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Evidence for the R8 phase of germanium

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The formation of R8 germanium is reported. The β -Sn phase is first induced by the indentation of amorphous germanium (a-Ge) and the resultant phases on pressure release are characterized by Raman scattering. The expected Raman line frequencies for the various phases of Ge are determined from first-principles calculations using density functional perturbation theory of the zone-center phonons in the diamond, ST12, BC8 and R8 Ge phases. In addition to the R8 phase, traces of BC8 may also be present following pressure release.

Phase transitions between the allotropes of germanium and silicon can be achieved through the application of pressure and are accompanied by dramatic changes in electronic properties.¹⁻³ These transitions are irreversible upon pressure release and various meta-stable phases result instead. Interestingly, these phases may be of great technological interest. For example, the rhombohedral (R8) phase of silicon has recently been identified as a narrow band gap indirect semiconductor with quite different, potentially very useful, properties to the common diamond crystal (DC) phase.^{3,4} It also has quite promising applications as a photovoltaic material⁵ or may be exploited for maskless nanoscale patterning.⁶ Such applications may be implemented by the use of a small pointed tip to induce localized phase transitions. The ability to locally modify the band structure of such widespread semiconductor materials as Ge and Si on the nano-scale by pressure application and without thermal treatments can easily be envisaged to form an integrated part of future electronic and optical device fabrication. Compared to Si, however, significantly less is known about Ge although it is becoming a more important material for the semiconductor industry. Moreover, such pressure-induced phases of Ge may be of equal technological interest, if it is possible to isolate a semiconducting R8 Ge phase at room temperature. Until now, however, the exact sequence of phases upon pressure release remains unclear and convincing evidence of a R8 Ge phase has been scarce due to a lack of experimental repeatability,⁷ the coexistence of multiple phases or the use of highly impure Ge.^{8,9} It is therefore of utmost fundamental importance to understand how this important semiconductor behaves upon pressure-release and which phases form.

It has long been known that a metallic phase with a β -Sn structure is formed on hydrostatic loading of the DC phase at around 10-12 GPa for both Ge and Si.^{1,10} From the β -Sn structure various meta-stable phases are obtained depending on the depressurization rate. Upon slow unloading of β -Sn Ge, the distorted simple tetragonal phase (ST12)¹¹ is obtained.¹² This phase is stable under ambient conditions but transforms back to DC upon heating to around 200°C.^{12,13} A similar transformation of ST12 Ge to DC Ge can be achieved under laser illumination such as during a Raman experiment.^{14,15}

For β -Sn Si, slow depressurization results in the body-centered-cubic (BC8) structure (forming at 2 GPa) via an intermediate R8 phase (forming at 9.4 GPa).¹⁶ For Si, both BC8 and R8 co-exist stably under ambient conditions.¹⁷ Upon rapid release, β -Sn Si transforms to an amorphous structure² while Ge is reported to transform to the BC8 phase.¹⁸ BC8 Ge is

observed to be stable at dry ice temperatures but quickly transforms (within several hours) to a hexagonal diamond phase (HEX, also known as lonsdaleite) under ambient pressures and temperatures.^{18,19} At temperatures above 500°C, HEX in turn transforms back to DC Ge.¹³ What is surprising, in comparison with Si, is that no R8 Ge phase has been observed.

As indicated above, the pressure required to induce a phase transition to β -Sn can be produced by using either a diamond anvil cell (DAC) or the localized pressure-application of a small diamond tip,²⁰ which is the method employed here. It should be noted, that this latter method is technologically more useful as it could allow for pressure-induced nano-engineering. In this current study, the starting material is pure amorphous Ge (a-Ge) formed by ion implantation so as to avoid deformation by the motion of dislocation type defects which can form in lieu of phase transformations in the indentation loading of DC Ge.²¹ Furthermore, unlike previous studies, by using this form of Ge the possible role of nano-structures and impurities is also avoided.²² The samples were cooled immediately after indentation and the high pressure phases of Ge were clearly and reproducibly observed. Since no authoritative Raman spectra for the Ge meta-stable phases exists, density functional perturbation theory (DFPT) calculations for the zone-center phonons in DC, ST12, BC8 and R8 Ge have been performed to aid in the phase identification. The existence of R8 is thus reliably demonstrated for the first time both through these DFPT calculations and comparisons with similar indents in Si.

A Cz-grown (100) Ge wafer was implanted with 3 MeV Ge ions to a fluence of 1×10^{15} Ge/cm² while held at liquid nitrogen temperature to form a 1.8 μm thick, homogeneous and voidless surface a-Ge layer. Indentation was performed into the surface of six samples using a 20 μm spherical tip and maximum loads of 700 mN. The transformed region extended to a depth of 1.2 μm , well within the amorphous layer. Immediately after indentation, the wafers were placed on dry ice to limit the time spent at room temperature before measurement. Raman micro-spectroscopy was conducted with a Renishaw 2000 Raman imaging microscope using 1.5 mW/ μm^2 of the 632.8 nm excitation line of a helium-neon laser with a 4x30 s exposure. The laser conditions were optimized so as not to alter the a-Ge film and to cause minimal change to the metastable Ge phases due to annealing.

Figure 1 shows a typical Raman spectrum from an indent immediately after removal from dry ice and brought to room temperature. This spectrum clearly indicates that a phase transformation has occurred on loading with the spherical indenter tip at room temperature. The

FIG. 1. (color online) Experimental Raman spectra of the indented a-Ge immediately after indentation fit with a series of Gaussian fits (solid lines). An a-Ge line-shape was included in the fit (dashed line). The inset shows the low frequency region from (i) the indented a-Ge and (ii) pure a-Ge showing the broad TA a-Ge Raman band.

spectrum in the 100-400 cm^{-1} range can be fit with a series of seven Gaussian line-shapes.²³ Given the clear presence of the broad a-Ge transverse acoustic (TA) ($\sim 80 \text{ cm}^{-1}$) phonon band arising from a-Ge,²⁴ we have included an a-Ge line-shape of an ion-implanted a-Ge substrate when fitting. This line-shape may differ subtly from that of the a-Ge contained inside the indent. The meta-stable crystalline phases give rise to lines with Raman frequencies of 85.4 ± 0.5 , 95.0 ± 0.5 , 202.3 ± 0.7 , 224 ± 1 , 246.3 ± 0.9 , 277 ± 2 and $287 \pm 5 \text{ cm}^{-1}$ (errors are the standard deviation from the six separate indents studied). The 202.3 cm^{-1} line has a small shoulder at $213 \pm 1 \text{ cm}^{-1}$. This line was included in the fit so as to accurately determine the peak positions. Although it is much smaller in intensity than the other lines, the sum of the residual intensities squared is up to a significant 40% smaller in the 190-240 cm^{-1} range when it is included in the fit.²³ A broad band centered at $\sim 150 \text{ cm}^{-1}$ is also included in the fit.

The phases formed are unstable at room temperature and rapidly transform. Indeed, in this work most of the Raman lines observed initially decrease significantly in intensity during observation at room temperature, while the band at 287 cm^{-1} increases. After 150 hours, this latter band dominates the spectrum with only the 224 cm^{-1} line remaining with a greatly reduced intensity. The 287 cm^{-1} line arises from the E_2 phonon in HEX Ge.²⁵ The presence of HEX Ge is confirmed by selected area diffraction measurements with no

FIG. 2. (color online) Experimental Raman spectra (i) from Fig. 1 compared to (ii) that of an indent formed under similar conditions in a-Si. The Raman shift has been normalized by the average bond length²³ ($b_{Ge} = 2.474 \text{ \AA}$ and $b_{Si} = 2.331 \text{ \AA}$) and mass using Eq. 1. The intensity has been scaled for comparison. The inset shows the low frequency region from the indented (i) a-Ge and (ii) a-Si.

DC Ge observed.²⁶ Since ST12 is expected to be stable at room temperature, especially in the nano-crystalline state of an indent,¹⁵ and to transform to DC on annealing, the rapid formation of HEX Ge is an excellent indication that no ST12 was initially formed. The phase evolution during annealing, however, will be discussed in detail elsewhere as it is outside the scope of this letter.^{26,27}

In order to investigate the nature of these lines, a comparison of the Ge spectra may be made to the R8/BC8 Si Raman spectrum. This is shown in Fig. 2. Noting that the spring constants vary with the 1.5 power of the bond length by the square root of the mass,^{24,28,29} the frequencies of like phonons existing in two different materials, A and B , having similar crystallographic structures can simply be related via the equation,

$$\frac{\omega_A}{\omega_B} = \frac{(b^{1.5}m^{0.5})_B}{(b^{1.5}m^{0.5})_A} \quad (1)$$

where ω , b and m are the Raman shift, average bond length and mass ($m_{Si} = 28.0855 \text{ u}$, $m_{Ge} = 72.64 \text{ u}$), respectively. The bond lengths used here are given in Ref. 23. This equation does not take anharmonic effects into account, yet the measured Raman spectra of the meta-stable phases of Si and Ge shown in Fig. 2 are indeed strikingly similar, an observation previously made for the Si and Ge phases during pressure release in a DAC.¹⁹

TABLE I. The Raman frequencies of the meta-stable phases observed in indented a-Ge compared to the Si values re-normalized assuming either an R8 or BC8 structure (all in cm^{-1}). A theoretically predicted BC8 line at 259.1 cm^{-1} does not correspond to any of the observed Raman lines.

Ge	Si, re-norm[R8/BC8]	DFPT [phase/symmetry]
85.4 ± 0.5	163.0, [94.2/91.3]	83.3 [R8/ A_g]
		87.0 [BC8/ T_g]
95.0 ± 0.5	165.3, [95.5/92.5] 180.1, [104.0/100.8]	89.8 [R8/ E_g]
		87.0 [BC8/ T_g]
202.3 ± 0.7	349.0, [201.6/195.4]	202.8 [R8/ A_g]
213 ± 1	370.1, [213.8/207.2]	211.6 [R8/ E_g]
		214.3 [BC8/ T_g]
224 ± 1	381.0, [220.1/213.3] 394.0, [227.6/220.6]	222.9 [R8/ A_g]
		227.1 [BC8/ A_g]
246.3 ± 0.9	434.8, [251.2/243.4]	243.7 [R8/ A_g]
		247.4 [R8/ E_g]
		246.2 [BC8/ T_g]
277 ± 2	Not applicable ^a	277.9 [R8/ E_g]

^a For Si, only the a-Si line at 485.0, [281.1] is observed in this vicinity.

The meta-stable Si phases were formed under similar conditions to the Ge indent in pure a-Si so that extrinsic stresses were kept to a minimum.³⁰ Both R8 and BC8 are expected to coexist in a Si indent formed under these conditions¹⁷ but the main line observed here at 349 cm^{-1} in the Si spectrum arises from the R8 phase.^{31,32} The renormalized Raman frequency of this line is 201.6 cm^{-1} which is in excellent agreement with the 202.3 cm^{-1} Ge line. All observed Si Raman modes are given in Table I renormalized for comparison with the Ge line positions. This comparison clearly suggests the presence R8 Ge.

Indeed, this comparison reveals further insight into the phases present upon pressure release. For Si, the transition pressure for $R8 \rightarrow BC8$ is 2 GPa.¹⁶ In comparison to previous DAC results by Olijnyk and Jephcoat, the Raman spectra of the Si indents we have formed do indicate that a residual stress of $\sim 1.5 \text{ GPa}$ may be present,¹⁴ and this results in the

presence of significant amounts of R8 Si in indents. Clearly, a similar stress is expected in the Ge indents. According to first principles total energy calculations, however, Ge makes this same transition on pressure release but at the lower pressure of 0.65 GPa.³³ It might therefore be expected that the Ge indent, confined within the substrate, may contain a greater volume of R8 than the equivalent Si indent. Thus it may well be possible that solely R8 is present after final indentation pressure release which would account for the slight differences observed between the Ge and Si spectra.

To further aid the interpretation of our experimental results, we have performed first principles calculations of the zone-center phonon frequencies in the DC, ST12, BC8 and R8 phases of Ge. These calculations were done using the DFPT approach³⁴ as implemented in the **QUANTUM ESPRESSO** package.³⁵ We used a norm-conserving pseudo-potential within the local density approximation (LDA) to density functional theory (DFT) with a plane wave energy cutoff of 40 Ry. Nonlinear core corrections were included in the pseudo-potential to take into account the overlap between the $3d$ states treated as core states and the $4s^2 4p^2$ states taken as valence states.³⁶ Tests performed on the DC Ge phase resulted in a lattice constant of 5.58 Å, which underestimates the experimental lattice parameter by 1.4%.³⁷ The calculated bulk modulus is obtained as 77.2 GPa, which is very close to the experimental value of 75.8 GPa.³⁸ In DC Ge we also obtain a value for the zone-center optical mode of 298.2 cm^{-1} . This value is in excellent agreement with the experimental value of 300.6 cm^{-1} ³⁹ and confirms the predictive power of our method. All of our phonon frequencies are calculated in the theoretically obtained structures, as is necessary due to the lack of any experimental information on the lattice and internal parameters that Ge would take in the R8 structure. Further details on our structural relaxations and phonon frequency calculations can be found in Ref. 33. A full list of the phonon frequencies also appears in the supplement.

The Raman frequencies determined by DFPT are shown in Fig. 3(a) and compared to the experimentally determined line positions extracted from Fig. 1. The DFPT results are not corrected for the $+2.4 \text{ cm}^{-1}$ difference between the experimental (300.6 cm^{-1}) and theoretical Raman mode (298.2 cm^{-1}) in DC Ge. The crystals in the transformed zone are expected to be 5-30 nm in diameter so that phonon confinement effects may also shift the Raman frequencies down as will any residual compressive stress in the indents. An upper limit is calculated to be -2 cm^{-1} for DC Ge with the phonon confinement model.⁴⁰

FIG. 3. (color online) (a) Raman-active mode frequencies determined by DFPT for various Ge phases. The upper bars (colored online) are the experimentally observed peak positions, the width of the bar being the associated standard deviation of the six indents measured. The color of the bar is the same as the corresponding Gaussian fit in Fig.1. (b) The calculated ST12 Raman spectra. The R8 and BC8 intensities could not be calculated since they are metallic within the calculations.

The frequency of the dominant line on pressure release at 202.3 cm^{-1} is in excellent agreement with the R8 line at 202.8 cm^{-1} . No other calculated Raman lines are observed in the vicinity. We therefore suggest that R8, giving rise to the dominant 202.3 cm^{-1} line, is present on pressure release. In addition, all other observed lines at 85.4 , 95.0 , 213 , 224 , 246.3 and 277 cm^{-1} are very close to the calculated phonon frequencies for R8.

For completeness, we have also calculated the ST12 Raman intensities (Fig. 3(b)). This is the only non-metallic meta-stable phase considered in this work and thus the only phase for which the Raman intensity can be simulated. In this case, the two dominant lines calculated at 249 and 275 cm^{-1} agree well with the experimentally determined Raman peak positions of ST12 Ge formed in a DAC at 246 and 273 cm^{-1} .⁴¹ Earlier DFT based ST12 calculations appear to underestimate the phonon frequencies compared to those in Fig. 3 possibly leading to an incorrect assignment.⁴² It is difficult to ascertain the cause of this discrepancy, however, we note that the DC phonon frequency in that work was calculated to be 292 compared to our 298.2 cm^{-1} indicating the robustness of our method, when compared with the experimental value of 300.6 cm^{-1} . Importantly, our observed 202.3 cm^{-1} line is

clearly not part of the ST12 Ge spectrum and shows that the indent does not contain any detectable trace of ST12. Again, the main Raman band must be attributed to R8 Ge.

Although most of the observed lines compare well with the calculated R8 lines, the four lines at 85.4, 213, 224 and 246.3 also coincide with those calculated for BC8 Ge. An additional theoretically predicted BC8 line at 259.1 cm^{-1} does not correspond to any of our observed Raman lines. Since the Raman intensities cannot be calculated for the R8 and BC8 phases, the observed Raman intensities do not support the presence of one phase over the other. Therefore, the presence of BC8 cannot be ruled out entirely. In any case, all observed lines are represented by either R8 or BC8 Ge.

In conclusion, we have shown that Ge can also exist in the R8 phase. This was achieved through recording Raman spectra of the meta-stable Ge phases after pressure release of a diamond tip. A dominant line was observed at 202.3 cm^{-1} . Comparison with similar Si indents and DFPT calculations clearly indicate that this line is due to R8 Ge. The positions of all the other observed Raman lines are also consistent with an R8 assignment, but the presence of some BC8 Ge can not be ruled out. In contrast, however, no ST12 Ge is present in our case. This work is thus the first experimental evidence of R8 formed from pure Ge without the presence of any ST12. We fully expect that further characterization of this intriguing semiconducting R8 phase of Ge, experimentally and ab-initio, will open exciting new options for nano-scale engineering. If the R8 phase can be stabilized at room temperature (within strained Ge or Si-Ge layers, for example), we anticipate that band-gap engineering via localized nano-scale pressure application may provide a means to realize new optical and electrical devices.

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