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Cite as: J. Appl. Phys. **126**, 105901 (2019); <https://doi.org/10.1063/1.5108751>

Submitted: 02 May 2019 . Accepted: 19 August 2019 . Published Online: 09 September 2019

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Submitted: 2 May 2019 · Accepted: 19 August 2019 ·

Published Online: 9 September 2019

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ABSTRACT

Novel phases of Si that are predicted to have industrially desirable properties can be recovered after indentation-induced pressure. However, the thermal stability of these phases is not well understood. Furthermore, in the past, different methods of annealing have resulted in conflicting reports on annealing stability and transformation pathways. This study investigates the thermal stability of several metastable Si phases called r8-Si, bc8-Si, hd-Si, and Si-XIII under furnace annealing, incremental annealing, and laser annealing using Raman microspectroscopy and electron diffraction. The temperature range of stability for these metastable phases is thus determined. Of particular interest, hd-Si is stable to a much higher temperature than previously reported, being the predominant phase observed in this study after annealing at 450 °C. This finding was enabled through a new method for confirming the presence of hd-Si by detailed electron diffraction. This high thermal stability generates renewed interest in exploiting this phase for industrial applications, such as strain-tailored solar absorption.

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I. INTRODUCTION

The metastable phase diagram of silicon (Si) has attracted much attention as many of these metastable phases of Si have displayed technologically interesting properties.^{1–7} These metastable structures are crystalline phases that can be recovered to ambient conditions but are not at the lowest-energy state, which is diamond-cubic (dc) Si. For example, the rhombohedral phase (r8) is predicted to be a narrow bandgap semiconductor with far greater absorption than the diamond-cubic (dc) phase across the solar spectrum.^{2,8} The body-centered cubic phase, bc8-Si, is expected to be highly useful for solar power conversion in the form of a hydrogenated nanoparticle.⁴ Furthermore, the application of strain to the hexagonal diamond phase (hd) has also been predicted to be an effective way to tailor its absorption to be more favorable to solar absorption.³ However, despite the clear potential of these phases in many future applications, their thermal stability is often not known or poorly understood. This clearly limits any potential application, as

technological silicon processing typically requires several hundred degrees Celsius.

In fact, the thermal stability of even these more conventional metastable silicon phases, bc8-Si, r8-Si, and hd-Si, that can be readily made in a diamond anvil cell (DAC) or by the indentation is not well characterized. In a DAC, dc-Si undergoes a phase transition to the metallic phase (β -Sn)-Si (space group $I 4_1/a m d$) at ~ 11 GPa.^{9,10} Upon slow pressure release, (β -Sn)-Si transforms to r8-Si (space group $R \bar{3}$) at ~ 9 GPa,^{11,12} which further transforms to bc8-Si (space group $I a \bar{3}$) at ~ 2 GPa. This phase is kinetically stable after total pressure release.¹³ Subsequent furnace annealing of the bc8-Si formed in a DAC yields a transition to hd-Si (space group $P 6/3 m c$) at a temperature of 200 °C before returning to dc-Si at a temperature of 750 °C.¹⁴ In indentation studies, dc-Si undergoes a similar phase transformation to β -Sn on loading,^{15,16} but the transition has been reported to have a lower critical pressure due to the presence of shear stress that varies with the indenter tip geometry.^{17,18} However, upon

pressure release, β -Sn formed via the indentation transforms directly to a bc8/r8 composite material at ~ 5.7 GPa.¹⁹ Both phases remain after total pressure release, with a recent spherical indentation study showing the final composite composed of 70% r8-Si due to a unit cell volume reduction in the material resulting from uniaxial, nonhydrostatic pressure release.²⁰ Annealing of the bc8/r8 composite causes a transformation pathway that ends in dc-Si,²¹ but there is no consensus on the exact pathway, nor the critical temperatures required for the formation of the intermediate phases such as hd-Si. At least one other phase exists, so-called Si-XIII with an as yet unidentified crystal structure,^{22,23} which forms during thermal annealing. Besides the difference in transformation pathways, the indentation also differs from DACs in the geometry of a transformed material. While the material formed via DACs or also multianvil presses is limited in their geometry to a solid round pellet, large arrays of indentations can be made that result in a thin film of metastable Si on a standard silicon wafer. Thus, the bc8/r8 composite formed via indentation (and the phases subsequently formed via annealing) is readily exploitable for technological applications. While the transition temperatures between these phases are of vital importance, there is no consensus in the literature for when these transitions occur, if they occur at all.

For example, Ge *et al.* investigated the annealing of the bc8/r8 composite material made by the indentation using an *in situ* transmission electron microscopy (TEM) hot stage. This work showed a transition from bc8/r8 to Si-XIII at ~ 150 °C. A subsequent transformation to hd-Si occurs at 200 °C followed by a transformation to dc-Si at 600 °C.²² However, Ruffell *et al.* observed the presence of hd-Si alongside Si-XIII after furnace annealing at 200 °C. They further suggested that, based on Raman spectroscopy data, the transition from hd-Si to dc-Si can occur at temperatures as low as 200 °C, provided annealing times are sufficiently long.²¹ Equally based on Raman analysis, Zeng *et al.* reported that laser annealing of bc8/r8 can cause a rapid bc8/r8 to dc-Si transition within 1 s at 320 °C. This temperature was calculated by observing the temperature dependent shift of the main dc-Si Raman peak at 521 cm^{-1} . They further noted that prolonged laser exposure at 730 °C yielded recrystallization from nanocrystalline to single-crystal dc-Si. It has been suggested that the variability in the reported results for the transformation pathway and transition temperature is due to differences in the annealing method.²⁴

In this study, we present furnace annealing, ramped annealing via heater stage, and laser annealing results of the indentation-induced bc8/r8 material. *In situ* Raman spectroscopy is used to map the evolution of the phases during annealing, and *ex situ* cross-sectional transmission electron microscopy (XTEM) is used to unambiguously confirm the presence or absence of phases that are not discernible solely by Raman spectroscopy. We demonstrate that, while the heater stage/furnace annealing and laser annealing lead to slight differences in the transformation pathways, both Si-XIII and hd-Si are present within both pathways. We further demonstrate that the temperature range in which hd-Si is stable is significantly wider than previously reported and aligns more with diamond cell observations.

II. EXPERIMENTAL METHODS

Indents were formed in Czochralski grown Si (100) wafers, p-doped with boron to a resistivity of $8\text{--}10\ \Omega\text{ cm}$ using an Ultra-Micro-Indentation-System 2000 equipped with a $\sim 17\ \mu\text{m}$

radius spherical indenter tip. 5×2 arrays of single cycle indents with $50\ \mu\text{m}$ separation were performed to a maximum load of 700 mN with the unloading performed in 200 increments (average unload rate $\sim 1.3\text{ mN s}^{-1}$). No hold duration was included during the indentation. This ensured that a pop-out event occurred on unloading, indicating that the phase transformed zone [of size around $10\ \mu\text{m}$ in diameter with a maximum depth of 400 nm as indicated in Fig. 1(a)] contained the bc8/r8 composite.^{15,21,25}

For the Raman measurements, the 532 nm line of a frequency doubled Nd:YAG laser was focused onto the sample with a confocal microscope in a backscattering geometry. Great care was taken not to anneal the metastable phases with the Raman laser, and, thus, the laser power was kept very low at 13 kW cm^{-2} . Note that problems with laser annealing prevented us from using a laser with a shorter wavelength (and hence a lower penetration depth) for this experiment. A long working distance $50\times$ objective lens resulted in a $\sim 4\ \mu\text{m}$ laser spot size and was used for all measurements. This laser spot is smaller than the overall extent of the phase transformed volume of metastable Si phases. Spectra were collected with a Renishaw InVia Reflex 0.25 working distance micro-Raman spectrometer with a 2400 grooves/mm grating. The overall wave number uncertainty was estimated to be $\pm 0.5\text{ cm}^{-1}$. The reported Raman frequencies for the phases of Si observed after indentation and subsequent annealing are given in Table I.

In a recent study, the current authors showed that the Raman spectra of the bc8/r8 composite material recovered after indentation were best fit with density functional theory (DFT) calculations that took into account a reduction in unit cell volume due to residual stress.²⁰ Calculations using the same method are performed in this study for dc-Si and hd-Si to produce a self-consistent set of DFT data for comparison with the experimentally observed peak positions. Calculations were performed using the pseudopotential and plane waves method of calculation, as implemented in the VASP DFT code.^{26,27} The outermost 3s and 3p valence electrons of the Si atoms were dealt with explicitly in the calculations (while the inner 1s, 2s, and 2p electrons were considered frozen at the core) within a projector augmented-wave (PAW) scheme^{28,29} and a generalized gradient approximation for the exchange-correlation functional³⁰ using a kinetic-energy cutoff in the plane wave expansions of 320 eV. The calculations correspond to zero hydrostatic pressure and temperature, with the small effect of zero-point motion neglected. The DFT calculated peak positions (from this study and Ref. 20) are also given in Table I.

A Linkam temperature stage (THMS600) with a quartz window was used to heat the indented sample from 20 to 240 °C in 10 °C increments in a flowing N_2 atmosphere. *In situ* Raman spectra were taken with an exposure time of 200 s at each temperature. This ramped anneal can be approximated by a constant heating rate of 0.03 °C s^{-1} . *Ex situ* furnace annealing was performed at a temperature of 240 °C, 450 °C, and 750 °C in a N_2 atmosphere for two hours in a tube furnace. Samples were loaded/unloaded in less than 1 min; thus, any incidental annealing during the loading is negligible. *In situ* laser annealing was also performed in the Raman system detailed above using a $50\times$ objective lens at a laser power of 400 kW cm^{-2} . During laser annealing, the beam was raster-scanned across the sample at a speed of $1\ \mu\text{m s}^{-1}$. This ensured that the transformed zone was relatively homogeneous

FIG. 1. (a) A typical BF TEM image of the transformed region. The central region is brighter as it has been further thinned than the outer regions. SADPs were taken from the thinned central region. The circle indicates the size and general positioning of the select area aperture used for all SADP shown in this study. (inset) A typical SEM image of the residual impression after indentation. SADPs from indents furnace annealed to (b) 240 °C, (c) 450 °C, and (d) 750 °C. The observed reflections can be associated with either hd-Si (yellow) or both hd-Si and dc-Si (green). The d -spacing associated with nanocrystalline dc-Si displays a characteristic spotty ringlike structure.

for subsequent characterization. Raman spectra were collected *in situ* to observe the shift in Raman peaks due to annealing as well as *ex situ* at a laser power of 13 kW cm^{-2} , which is low enough to not modify the sample.

TABLE I. The experimentally reported Raman frequencies associated with the Si phases (dc-Si, bc8-Si, r8-Si, hd-Si, Si-XIII) observed after indentation-induced phase transformation and subsequent annealing. The DFT modeled positions and phonon modes are also presented. The values for hd-Si and dc-Si are at ambient pressure, as calculated for this study. The bc8-Si and r8-Si values are from Ref. 20, which are experiencing a compressive indentation-induced residual stress as described therein. The most prominent frequency for each phase is in bold.

Phase	Raman shift (experimental)	Reference	Raman shift (DFT)	Phonon
dc-Si	302	31		
dc-Si	520	31	509	T_{2g}
bc8-Si	182	32	163	T_g
bc8-Si	373	32	379	A_g
bc8-Si	384	32	380	T_g
bc8-Si	438	20	425	T_g
bc8-Si	463	32	467	E_g
r8-Si	165	32	166	A_g
r8-Si	170	32	171	E_g
r8-Si	352	32	348	A_g
r8-Si	373	32	379	E_g
r8-Si	397	32	400	A_g
r8-Si	413	20	435	E_g
r8-Si	433	20	435	A_g
r8-Si	495	20	502	E_g
hd-Si	496	33	492	E_{2g}
hd-Si	514	33	505	A_{1g}/E_{1g}
Si-XIII	200	22		
Si-XIII	330	22		
Si-XIII	475	22		
Si-XIII	497	22		

After annealing, samples were prepared for cross-sectional transmission electron microscopy (XTEM) using a FEI Helio 600 NanoLab dual-beam focused ion beam (FIB) system. A Pt protective layer is deposited over the indent via an electron beam and then an ion beam before any ion beam milling is performed to minimize the unwanted ion beam amorphization of the sample surface. Bright-field images and selected electron diffraction pattern (SADP) results were collected using a Philips CM 300 operating at an accelerating voltage of 300 kV. As several phases have d -spacings within close proximity to one another, care was taken that the reflections observed in SADP were correctly attributed. Table II lists the reported d -spacing for phases commonly found in indented Si from Ref. 23. The highlighted d -spacings are the ones used in this study to positively identify the presence of their respective phases. Due to the reciprocal nature of SADPs, the uncertainty is increased for the reflections with a larger d -spacing (i.e., $\pm 0.1 \text{ \AA}$ is used for the $4.4 \text{ \AA}$ and $4.8 \text{ \AA}$ d -spacings, whereas $\pm 0.05 \text{ \AA}$ is used for the others).

III. RESULTS

A. Furnace annealing

Figure 1 shows typical SADPs taken from three indents that were furnace annealed to 240 °C, 450 °C, or 750 °C. No significant

TABLE II. The reported d -spacings associated with the Si phases (dc-Si, bc8-Si, r8-Si, hd-Si, Si-XIII) observed after indentation-induced phase transformation and subsequent annealing (from Ref. 23). The most characteristic spacings for each phase are in bold and are used in this study to positively identify the presence of their respective phases. No hkl values are given for Si-XIII as the crystal structure is as yet unknown. The r8-Si phase is listed here for completeness, but it was not observed in the SADPs presented in this study.

dc-Si		bc8-Si		hd-Si		r8-Si		Si-XIII	
hkl	d -spacing (Å)	hkl	d -spacing (Å)	hkl	d -spacing (Å)	hkl	d -spacing (Å)	hkl	d -spacing (Å)
111	3.13	110	4.70	100	3.29	1 $\bar{1}$ 0	4.59	N/A	5.6
220	1.92	200	3.32	002	3.14	100	4.49	N/A	4.8
311	1.64	211	2.71	101	2.91	11 $\bar{1}$	3.21	N/A	4.4
400	1.36	220	2.35	102	2.27	11 $\bar{2}$	2.65		
		321	1.77	110	1.90	20 $\bar{1}$	2.63		
		400	1.66	103	1.77	110	2.57		
				200	1.65	21 $\bar{3}$	1.74		

difference in the d -spacing was observed between patterns taken from the same sample. A careful analysis of the SADP taken from the indent annealed to 240 °C, shown in Fig. 1(b), shows that the reflections around the first a-Si ring (which arises most likely from ion beam milling and is centered on ~ 3.13 Å) do not belong entirely to the commonly observed 3.13 Å d -spacing representing the (111) reflection of dc-Si. Instead, the most prominent reflections around this d -spacing lie on two distinct rings. There are two different d -spacings present, one at 3.25 Å and one at 2.95 Å, both of which correspond to hd-Si (in bold in Table II). Reflections are also observed at 3.15 Å, 1.90 Å, and 1.65 Å but such reflections cannot be positively identified as either hd-Si or dc-Si as both phases have reflections at this d -spacing.

Figure 1(c) shows a SADP taken from an indent furnace annealed to 450 °C. Around the first a-Si ring, d -spacings of 3.25 Å, 3.15 Å, and 2.95 Å are observed. The presence of reflections with more than one d -spacing around the first a-Si ring confirms the presence of hd-Si. The other reflections at 1.90 Å and 1.65 Å can be attributed to either dc- or hd-Si.

Figure 1(d) shows a SADP taken from an indent annealed to 750 °C. At this temperature, instead of a small number of diffuse reflections at each d -spacing, a larger number of sharper reflections begin to form spotty rings at each d -spacing. This suggests that we have obtained a nanocrystalline material with a larger number of differing orientations. These spotty rings are at a d -spacing of 3.15 Å, 1.90 Å, and 1.60 Å. Further, the reflections at 3.25 Å and 2.95 Å that are characteristic of hd-Si are no longer present, indicating that hd-Si is no longer present in the sample. We suggest that such spotty rings, with many individual reflections at each d -spacing, are indicative of nanocrystalline dc-Si in the transformed region.

It should, however, also be noted that the bc8, r8, and hd-Si formed via indentation and subsequent annealing are also polycrystalline. This raises the question, why have such spotty rings, the characteristic of a reasonably good powder, not reported for any other phase? We suggest that these phases form with a preferred orientation due to point loading.²⁰ Such a preferred orientation leads to fewer observed reflections in SADPs. Further, the high temperature at which the nanocrystalline dc-Si is formed here allows for greater relaxation of the sample leading to a less defective material. Thus, the reflections from the nanocrystalline dc-Si are sharper and reflections that would not be clearly observed in a more defective material can be seen.

While many reflections are observed around the 3.15 Å region after annealing at 450 °C [Fig. 1(c)], these reflections are attributed to three separate d -spacings, with each spacing having only a few reflections. Further, the diffuse nature of the reflections is far more comparable to the reflections observed in Fig. 1(b) than the reflections observed in Fig. 1(d). This suggests that at 450 °C, hd-Si is the predominant phase and no substantial transformation to nanocrystalline dc-Si has begun.

Figure 2 shows the corresponding Raman spectra of indents annealed at 240 °C, 450 °C, and 750 °C. Twenty indents were measured for each temperature, with representative spectra presented. All spectra show features on the low wave number side of the TO single-crystal dc-Si peak at 521 cm⁻¹. This can be attributed to a number of different phases, which include hd-Si, Si-XIII, and nanocrystalline dc-Si. For the 240 °C annealed sample shown in Fig. 2(a), three curves are required to fit the spectra between 450 and 550 cm⁻¹ accurately. This includes a peak we attribute to a dc-Si signal arising from the substrate (discussed further below) and peaks at 479 cm⁻¹ and 513 cm⁻¹. The peak at 513 cm⁻¹ is associated with hd-Si. The peak at 479 cm⁻¹ may be attributed to either a Si-XIII peak at 475 cm⁻¹, the secondary hd-Si peak at 492 cm⁻¹, or a broad a-Si peak at 480 cm⁻¹. The peak is most likely to originate from a-Si, which can be confirmed to be present in the sample due to the presence of broad peaks associated with a-Si in the <200 cm⁻¹ range. The width of the hd-Si peak at 512 cm⁻¹ is much broader than previously observed for hd-Si spectra³³ and indicates a poorer crystal quality. A similar result is observed from the sample annealed to 450 °C shown in Fig. 2(b), with a peak at 490 cm⁻¹ that is most probably attributed to a-Si and a peak at 511 cm⁻¹ that is indicative of hd-Si, which is consistent with the observation from the SADP that indicated that no substantial transformation to nanocrystalline dc-Si has begun. The peaks in the 750 °C annealed sample spectrum shown in Fig. 2(c) also show several peaks in the 450–550 cm⁻¹ range, but at a much-reduced intensity for all but the main dc-Si peak. This suggests that a full transformation to dc-Si has occurred. This spectrum also contains a peak at 519 cm⁻¹, which we attribute to nanocrystalline dc-Si rather than hd-Si due to the observation in the corresponding SADP [Fig. 1(d)] of spotty nanocrystalline dc-Si reflections and the absence of characteristic hd-Si reflections. This is expected, as hd-Si and Si-XIII transform to nanocrystalline dc-Si before returning to single-crystal dc-Si.

FIG. 2. Raman spectra taken from an indented region annealed at (a) 240 °C, (b) 450 °C, and (c) 750 °C for two hours (grey-dotted) with the peaks fitted (black). The peaks (red) have been offset for clarity and the peaks in the 450–550 cm^{-1} region of interest has been labeled (cm^{-1}). (inset in b) The difference spectrum between the 750 °C and 450 °C spectra, indicating a clear hd-Si Raman signal at 511 cm^{-1} after annealing at 450 °C that is not observed after the higher temperature anneal.

Interestingly, the peak at 512 cm^{-1} may suggest that, even though the SADP at this temperature shows predominantly dc-Si, trace amounts of hd-Si still remain. However, the results indicate that hd-Si is not kinetically stable at 750 °C and this trace would most likely be removed after a longer anneal at this temperature.

B. Heat stage annealing

Figure 3 shows Raman data collected from the samples annealed via heat stage. Figure 3(a) indicates previously reported peak positions taken from experimental data of the Si phases (black) and the peak positions calculated using DFT in this study and in Ref. 20 (red) as shown in Table I. There is in agreement with the previously reported peak positions for hd-Si and the positions calculated via DFT for hd-Si under no residual stress. This suggests that the residual stress that results in a volume reduction in the bc8/r8 composite material after indentation is relaxed during the transformation to hd-Si.

Figure 3(b) shows Raman spectra collected at room temperature after anneals in the 20–240 °C range. Before commenting on the phase present in the indented region, the detection of the main dc-Si peak will be discussed as it is not expected within the transformed region. The main peak for dc-Si can be seen at 520 cm^{-1} at

FIG. 3. (a) The experimentally reported Raman peak position for each phase (black) alongside the peak positions as calculated using DFT (red) in this study and in Ref. 20. (b) Raman spectra of an indented sample measured at room temperature after anneals at 20–240 °C in 10 °C increments. The bottom-most spectrum in the series (i.e., highest temperature) was from an indent annealed at 240 °C. A dc-Si spectrum is shown for comparison (dashed line). (c) The bc8/r8 intensity ratio calculated from the 353 cm^{-1} (r8) and 437 cm^{-1} (bc8) peaks as a function of anneal temperature extracted from (a). (inset) The spectrum after annealing at 100 °C, showing a peak at 475 cm^{-1} (red arrow) associated with Si-XIII.

all temperatures. When using a lower wavelength excitation laser or a higher numerical aperture objective, this peak reduced in intensity. Thus, this dc-Si peak most probably originates from the dc-Si below the transformed region.

Before annealing, the main Raman line for bc8- and r8-Si can be seen at 437 cm^{-1} and 353 cm^{-1} , respectively. Upon annealing, these lines are slowly replaced by lines in the 450 cm^{-1} – 550 cm^{-1} range, which may be attributed to either hd-Si or Si-XIII. The intensity ratio between the 353 cm^{-1} r8 peak and the 437 cm^{-1} bc8 peak as a function of anneal temperature is presented in Fig. 3(c). The ratio remains constant below 100°C , while above this temperature, the 353 cm^{-1} peak decreases at a faster rate. This confirms that these two peaks are from different phases since they have a different dependence on temperature. It also suggests that transformation out of the bc8/r8 composite material occurs at 100°C , with r8-Si transforming at a greater rate than bc8-Si. The Raman spectrum after annealing at 100°C [shown in the inset of Fig. 3(c)] has a peak at 475 cm^{-1} which is associated with Si-XIII, suggesting r8-Si transforms to Si-XIII at this temperature. Due to the overlap of the hd-Si and Si-XIII Raman peaks in the 450 cm^{-1} – 550 cm^{-1} range, we now turn to TEM to investigate the phases present after incremental annealing to 240°C .

Figure 4(a) shows SADP taken from the indent after incremental annealing to 240°C [bottom spectrum in Fig. 3(b)] within 1 day of the initial thinning. The presence of diffuse reflections at

FIG. 4. SADPs from an indent after incremental anneal to 240°C (a) 1 day after thinning and (b) 20 days after thinning. The observed reflections can be associated with either hd-Si (yellow), both dc-Si and hd-Si (green), or Si-XIII (red).

both 3.15 Å and 3.25 Å indicates the presence of hd-Si, as established above. There are also reflections at d -spacings of 4.4 Å and 4.7 Å , which indicate the presence of Si-XIII. Another SADP was taken from the same area 20 days after the initial thinning [shown in Fig. 4(b)]. In this SADP, the Si-XIII reflections are no longer observable and the ring at 3.15 Å has broadened, representing the conversion of Si-XIII to disordered dc-like Si after thinning.

C. Laser annealing

Figure 5(a) shows a Raman spectrum taken from a sample after laser raster annealing. Raman peaks at 353 cm^{-1} and 437 cm^{-1} , associated with bc8- and r8-Si, remain present after annealing. Broad peaks associated with a-Si can also be observed in the $<200\text{ cm}^{-1}$ range. Importantly, multiple peaks are observed within the 450 – 550 cm^{-1} range, indicating intermediate phases are present after laser annealing. Peaks at 475 cm^{-1} , 485 cm^{-1} , 500 cm^{-1} , and 520 cm^{-1} are present. Figure 5(b) shows a SADP that was taken from the same indented region. Reflections at 4.4 Å , 2.95 Å , and 2.70 Å indicate the presence of Si-XIII, hd-Si, and the bc8-Si respectively, as

FIG. 5. (a) Raman spectrum and (b) SADP taken from an indented region after laser raster annealing. A Raman spectrum taken from an as-indented sample (dotted line) has been included for reference. The reflections observed in the SADP can be associated with either hd-Si (yellow), Si-XIII (red), or bc8-Si (orange).

these d-spacings are unique to their respective phase. This confirms that, at lower laser power, the intermediate hd-Si and Si-XIII phases can indeed be formed.

During the laser annealing, the position of the main r8-Si peak at $\sim 350\text{ cm}^{-1}$ was measured. This was compared against the shifts observed in the *in situ* anneal Raman measurements with the heat stage to calculate an equivalent thermal annealing temperature. Based on this, the temperature was estimated to be between 40 and 60 °C during the laser anneal. A temperature can also be calculated using the shift of the main dc-Si peak at 520 cm^{-1} and by comparing the ratio between the bc8- and r8-Si peaks as seen in Fig. 3(c). Using the dc-Si Raman peak, a much higher equivalent thermal annealing temperature of 195 °C was calculated. Similarly, when compared to the heat stage anneal ratio shown in Fig. 3(c), the bc8/r8 intensity ratio is equivalent to an anneal temperature of $\sim 190\text{ °C}$. We propose that the discrepancy may be due to differences in the thermal and optical absorption properties of the different phases, which suggests that there is a degree of unreliability between different temperature calculation methods. For example, for the laser heating, one has to consider that the 353 cm^{-1} peak typically has the largest Raman response. Thus, laser heating is also concentrated on the source of the 353 cm^{-1} peak. Consequently, r8 is annealed out more rapidly during laser annealing than bc8, which leads to a ratio that corresponds to a far higher temperature heat stage anneal. Such considerations are not an issue with furnace and heat stage anneals as the entire sample is heated up to the same temperature and sufficient time is given for the phases to reach a stable state. These discrepancies clearly need to be considered when reporting an equivalent temperature under laser annealing.

IV. DISCUSSION

While it is generally accepted that the bc8/r8 composite formed via indentation transitions to an end phase of dc-Si with hd-Si and Si-XIII forming as intermediate phases, the transition temperatures are not agreed upon. Here, we have shown that dc-Si, Si-XIII, and hd-Si are difficult to distinguish through Raman spectroscopy alone, especially when dc-Si is in a nanocrystalline form. However, these phases have distinct characteristics in the TEM SADPs. Thus, both Raman spectroscopy paired with electron microscopy are needed to understand the thermal stability of the bc8-, r8-, hd-Si, and Si-XIII phases. By drawing on both Raman and electron microscopy results, we present a more unified understanding of the thermal stability of the phases present and the corresponding transition pathways below.

A. Furnace annealing

When furnace annealed, we observed that bc8/r8-Si transforms to hd-Si after annealing to 240 °C for two hours. The hd-Si remained stable after annealing at 450 °C for two hours but further transforms to nanocrystalline dc-Si after annealing to 750 °C for two hours. Interestingly, the nanocrystalline dc-Si reflections in the 750 °C sample SADP were not discrete spots as is commonly seen in SADPs of the phases formed via nanoindentation (see below for discussion). Instead, they displayed a characteristic spotty ringlike behavior. This behavior is due to far more crystal orientations being present within the selected area, which is directly linked to the crystallinity of the structure. Thus, these spotty rings act as a clear indicator of the

presence of nanocrystalline dc-Si rather than hd-Si (which exhibits many similar d-spacings to dc-Si). This demonstrates the necessity for the identification of nanocrystalline dc-Si via SADP rather than only via Raman, as the Raman peak shifts of both phases occupy the same shift range. Thus, electron microscopy enables a new insight into the phase evolution upon thermal annealing.

With this new understanding, it is possible to reconsider the previously reported statement that the hd-Si phase transforms completely to nanocrystalline dc-Si at 200 °C.²¹ We suggest that, due to the similarity between the appearance of nanocrystalline dc-Si and hd-Si in Raman and the similarity of dc-Si and hd-Si in SADP, hd-Si had been mistakenly reported as nanocrystalline dc-Si. The broad shoulder on the main dc-Si peak in the 300 °C furnace annealed Raman spectra in Ref. 21 can be attributed to either hd-Si or nanocrystalline dc-Si, but cannot be explained by the presence of single-crystal dc-Si alone. However, in Ref. 21, the SADPs presented of the bc8/r8 composite annealed to 450 °C do not exhibit the characteristic spotty ringlike behavior. Thus, they should be attributed to hd-Si or single-crystal dc-Si but not to nanocrystalline dc-Si. Clearly, the reflections in these SADPs also do not stem from single-crystal dc-Si and thus this strongly suggests that hd-Si is the only phase present in the transformed region at 450 °C. Furthermore, this also implies that the Raman spectra shown upon the full “annealing out” of r8/bc8-Si and Si-XIII at 200 °C most likely consist of pure hd-Si instead of dc-Si as stated previously. Based on electron microscopy [see Fig. 1(c)], hd-Si is still present even after furnace annealing at 450 °C for two hours.

B. Ramped and laser annealing

Conversely, based on Raman spectroscopy, Zeng *et al.* report that laser annealing at 730 °C for 240 s is sufficient for a complete change in the frequency, width, and intensity of the Raman peaks.²⁴ Zeng *et al.* based this on the transition from hd-Si to dc-Si. This is also supported by Ref. 21. However, as discussed above, evidence suggests that hd-Si forms a significant component of the resultant indent after anneals of 240 °C and 450 °C. This is in contrary to these previous reports where the conclusion is based only on Raman results in which hd-Si and nanocrystalline dc-Si appear in the same wavenumber range. In both studies, an asymmetric peak with a lower wavenumber shoulder is observed at 521 cm^{-1} after annealing, which is attributed to a composite of bulk dc-Si (peak at 521 cm^{-1}) with nanocrystalline dc-Si (shoulder). In this study, we have shown that such an asymmetric peak is better fitted by a composite material comprised of bulk dc-Si, hd-Si, and a-Si (as shown in Fig. 1). This interpretation is supported by the observation of the a-Si peaks observed in the 100–200 cm^{-1} range in the Raman spectra presented in Refs. 21 and 24.

In addition to past mislabeling by Ruffell *et al.*, we suggest that there is a further reason that contributes to this significant apparent difference in the reported stability of hd-Si, which is a difference in the heat distribution between furnace and laser annealing. In the present study, the peak ratios of the laser annealed sample are similar to those of a heat stage anneal to $\sim 190\text{ °C}$, in close agreement with the equivalent thermal annealing temperature calculated using the 520 cm^{-1} dc-Si peak. However, the temperature calculated from the temperature dependent peak shift of the 353 cm^{-1} peak is

only 40–60 °C. These discrepancies may in part be correlated to different laser absorption cross sections, particularly for r8-Si as detailed earlier. Similarly, the Raman intensity and thus response to the laser of the peaks associated with hd-Si presented in this study and in Ref. 24 are significantly lower than those of nanocrystalline dc-Si. Thus, the temperature experienced by the hd-Si regions, with its lower laser absorption cross section, may be substantially lower than the dc-Si regions from which the reported laser annealing temperature of 730 °C is calculated. As hd-Si and dc-Si are both semiconductors of similar bandgap, the difference in laser absorption cross section between these two materials could easily be due to the defective nature of the hd-Si initially formed at 200 °C.

Given these two factors, i.e., that the analysis by Zeng *et al.* may have been influenced by Ruffell *et al.*'s misattribution of the hd-Si Raman signal to dc-Si, as well as an overestimation of the annealing temperature experienced by hd-Si under laser annealing, we suggest that the Raman spectra shown in Ref. 24 do not indicate the absence of hd-Si. Instead, hd-Si is present and remains present throughout their annealing as laser heating is concentrated on the nanocrystalline dc-Si, which anneals out to single-crystal dc-Si over time and the hd-Si remains relatively unchanged. This is supported by the asymmetric nature of all the Raman spectra in Ref. 24, which is indicative of a hd-Si peak at 505 cm⁻¹ alongside the main dc-Si peak.

C. Stability after thinning

Ge *et al.* observed that the thickness of their sample affected the transformation pathway of their material by *in situ* annealing samples thinned to electron transparency (~100 nm). For example, Si-XIII was never observed in their thinner samples and r8-Si was not observed in their thinnest sample.²² This is in agreement with the results seen in Fig. 4, where Si-XIII is observed immediately after thinning but has decayed out within 20 days. It should also be noted that no r8-Si reflections are present in any of the SADP presented in this study. It follows that a thinned sample plays a key role in the thermal stability of these phases, especially that of Si-XIII. Thus, the presence of Si-XIII after incremental annealing at 240 °C is not unexpected. In fact, it suggests that the stable range of Si-XIII is higher than previously reported. Similarly, it is unsurprising that hd-Si is still observed after furnace annealing at 750 °C for 2 h compared to the 600 °C transition temperature reported in Ref. 22. From this result, we further suggest that the stability of Si-XIII and r8-Si is connected to the presence of residual stress in the sample due to indentation. When the residual strain is removed via thinning, the Si-XIII and r8-Si phases decay rapidly.

D. Range of thermal stability

Figure 6 is an updated schematic of the changing phase composition during annealing. Before annealing, the as-indentated sample consists of a bc8/r8 composite.²⁰ Upon annealing, this bc8/r8 composite transforms to the hd-Si and Si-XIII phase. At 100 °C, r8-Si is no longer stable and begins to transform to Si-XIII. Ruffell *et al.* reported that r8-Si peaks remained after annealing at 200 °C for two hours,²¹ while the results presented within this study show that only hd-Si remains after annealing at 240 °C for 2 h. This indicates that r8-Si can be rapidly transformed to Si-XIII at a temperature between 200 and 240 °C. Further, Si-XIII is also reported to be partially stable

FIG. 6. A plot showing the presence of the exotic Si phases after thermal annealing at varying temperatures. Fading color represents temperatures at which the phase is gradually transforming. The temperature at which the bc8- to hd-Si transformation begins is an estimate only.

at 200 °C,²³ suggesting that Si-XIII also fully anneals out at a temperature between 200 and 240 °C, transforming to hd-Si. Incremental annealing suggests that bc8-Si remains stable at a higher temperature than r8-Si, but is also fully transformed after annealing at 240 °C for 2 h. Thus, all other metastable phases made by indentation have annealed out and transformed to hd-Si at the same temperature of 240 °C. This hd-Si begins to transform to nanocrystalline dc-Si at 750 °C but traces remain present after annealing at this temperature for 2 h. This is slightly different to DAC studies, where bc8-Si also transforms directly to hd-Si at 210–250 °C¹⁴ but r8-Si transforms directly to dc-Si at above 250 °C.²³

Under furnace, laser, and heat stage annealing, hd-Si has formed at relatively low anneal temperatures and has remained present for the entirety of the anneal. Indeed, hd-Si is the only phase present between 240 and 450 °C. Upon cooling, hd-Si remains present as detected by SADP. By refining our understanding of hd-Si in Raman and SADP, it appears that considerably higher energy is required for the hd-Si to dc-Si transition than previously reported even for a thin film of hd-Si. Interestingly, this result indicates that a thin film of hd-Si made by indentation is at least as thermally stable as a-Si, a material widely used on an industrial scale. Clearly, this makes hd-Si of great technological interest, as it allows for easier hd-Si integration into industrial Si devices using current industrial processes that already involve a-Si. It should also be noted that a hd-Si to dc-Si transition temperature of 750 °C for these indentation-made samples is in close agreement to the reported transition temperature in samples made via DACs (730–780 °C¹⁴). We propose that the differences in residual and shear stress, that cause the observation of different phase transformation pathways in nanoindentation compared to DACs below 250 °C, are annealed out during the annealing process before 750 °C. This proposal is supported by the DFT modeling, which indicates that there is a good agreement between the experimentally observed hd-Si Raman peak positions with the modeled peak positions at ambient pressures (i.e., no residual stress). Thus, there exists a region within the thermally stable range of hd-Si in which samples formed via DAC or nanoindentation both behave similarly. This allows for integration of both pressure-inducing techniques for the creation of hd-Si within this temperature range. Finally, the presence of Si-XIII at above the previously reported 200 °C generates interest in probing the structure and properties of this phase due to its greater range of thermal stability.

V. CONCLUSION

Here, we have measured the thermally stable range of a bc8/r8 composite, hd-Si, and Si-XIII made by spherical indentation. We have demonstrated a new indicator for the presence of nanocrystalline dc-Si using electron diffraction, which suggests that samples previously reported as nanocrystalline dc-Si based on Raman spectroscopy may in fact contain substantial amounts of hd-Si. We have also considered the difference between furnace and laser annealing and have shown that both methods follow the bc8/r8 $\rightarrow$ Si-XIII/hd-Si $\rightarrow$ hd-Si $\rightarrow$ dc-Si pathway if the starting bc8/r8 composite is made by indentation. Si-XIII is present at 100 °C and remains present until 240 °C. The hd phase is also present at 200 °C and remains even after annealing at 450 °C. Interestingly, hd-Si is the only crystalline phase observed in the transformed region after annealing to 240 °C–450 °C. Laser annealing differs from furnace annealing due to the concentration of laser heating on materials with a greater absorption cross section. This leads to an even greater stable range of hd-Si due to the strong absorption cross section of hd-Si's precursor phases and the relatively weaker absorption cross section of the hd-Si itself. The greater thermal stability of hd-Si generates renewed interest in utilizing this novel phase for technological applications.

ACKNOWLEDGMENTS

J.E.B. would like to acknowledge the Australian Research Council (ARC) (No. FT130101355). A.M. acknowledges support from MINECO (Spain). B.H. gratefully acknowledges funding through a Weinberg Fellowship sponsored by the Laboratory Directed Research and Development Program of Oak Ridge National Laboratory, managed by UT-Battelle, LLC, for the U. S. Department of Energy (DOE) and ORNL's Neutron Facilities, a DOE Office of Science User Facility operated by the Oak Ridge National Laboratory.

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