peaks (cm^{-1})	165.9 ± 1.2	165.4 ± 0.8	167.3 ± 0.8	167.0 ± 0.7
	184.1 ± 1.4	182.4 ± 0.8	184.9 ± 1.1	183.5 ± 1.0
	354.6 ± 1.1	352.3 ± 1.1	354.3 ± 0.8	352.9 ± 0.8
	377.0 ± 1.8	373.3 ± 1.2	377.2 ± 1.5	374.4 ± 1.4
	386.1 ± 1.2	383.9 ± 1.0	386.6 ± 0.9	384.6 ± 0.8
	398.5 ± 1.5	396.3 ± 1.1	399.6 ± 0.8	397.6 ± 0.8
	440.4 ± 3.1	438.7 ± 2.8	440.0 ± 2.3	437.5 ± 2.0

and c-Si matrices are shown. For comparison, annealing data for small indents in c-Si (which can be compared directly with those made here in a-Si) are plotted from Ref. 18. Over the temperature range studied here, annealing of the high pressure phases was slower for the larger indents by at least an order of magnitude. In addition, the surrounding matrix has a significant effect on the annealing kinetics of the small indents compared to those of the large indents.

Table I shows the average of the ratio of the intensity of the Si-III peak at ~438 cm^{-1} to that of the Si-XII peak at ~353 cm^{-1} for small and large indents made in c-Si and a–Si without any annealing. This ratio provides an estimate of the ratio of the volume of Si-III to Si-XII within the transformed zone. For each type of indent, spectra from 20 indents were analyzed. Although this ratio has some variation for different indents made under identical conditions, no significant difference in this average ratio can be observed by Raman between the indents made under the different loading conditions in the different matrices here. In all cases, Si-XII is around 80% of the transformed volume.

Although the Raman measurements reveal no significant differences in the ratio of Si-III to Si-XII between the indents made under different conditions, close inspection of the peak positions reveal differences in the residual stress within the indents. Table II shows the average position of the peaks

associated with Si-III and Si-XII extracted from measurements of 20 indents in both small and large indents in a-Si and c-Si. No significant difference in peak positions is observed between small and large indents but the peaks in a-Si are consistently shifted to lower wave numbers (approximately 2 cm^{-1}) relative to the indents in c-Si. Based on peak shift measurements made for crystalline Si-I, the difference in position of the Si-III/XII peaks observed here would indicate that there is a higher residual compressive stress in the indents created in c-Si corresponding to approximately 0.5 GPa.[23] The peak positions for the high pressure phases in a-Si are close to those reported from measurements made on samples formed in a high pressure cell, i.e., stress-free.[20,24]

Figure 2 shows representative XTEM bright field images taken from small and large indents before and after annealing at 450 °C for 30 min. For the large and small indents, the phase transformed zone is composed of Si-III/XII (confirmed by selected area diffraction) and has a polycrystalline microstructure before annealing. No significant differences in grain size and orientation are observed between the two cases from this TEM. After annealing, only polycrystalline Si-I was found in the transformed zone as evident from the selected area diffraction patterns shown as insets in the TEM micrographs. Again, no significant differences in the polycrystalline microstructure can be observed from the TEM images. Furthermore, TEM investigations of indents made in the a-Si matrix (images not shown here) show no significant differences to those shown here in the c-Si matrix. To date, many indents studied by the authors exhibit similar microstructure to these indents.[1,7,11,13,16,21,25]

Figure 3 shows typical Raman spectra taken from unannealed indents and of the respective unindented matrices. Figure 3(a) shows the spectra for the a-Si matrix and Fig. 3(b) shows equivalent spectra for the c-Si matrix.

Figures 4 and 5 show representative Raman spectra taken from (a) small and (b) large indents formed in a-Si and annealed at 200 (Fig. 4) and 280 °C (Fig. 5) for a range of times. The evolution of the indentation-induced phases can be observed and, since the Raman spectra taken from indents in c-Si show qualitatively the same evolution, we show only
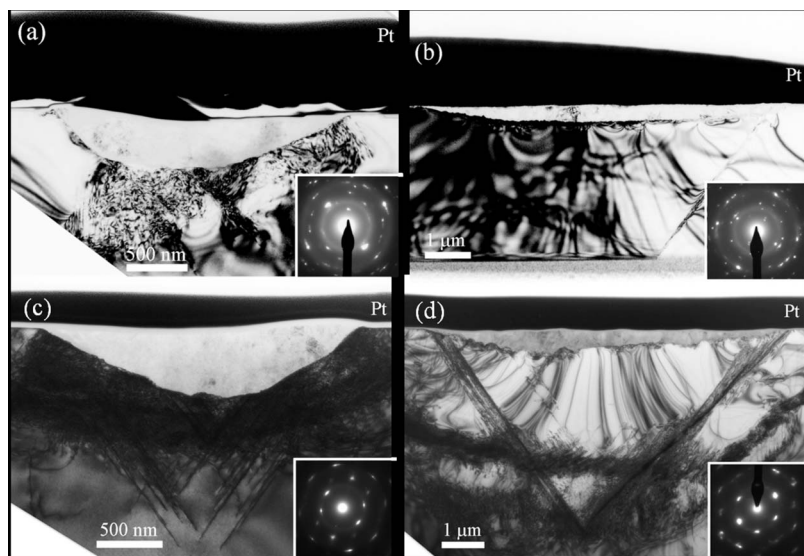

FIG. 2. Bright field XTEM images taken from small and large indents made in c-Si before [(a) and (b)] and after [(c) and (d)] annealing at 450 °C for 30 min. Selected area diffraction patterns are shown as an inset in each image. The protective Pt layer above the surface of the Si is labeled. Before annealing the zone created in c-Si consists of polycrystalline Si-III/Si-XII, while it has completely transformed to polycrystalline Si-I after the anneal. No significant microstructural differences in the phase transformed zones formed by the large and small indenters can be observed from this TEM (see selected area diffraction patterns). Similar microstructure is observed for indents made in an a-Si matrix (not shown here).
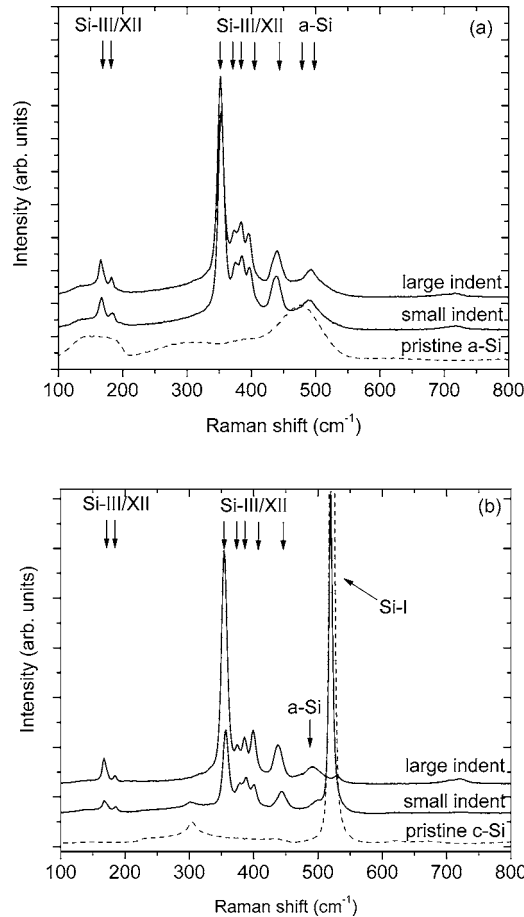
FIG. 3. (a) Raman spectra of pristine relaxed a-Si, a small indent made in a-Si, and a large indent made in a-Si. The load was 80 mN in the case of the small indent and 750 mN in the case of the large one. Extra peaks associated with Si-III/XII are observable in the spectra taken from the indents. (b) Raman spectra of pristine c-Si, a small indent made in c-Si, and a large indent made in c-Si.

FIG. 4. Raman spectra from indentations made in a-Si and annealed at 200 °C for times of 6 to 10 100 min. (a) Small indents made in a-Si. (b) Large indents made in a-Si. The peaks associated with Si-III and Si-XII diminish with annealing time. Extra peaks associated with Si-XIII and Si-IV are observed for intermediate annealing times. The peaks corresponding to Si-III/XII and Si-XIII and Si-IV are no longer present after annealing is complete.

those in a-Si here. Although peaks from intermediate phases (Si-XIII and Si-IV) are visible for the indents in c-Si, compared with an a-Si matrix, it is more difficult to monitor peaks closer to 521 cm^{-1} where there is a large peak originating from the surrounding Si-I. Three changes can be observed by Raman during annealing: (1) the peaks associated with Si-III/Si-XII diminish, (2) a peak corresponding to Si-I at ~520 cm^{-1} appears and grows, and (3) new peaks associated with intermediate phases appear and then diminish again with annealing time. For example, for annealing at 200 °C, small peaks at ~202, ~333, ~478, and possibly 500 cm^{-1} emerge during annealing. These peaks are more visible in the Raman spectra taken from the large indents [Figs. 4(b) and 5(b)]. The final spectrum for each indent type shows the final structure of the phase transformed zone following annealing, i.e., further annealing did not further modify the spectrum. For these spectra no peaks associated with Si-III/Si-XII are visible, no peaks associated with intermediate phases are visible, and a peak at ~520 cm^{-1} corresponding to Si-I is visible. The peak corresponding to Si-I has either a broad a-Si peak next to it at lower wave numbers (small indents in a-Si) or has a broad shoulder on the low wave number side for the larger indents (possibly a-Si or highly disordered Si-I).
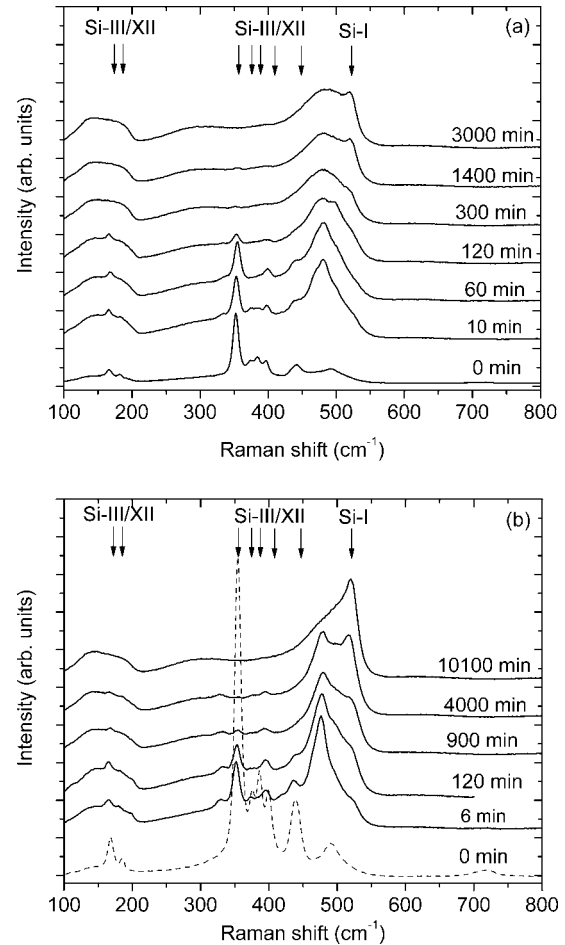
In Fig. 6 the spectrum of an unannealed large indent in a-Si and of an indent annealed for 60 min at 200 °C (incomplete annealing) is shown and the peaks indicating different phases are labeled accordingly. New peaks at 202, 333, and 478 cm^{-1} are visible. Previously peaks at 202, 333, and 478 cm^{-1} have been assigned to Si-XIII.[17] The region from 400–550 cm^{-1} can be decomposed into three peaks at 478, 500, and 518 cm^{-1}. The peak at 518 cm^{-1} corresponds to Si-I, the peak at 478 cm^{-1} has been assigned to Si-XIII, but it is more difficult to assign a phase corresponding to the peak at 500 cm^{-1}. The reason for that will be explored in more detail below.

Examination of the ratio of peak intensities in the Raman spectra provides an estimation of the volume ratio of the respective phases associated with the peaks. In principle, this could be used to track the evolution of the ratios with annealing time which in turn may be used to determine the exact sequence of phase transformations during annealing. However, this proved to be difficult here due to the limited number of spectra containing all peaks (that are discernable from the background) corresponding to starting phases, intermediate phases, and Si-I. The only clear ratio that could be
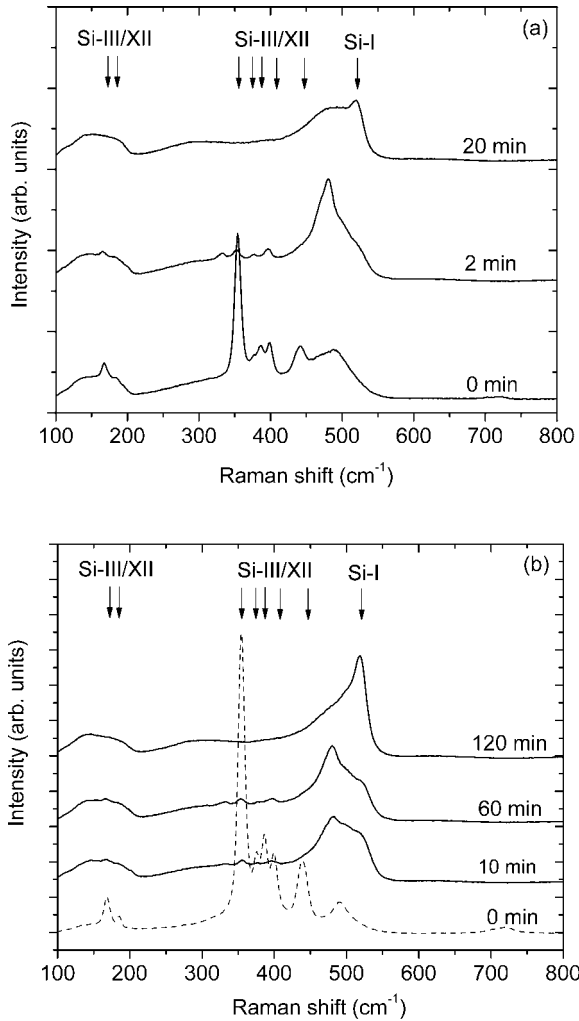
FIG. 5. Raman spectra from indentations made in a-Si and annealed at 280 °C for times of 2–120 min. (a) Small indents made in a-Si. (b) Large indents made in a-Si. The peaks associated with Si-III and Si-XII diminish after long annealing times. The peak at 330 is visible for the small as well as for the large indent and there is a large peak at 475 too. Extra peaks associated with Si-XIII and Si-IV are observed for intermediate annealing times. The peaks corresponding to Si-III/XII are no longer present after annealing is complete.

extracted was the volume of Si-III to Si-XII (peaks at 438 and 353 cm^{-1}, respectively). This ratio, as a function of time for annealing at 200 °C, is shown in Fig. 7. The case of the all indents in a-Si and the large indents in c-Si, this ratio decreases with increasing annealing time indicating that the ratio of Si-III to Si-XII decreases. For most annealing times and temperatures in this study, it is difficult to extract such detailed data for all temperatures, but in all cases the Raman peaks associated with Si-III diminish sooner than those corresponding to Si-XII or Si-XIII. Interestingly, in the previous study this ratio appeared to increase with annealing time.[21]

IV. DISCUSSION

A. Annealing kinetics

We will first discuss the kinetics of the overall phase transformation from Si-III/Si-XII to Si-I then return to the exact phase transformation pathways later in this section. Over the temperature range studied here, the time for the
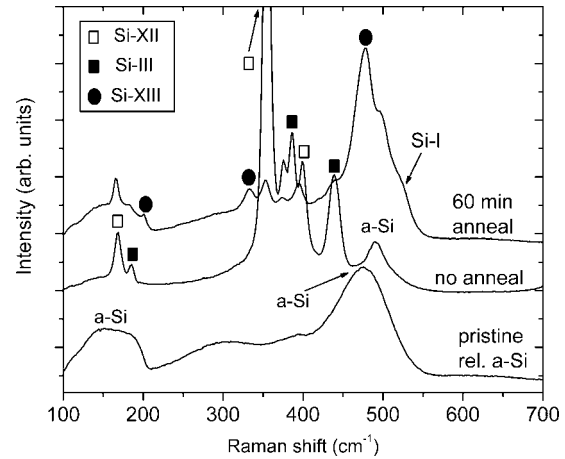

FIG. 6. Raman spectra of pristine relaxed a-Si, an unannealed large indent, and a large indent annealed for 60 min at 200 °C. The indentations were performed using the ~17.7 μm spherical indenter applying a maximum load of 750 mN. The peaks associated with Si-III, Si-XII, and Si-XIII are labeled.

Si-III/Si-XII to Si-I phase transformation shows an exponential dependence on annealing temperature. The data also show that, for small indentations, the zones of Si-III/Si-XII created in a-Si are more thermally stable than those created in c-Si. Furthermore, the large indents are more stable than the small indents and for these cases the form of the surrounding Si matrix has less of an influence on the subsequent annealing kinetics.

In terms of interpreting the annealing kinetics, the following observations are relevant. To date, comparison of TEM measurements of indents has not revealed any significant microstructural differences between identical indents made in the two materials (see Fig. 2) but more detailed studies are underway.[25] Regardless of indent size or the surrounding matrix, the Si-III to Si-XII ratio did not vary significantly from 0.2 for indents before annealing (Table I). However, careful inspection of the Raman spectra extracted from a series of unannealed indents made in a-Si and c-Si reveal a difference in residual stress (see Table II) between these two cases. In the case of c-Si all Raman bands are
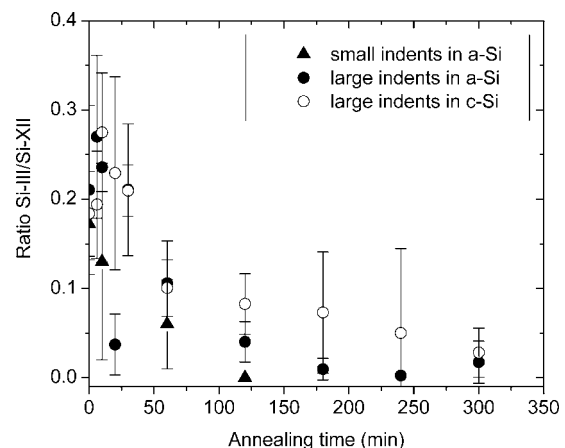

FIG. 7. Development of the ratio of Si-III to Si-XII over annealing time for small indents made in a-Si and large indents made in a-Si and c-Si. All anneals were performed at 200 °C.

shifted toward higher wave numbers compared to a-Si, which indicates a higher residual stress within the transformed zone for those indents.[23] This difference may play a role in determining the annealing behavior. Indeed, Piltz *et al.*[19] modeled the effect of shear stresses on the residual phases formed in silicon. Any variation would be expected to change the subsequent annealing kinetics. Another difference that may play a role is related to the size of the starting Si-III/Si-XII zone. For example, if the surrounding matrix has an effect on the annealing behavior of the phase transformed zone, through, say, preferred nucleation at the interface created by the two, it would be expected that the larger indents would suffer less of an influence from the interface and the surrounding matrix. Various authors studied the size and rate effects on the formation of the high pressure phases and, again, variations in the form of the residual indented zone would be expected to effect the subsequent annealing.[1,2,20] Finally, the annealing kinetics may be sensitive to such differences as we explain below.

In terms of the annealing kinetics depicted in Fig. 1, there are two features that warrant discussion. The first is the lack of stability of Si-III/Si-XII within small indent zones in c-Si, compared with the a-Si matrix and the large indents. As indicated above, the matrix (c-Si) may act to "seed" phase transformation by "nucleation" of the Si-III/Si-XII phase in this case. This is a similar argument to the thermal crystallization of a-Si in contact with Si-I, whereby epitaxial crystallization on the seed crystal occurs much faster than nucleation of polycrystalline Si-I within an a-Si matrix. For the case of large indents, the larger volume-to-crystalline-interface ratio would suggest less sensitivity to interface seeding. The second feature is that the apparent activation energies (i.e., slopes of Arrhenius plots) are substantially different depending on the starting conditions. This would not be expected of an activated process dominated by a single activation energy. Possible explanations may be that there are multiple activated processes involved in the thermally induced transformations, depending on starting state, or that different transformation pathways (each with a dominant activation energy) are favored, again depending on starting conditions. In the former case, for the small zone in c-Si, the surrounding c-Si may lower the activation energy for nucleation such that the transformation kinetics are dominated by a growth term, whereas for the other cases, nucleation may be the rate limiting step. Strain differences between zones in a-Si and c-Si matrices may additionally raise (lower) the activation energy for thermal transformation in these cases. We discuss the second issue of different transformation pathways later.

From the data shown in Fig. 1 alone, it is impossible to determine which process dominates the annealing kinetics of Si-III/Si-XII in each of the cases. A detailed systematic study would be required to investigate each of the above effects.

B. Intermediate phases (Si-XIII and Si-IV)

Before discussion of the thermally induced phase transformation pathways, discussion of the intermediate phases and their peak assignments in the Raman spectra is war-

ranted. All of the Raman spectra taken in this study revealed additional peaks during annealing that eventually disappear after long times. The phases associated with these Raman peaks are discussed in the following paragraphs and can be assigned to Si-XIII and Si-IV.

A number of other studies identified the presence of Si-IV in the Raman spectra with the reported position of a single peak ranging from 500 to 520 cm^{-1}.[17,26,27] Furthermore, the position is reported to be dependent on measurement laser power.[26] Interestingly, the positions of peaks corresponding to other high pressure phases of silicon (e.g., Si-III and Si-XII) are not reported to depend on Raman measurement conditions making it unclear why the peak associated with Si-IV would have this dependency. On closer inspection of the results published by Ge *et al.*[17] an additional peak can be observed at $\sim$497 cm^{-1} on the shoulder of the broad peak at 475 cm^{-1}, which could be attributed to Si-IV. This confusion in the peak assignment for this phase makes it difficult to identify in this study. For small indents in c-Si, this phase was not observed[18] as it is either obscured by the large signal from crystalline Si-I (at 520 cm^{-1}) or from the broad peak at $\sim$480 cm^{-1} from a-Si. For the indents made in a-Si and the large indents made in c-Si here, a peak is observed at 498 cm^{-1} during annealing, which also disappears after long anneal times. This peak does not correspond to Si-III or Si-XII and has not previously been assigned to Si-XIII. We therefore suggest that this peak may be attributable to Si-IV. However, it is never present without the peaks corresponding to Si-XIII (at 202, 333, and 478 cm^{-1}, see next section). Therefore, it is impossible to determine unequivocally whether this is attributed to Si-IV or another peak associated with Si-XIII. Note that the bands at 202, 333, and 478 cm^{-1} have been attributed by Ge *et al.*[17] to a new, previously unidentified phase which they labeled Si-XIII. Evidence in the current study for this phase is observable in some of the spectra obtained from the annealed indents made with the 4.3 μm indenter [see Figs. 4(a) and 5(a)]. For these samples, a peak is clearly observable at 330 and 475 cm^{-1}. All three peaks corresponding to Si-XIII are clearly observed in all of the spectra taken from the large indents [Figs. 4(b) and 5(b)]. Finally, these peaks disappear with continued annealing and thus are not thermally stable.

C. Phase transformation pathways

Before discussing the possible phase transformation pathways that occur during annealing, we summarize the relevant observations from the experiment. During complete annealing the starting phases Si-III and Si-XII transform ultimately to Si-I (poly-/nanocrystalline). After long anneals (defined as those where the Si-III/XII phases are annealed out), the final spectra from the small indents consist of a peak at $\sim$518 cm^{-1} (corresponding to Si-I which may be nanocrystalline[14]) and a broad peak at 481 cm^{-1} (corresponding to a-Si for those made in an a-Si matrix). It has been confirmed by TEM that the resultant Si-I consists of nanocrystalline (or fine grained polycrystalline) material. From the data presented here it is clear that during annealing the Si-III/Si-XII zones transform to Si-I via intermediate

① Si-XII ⎤
  Si-III ⎦ ⟶ Si-XIII/Si-IV ⟶ Si-I

② Si-XII ⟶ Si-XIII/Si-IV ⟶ Si-I
  Si-III ⟶

③ Si-XII ⟶
  Si-III ⟶ Si-XIII/Si-IV ⟶ Si-I

④ Si-XII ⟶ Si-III ⟶ Si-XIII/Si-IV ⟶ Si-I
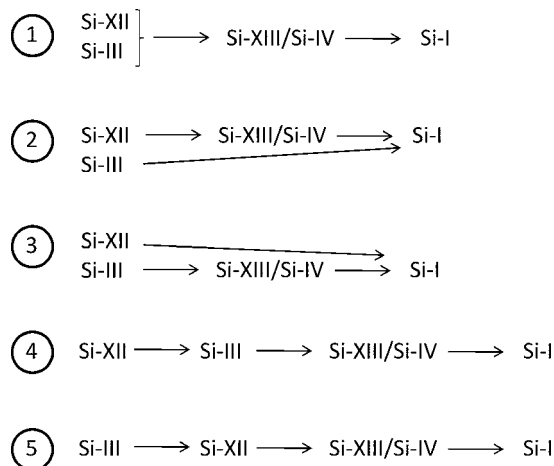
⑤ Si-III ⟶ Si-XII ⟶ Si-XIII/Si-IV ⟶ Si-I

FIG. 8. Transformation pathways that are possible during annealing of the zones of Si-III/Si-XII.

phases, i.e., Si-XIII and Si-IV. The peaks associated with these latter phases appear in the Raman spectra when the Si-III and XII phases anneal out and they in turn anneal out to the Si-I end state. Finally, the ratio of Si-III to Si-XII decreases with annealing time indicating two possibilities: one, Si-III transforms to Si-XII during annealing or, two, Si-III transforms to other phases (Si-I, Si-XIII, Si-IV) at a greater rate than Si-XII.

Based on results from annealing experiments of samples formed in diamond anvil cells, where Si-XII transforms first to Si-III, which in turn transforms to Si-I,[20] the sequence Si-XII→Si-III→Si-XIII/Si-IV→Si-I would seem the most likely transformation pathway for the indentation case. Evidence for Si-XIII or Si-IV was not observed in the diamond anvil experiments but for the case of zones of Si-III/Si-XII created by nanoindentation, high deviatoric stresses remain in the sample. These could be responsible for the formation of intermediate phases during annealing of the indentation cases. In a nanoindentation study by Ge *et al.*,[17] where TEM specimens were heated, they suggested the following transformation sequence: Si-XII→Si-III→Si-XIII→Si-IV or a-Si→Si-I. However, it seems unlikely that a-Si crystallizes to Si-I at these low temperatures (<300 °C).

Figure 8 shows a list of possible phase transformation pathways based on our observations. Scenario 1 seems unlikely based on diamond anvil experiments, since Si-XII (present in small volumes within Si-III) transforms to Si-III first before further transformation to Si-I. Also, based on the same results, scenario 3 seems unlikely as the intermediate phases (Si-XIII/Si-IV) are rarely observed in diamond anvil experiments even though the starting material is nearly 100% Si-III, whereas only ~20% of the starting material is Si-III in the indentation case. Additionally, scenario 5 is again unlikely since a Si-III to Si-XII transformation is inconsistent with diamond anvil results. Finally based on current results and previous diamond anvil work, scenarios 2 and 4 seem the most likely transformation pathways for the indentation annealing studies. Scenario 4 would be in agreement with the diamond anvil results, with the increased volumes of intermediate phases during annealing of indentation samples attributed to the stresses that remain in the indented material.

Scenario 2 could also be plausible as substantial volumes of Si-XIII and Si-IV observable in the indentation case could be a result of the increased volume of Si-XII compared to that in diamond anvil samples. Furthermore, the phase transformation may proceed through a combination of these two pathways with the dominant path being determined by the starting conditions (zone size and surrounding matrix). If there were two appropriate pathways (or if a combination of scenarios 2 and 4 is operative), the difference in activation energy observed between the small and large indent zones and between the small zones in an a-Si and c-Si matrix could be explained with this model.

A way to determine the phase transformation pathway during annealing would be to track the ratio of all combinations of peaks associated with the starting phases, intermediate phases, and Si-I. However, this proved to be impossible in the present case for a number of reasons. For example, for all of the annealing temperatures, a large number of anneal times would be needed in order to collect accurate time resolved data for the evolution of the intermediate phases such as Si-XIII. Moreover, the peaks associated with Si-III, Si-XIII, and Si-I are not intense enough, as they are superimposed on a large Raman background and/or neighboring peaks.

V. CONCLUSION

The evolution of phase transformed zones of silicon containing Si-III and Si-XII during low temperature ($200 < T < 300$ °C) thermal annealing has been studied by Raman microspectroscopy and TEM. The effect of the starting silicon matrix and volume of the zone on the annealing kinetics has been investigated by indentation in both relaxed ion-implanted a-Si and c-Si using two indenters, which create substantially different sized phase transformed zones.

The overall transformation is from Si-III/XII to polycrystalline Si-I. Furthermore, this phase transformation proceeds through intermediate phases, which are observed as additional peaks in the Raman spectra (Si-XIII/Si-IV). It is possible that Si-XII first transforms to Si-III before transforming through the intermediate phases to Si-I but a scenario in which Si-III goes directly to Si-I but Si-XII goes first to the intermediate phases before transforming to Si-I is also possible. Residual stresses in the indentation case may be the reason intermediate phases are observed in contrast with the diamond anvil case.

The larger phase transformed zones and the small zones in an a-Si matrix are more thermally stable than small zones in a c-Si matrix. We suggest that the crystalline matrix "seeds" the crystallization of Si-III/XII to Si-I such that the smaller indents in the crystalline Si matrix, where the c-Si interface area to Si-III/Si-XII volume is highest, will transform most easily. A combination of phase transformation pathways may also contribute to differences in apparent activation energies observed, with the dominant pathway (depending on the starting conditions) determining the measured activation energy.

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