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Raman Spectrum of Wurtzite Silicon*

R. J. Kobliska[†] and S. A. Solin

Department of Physics and The James Franck Institute, University of Chicago, Chicago, Illinois 60637

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The Raman spectrum of a metastable polycrystalline sample of wurtzite silicon is reported. The data are analyzed using a large-zone comparison with the diamond cubic phase of silicon and in terms of a simple force-constant model. These measurements are compared with the Raman spectrum of amorphous silicon and with the microcrystallite model of the amorphous phase.

Currently, there is considerable interest in the electronic[1] and vibrational[2,3] properties of the polymorphs of Si and Ge. This interest is warranted since the polymorphs may be regarded as intermediate between the well-characterized diamond cubic phase and the theoretically intractable amorphous phase. The polymorphs of Si and Ge are crystalline, tetrahedrally bonded, and are therefore amenable to a simple model calculation of the phonon frequencies. An experimental and theoretical study of the two polymorphs Si III (BC-8) and Ge III (ST-12) has previously been reported.[3] In this paper, we report the Raman spectrum of wurtzite silicon Si (2*H*-4)[4] which, in addition to being a polymorph of Si, is also a polytype of the diamond cubic phase labeled Si I (FC-2). Of the silicon polymorphs, wurtzite silicon is certainly the most important because the wurtzite structure is central to the microcrystallite theory of amorphous Si. Specifically, it has been suggested[5] that approximately 50% of the atoms of the amorphous phase are linked in a random network while the remainder are contained in wurtzite silicon microcrystallites.

The polycrystalline wurtzite silicon sample examined in this study was prepared by G. S. Cargill, III by annealing the previously studied Si III (BC-8) sample for 24 h at a temperature of 250 °C. Kahn determined from x-ray measurements that the sample was 60% Si (2*H*-4) and 40% Si I (FC-2).[6] The measured c/a ratio of 1.661 ± 0.03 is smaller than the ideal value of 1.663 for a wurtzite structure. The microcrystallites of which the sample was composed were estimated, from x-ray measurements, to have typical dimensions of 100 Å–1 μ.

The polarization-unanalyzed Stokes-Raman spectrum of wurtzite silicon shown in Fig. 1(a) was recorded at room temperature, in a backscattering geometry, with 100 mW of 5145-Å argon-ion-laser radiation focused onto the sample at Brewster's angle. An effective sample temperature of approximately 700 K was calculated from the measured Stokes–anti-Stokes ratio. The essential feature of the spectrum is the shoulder at 494 cm^{-1} which, when measured with a spectral slitwidth of 6 cm^{-1}, is barely resolvable from the intense peak at 513 cm^{-1}. From the polarized Raman spectra a depolarization ratio of 0.75 ± 0.1 was calculated for each of these Raman lines. We also observe an experimentally reproducible low-energy tail which extends from the two high-energy peaks to an energy as low as 420 cm^{-1}. In Fig. 1(b) is shown the Stokes-Raman spectrum obtained with the sample mounted in a Joule-Thompson flowing-exchange-gas dewar and under conditions in which the sample mounting block was cooled to 16 K. No anti-Stokes signal was observed; thus, we estimate an upper limit of 200 K for the effective sample temperature. Our attempts to deconvolute the spectra of Fig. 1, in each case, resulted in a peak at ~ 520 cm^{-1}, with a second peak approximately 20 cm^{-1} lower in energy. For comparison, the energy of the Γ_{25}^{+} symmetry zone-center phonon of Si I (FC-2) at room temperature is 520 cm^{-1}.[7]

Note that the low-temperature spectrum of Fig. 1 is broad and that the ratio of the intensity of the low-energy tail to the intensity of the 520-cm^{-1}

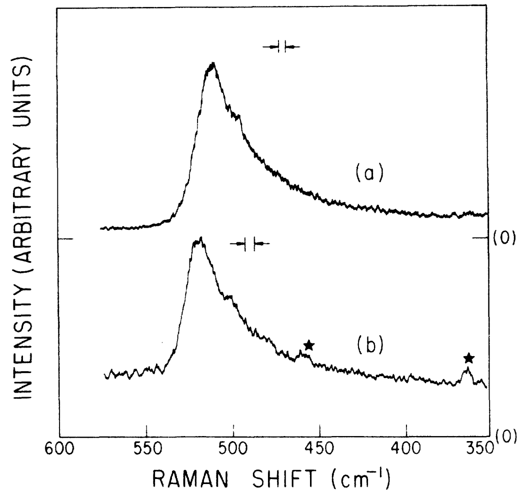

FIG. 1. Polarization unanalyzed Stokes-Raman spectra of wurtzite silicon recorded with effective sample temperatures of (a) 700 K and (b) < 200 K. The stars denote grating ghosts. The abscissa is linear in wavelength rather than wave number.

Raman peak is approximately constant for the two temperatures shown. This observed temperature dependence rules out the possibility that the low-energy tail is due to second-order Raman scattering. The possibility that finite-wave-vector effects may cause the low-energy tail in the spectra of Si (2*H*-4) has been disallowed on the grounds that a similar tail would be expected in the spectra of both the parent Si III (BC-8) and the daughter Si I (FC-2) crystals; no such tail was observed.

The constituent lines in the Raman spectrum of wurtzite silicon are very likely broadened by residual strains in the sample. In this regard, the widths of the Raman lines of the parent Si III (BC-8) crystal were in excess of 14 cm^{-1}.[3] A similar linewidth in Si (2*H*-4), when measured using a spectral slitwidth of 6 cm^{-1}, would account for the difficulty in resolving the lines observed at 520 and 500 cm^{-1}. When exposed to focused incident laser powers in excess of 200 mW, Si (2*H*-4) transformed to Si I (FC-2). Transformation to the cubic phase was signaled by the appearance of the single 13-cm^{-1}-wide zone-center phonon Raman line of Si I (FC-2) at 520 cm^{-1}. The 13-cm^{-1} linewidth was measured with an effective sample temperature of ~ 600 °C and an incident laser power of 65 mW. According to the measurements of Hart *et al.*,[8] the linewidth of the zone-center phonon of Si I (FC-2) is 7 cm^{-1} at 600 °C. Clearly nonthermal broadening mechanisms, possibly strain inhomogeneities and/or surface effects, are present in our Si I (FC-2) sample.

The Si (2*H*-4) structure has space-group symmetry D_{6h}^4 with four atoms per primitive cell and is equivalent to an ordinary wurtzite structure with every site occupied by a Si atom. Using group theory, it is possible to divide the 12 normal modes of Si (2*H*-4) into $\Gamma_1^+ + \Gamma_2^- + \Gamma_3^+ + \Gamma_4^- + \Gamma_5^+ + \Gamma_5^- + \Gamma_6^+ + \Gamma_6^-$ irreducible representations of the D_{6h} point group.[9] Of these, the Γ_1^+, Γ_5^+, and Γ_6^+ modes are Raman active; thus, the Raman spectrum of Si (2*H*-4) should contain at most three distinct lines.

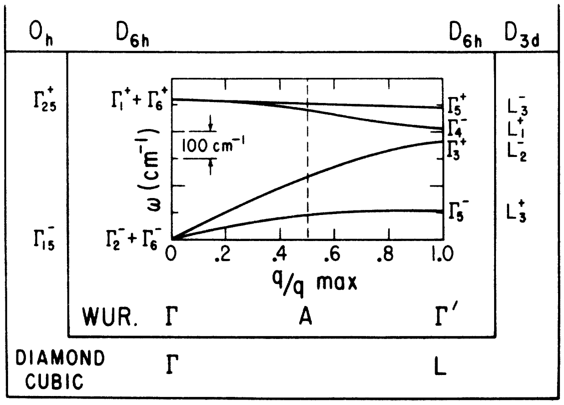

FIG. 2. Large Jones zone of wurtzite silicon. The first row gives the point group of the wave vector at the appropriate symmetry point in the large Jones zone (Brillouin zone) of wurtzite (diamond cubic) silicon. The L-point irreducible representations are related in the following way to those given in Ref. 10: $L_3^- \equiv L_3'$, $L_1^+ \equiv L_1$, $L_2^- \equiv L_2'$, $L_3^+ \equiv L_3$.

The essential difference between wurtzite silicon and diamond cubic silicon is in the stacking of the layers along the hexagonal *c* axis of Si (2*H*-4) or equivalently the [111] axis of Si I (FC-2). If perturbations due to the differences in layer stacking order are disregarded, the phonon dispersion curves corresponding to propagation along the *c* axis ($\Gamma \rightarrow A \rightarrow \Gamma'$) of the Jones zone[10] of Si (2*H*-4) are identical to the dispersion curves for propagation along the [111] axis ($\Gamma \rightarrow L$) of the Brillouin zone of Si I (FC-2). The dispersion curves along the *c* axis of the Jones zone of Si (2*H*-4) have been obtained from the neutron scattering measurements of the dispersion curves along the [111] axis of Si I (FC-2)[11] and are shown in Fig. 2.[12] The Brillouin zone of Si (2*H*-4) is obtained by reflecting the curves in the $A \rightarrow \Gamma'$ section of the Jones zone through a plane normal to the $\Gamma \rightarrow A \rightarrow \Gamma'$ axis at A. In order to correlate the L-point phonons of Si I (FC-2) with the Γ' point phonons of Si (2*H*-4) it is necessary to carefully consider the effect of the inversion operation. Inversion in Si I (FC-2) involves the interchange of the two atoms in the two-atom basis while inequivalent atoms in neighboring layers of Si (2*H*-4) are interchanged under inversion. The primitive cell of Si (2*H*-4) can be constructed by properly stacking two Si I (FC-2) primitive cells along the [111] direction. It is easily shown that the 180° phase factor introduced between modes in neighboring cells at the L point in Si I (FC-2) leads to a change of sign under inversion for the corresponding normal modes at the Γ' point of Si (2*H*-4). As can be seen from Fig. 2, L-point phonons which are even under inversion correspond to Γ'-point phonons which are odd under inversion and vice versa.

On the basis of the above analysis and Fig. 2, we expect the Raman spectrum of Si (2*H*-4) to contain only *two* lines, one at 520 cm^{-1} arising from the degeneracy of a Γ_1^+ singlet and Γ_6^+ doublet and another at 500 cm^{-1} corresponding to a Γ_5^+ doublet. Furthermore, for the symmetry assignments specified, we expect the following depolarization ratios: $\rho(520) \simeq 0.75$ and $\rho(500) \equiv 0.75$. Aside from the low-energy tail in the Raman spectrum of Si (2*H*-4), the Jones-zone analysis and experimental observations are in excellent agreement as can be seen from Figs. 1 and 2.

A theoretical analysis of the vibrational modes of Si (2*H*-4) based on a simple Raman Hamiltonian, and the Keating model of a tetrahedrally bonded solid has been carried out by Alben *et al.*[13] The details of this analysis which has been success-

TABLE I. Properties of the normal modes of wurtzite Si. The irreducible representations appropriate to the D_{6h}^4 space group are labeled according to Ref. 10. Only Γ_1^+, Γ_5^+, and Γ_6^+ are Raman active. The energy and relative intensity of Raman lines at ~500 cm^{-1} were deduced from the deconvoluted spectrum.

	Phonon Energy in cm^{-1}		Depolarization Ratios		Relative intensity—HH	
Symmetry	Expt.	Theoret.[a]	Expt.	Theoret.[a]	Expt.	Theoret.[a]
Γ_2^-	...	0	...	...	0	0
Γ_6^-	...	0	...	...	0	0
Γ_5^-	...	150	...	...	0	0
Γ_3^+	...	360	...	...	0	0
Γ_4^-	...	418	...	...	0	0
Γ_5^+	502 ± 3	498	0.75 ± 0.1	0.75	0.4 ± 0.1	0.8
Γ_1^+	520 ± 1	520	0.75 ± 0.1	0.75	1.0	0.6 } 1.0
Γ_6^+		520				0.4

[a] From Ref. 13.

fully applied to Si III (BC-8) and Ge III (ST-12) are given elsewhere.[2] The theoretical results of Alben *et al.* are compared with experiment in Table I. Agreement between theory and experiment is excellent for the energy shifts and depolarization ratios of the two observed Raman lines and reasonable for the relative intensities. It is not surprising that the relative intensities are in error. The wurtzite silicon sample studied contained 40% Si I (FC-2); therefore, the experimental Raman intensity at 520 cm^{-1} is artificially enhanced by scattering from the zone-center phonon of the diamond cubic phase. In the analysis of Alben and co-workers only first-nearest-neighbor interactions are considered.[2,13] Since differences in the layer stacking order between Si I (FC-2)and Si (2*H*-4) arise from the positions of the third nearest neighbors, the analysis of Alben and co-workers like the Jones-zone analysis, treats perturbations due to these differences as being negligible. The effect of nonnegligible third-neighbor interactions is to lift the degeneracy between the Γ_1^+ and Γ_6^+ modes. Yet our measurements of the polarized and unpolarized Raman spectra of Si (2*H*-4) put an upper bound on the Γ_1^+-Γ_6^+ splitting of 5 cm^{-1} or ~ 1% of the Raman shift. The exclusion of third-neighbor interactions from the Jones-zone analysis and the model of Alben and co-workers[2,13] is indeed justifiable *vis-a-vis* wurtzite silicon.

In connection with the microcrystallite theory of amorphous solids[5] it is fruitful to note that the Raman spectrum of wurtzite silicon and the spectrum of amorphous silicon reported by Smith *et al.*[14] are quite dissimilar; the former has negligible intensity between 0 and 450 cm^{-1} whereas the latter exhibits significant intensity in this region. Moreover, the high energy peak in the spectrum of amorphous silicon is much broader than and occurs at a lower energy than the corresponding peak for Si (2*H*-4). Nevertheless, the microcrystallite theory is based on crystallites of typical dimension ~ 15 Å[5] while the microcrystallites in the wurtzite silicon sample studied here had dimensions ≥ 100 Å. Our measurements cannot therefore be used to definitively disprove the microcrystallite theory but rather serve to set an upper bound of 100 Å on the microcrystallite size.

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