hcp-to-fcc Transition in Silicon at 78 GPa and Studies to 100 GPa

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The pressure-induced phase sequence of silicon has been studied up to 100 GPa by energy-dispersive x-ray diffraction techniques. A new phase transition from hexagonal close-packed to face-centered cubic was observed at a volume compression of $V/V_0 = 0.481 \pm 0.005$ and 78 ± 3 GPa, in excellent agreement with first-principles calculations of the phase stability of silicon at high pressures. This represents the lowest-atomic-number material for which a structural determination has been made up to 100 GPa.

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There has been considerable interest in the phase transitions in materials in the megabar (100 GPa) pressure range due to the recent advances in diamond-anvil-cell technology[1] and the development of ultrahigh-pressure x-ray diffraction techniques with synchrotron sources.[2] Also, first-principles calculations of the crystal energies for various phases as a function of volume have become sufficiently accurate to predict phase-transition sequences with decreasing volume for a variety of elements and compounds. McMahan and Moriarty,[3,4] in their calculation of structural phase stability of the third-period simple metals Na, Mg, Al, and Si, predict transition-metal sequences in all these materials at megabar pressures. These transition-metal sequences involve hcp, bcc, and fcc structures, and are driven by the lowering of $3d$ conduction bands at high pressures. These se-

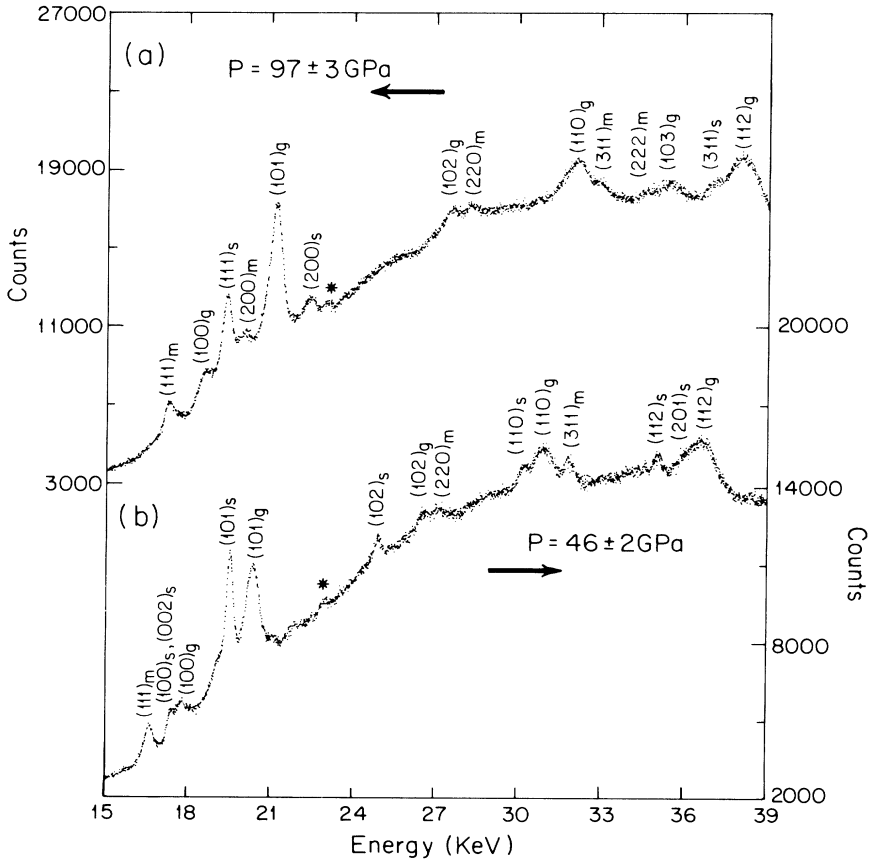

FIG. 1. EDXD patterns for Si-Au mixture. (a) Si in fcc phase at 97 ± 3 GPa. (b) Si in hcp phase at 46 ± 2 GPa. The diffraction peaks marked s are from the Si sample, marked m are from the pressure marker Au, and marked g are from the Fe in the gasket. In both spectra Au is fcc and Fe is hcp. The very weak peak at 22.9 KeV marked with an asterisk is constant in all spectra, and not diffraction from any sample. ($Ed = 36.92 \pm 0.02$.)

quences are similar to the ones observed in the nonmagnetic $3d$, $4d$, and $5d$ series of the periodic table as a result of the filling of the d band.[3] In the case of Si various first-principles calculations predict the hcp-to-fcc transition at 76 GPa[4] using linear muffin-tin orbitals (LMTO), at 80 GPa[4] using generalized pseudopotential theory (GPT), and at 116 GPa[5] using *ab initio* pseudopotential methods (AP). Therefore, an experimental verification of the existence of this transition in Si is critical, and will provide feedback to improve the various one-electron exchange and correlation terms used in these calculations.

Extensive experimental studies of the group-IV elements Si and Ge have been made in recent years. Motivations have included the rich variety of phase transitions and the existence of a simple hexagonal phase. Si shows the following phase-transition sequence in the pressure range 0–50 GPa: cubic diamond to β-Sn at 11 GPa, β-Sn to simple hexagonal (sh) at 13–16 GPa, sh to an intermediate phase at 34 GPa,[6] and finally to hexagonal close packed (hcp) above 40 GPa.[6,7] Ge has recently been investigated up to 125 GPa.[8] The same transition sequence as in Si is observed, with the exception of the hcp phase where a dhcp phase is found at 102 GPa.[8] The existence of the sh phase in Si and Ge is well understood theoretically.[9,10] A recent compilation of experimental results for Si in the pressure range 0–50 GPa has been done by Hu *et al.*,[11] and theoretical calculations are summarized by Chang and Cohen.[5]

We have extended the room-temperature phase diagram of Si to 100 GPa by energy-dispersive x-ray diffraction techniques (EDXD) using a white-beam station at the Cornell High Energy Synchrotron Source (CHESS). The details of the experimental technique are described by Brister, Vohra, and Ruoff.[12] Silicon crystals of 99.9999% purity were ground to fine powder, mixed with 15 wt.% of gold (Au), and loaded into a 50-μm-diam sample chamber with a spring steel gasket. Diamonds with a 300-μm culet and 10° bevel angle approaching a flat of 100 μm were used in the present experiment. The gold acts as an internal pressure marker, and pressures were calculated from the isothermal equation of state of gold by Jamieson, Fritz, and Manghani[13] deduced from shock-wave data. The experiment was terminated when scheduled time at CHESS ended.

Lattice constants were determined with the use of at least the (111), (220), and (311) diffraction peaks of fcc Au [in some cases the (200) and (222) were also observed]; the (100), (101), (102), (110), and (112) peaks of hcp Si [in some cases the (201)]; and the (111), (200), and (311), peaks of fcc Si [and in some cases the (220) and (222)]. Also, the hcp peaks of the iron in the gasket and the equation of state of Fe by Brown and McQueen[14] were used to confirm the sample pressure. Figure 1 shows diffraction patterns for both hcp and fcc phases of Si. It should be noted that diffraction peaks of the weak scatterer Si are an appreciable fraction of the peaks from the strong scatterer Fe. Table I presents the indexing of fcc Si at 87 ± 7 GPa. The disappearance of the (101) and (102) peaks of hcp Si, along with the appearance of the (111) and (200) peaks of fcc Si, makes the phase transition quite distinct (see Fig. 1).

Table II summarizes the phase-transition results of this experiment, and compares them to the theoretical results. Our fractional volume of hcp Si at the transition, $V/V_0 = 0.481 \pm 0.005$, agrees most favorably with the GPT result of McMahan and Moriarty.[3] Although they do not report the change in V/V_0 at the phase transition, our result of 0.006 ± 0.006 agrees, within experimental error, with the value of 0.009 calculated by Chang and Cohen.[5] The pressure of the transition is 78 ± 3 GPa, which agrees with both the LMTO and GPT calculations.

The equation of state (EOS) of Si in the hcp and fcc phases up to 100 GPa is shown in Fig. 2. The error bars have been estimated for each spectrum by taking the worst-case deviation of an observed diffraction peak energy from the energy predicted by a least-squares fit to all the peaks of the element. Dividing this deviation by the diffraction peak energy gives an estimate of the fractional error in the lattice constants. Our EOS agrees well with the lower-pressure EOS of Olijnyk, Sikka, and Holzapfel.[6] The Birch first-order EOS fitted to the hcp data gives $B_0 = 71 \pm 2.0$ GPa, $B_0' = 3.91 \pm 0.07$, and V/V_0, the zero-pressure fractional volume for hcp with respect to the diamond phase, of 0.75 ± 0.01. This V/V_0 is in reasonable agreement with the LMTO result of McMahan and Moriarty.[3]

Figure 3 shows the measured c/a for Si in the hcp

TABLE I. Observed and calculated d spacings for fcc Si at 87 ± 7 GPa. $a = 3.34 \pm 0.010$ Å.

hkl	d_{obs} (Å)	d_{calc} (Å)
111	1.929	1.929
200	1.671	1.670
220	1.177	1.181
311	1.004	1.007
222	0.969	0.964

TABLE II. Comparison of transition volumes and transition pressures for hcp-to-fcc transition in silicon.

	$(V/V_0)^{hcp}_{transition}$	$(V/V_0)^{fcc}_{transition}$	Pressure (GPa)
Theory			
GPT[a]	0.482	· · ·	80
LMTO[a]	0.496	· · ·	76
AP[b]	0.465	0.456	116
Present expt.	0.481 ± 0.005	0.475 ± 0.005	78 ± 3

[a]Reference 3. [b]Reference 5.

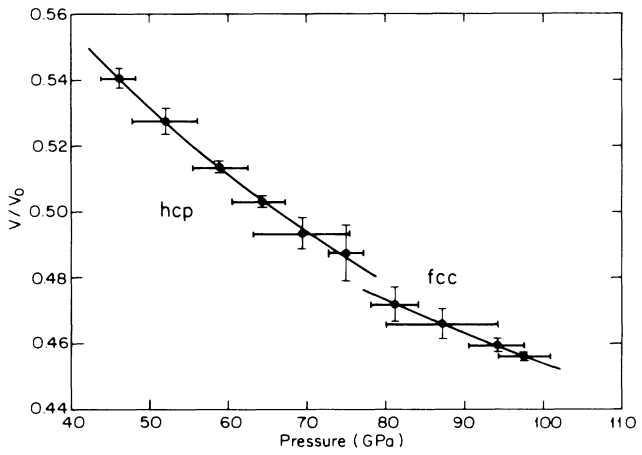

FIG. 2. The equation of state of Si at room temperature in the hcp and fcc phases. Error bars represent the worst-case estimate; see text. The curves are Birch first-order fits.

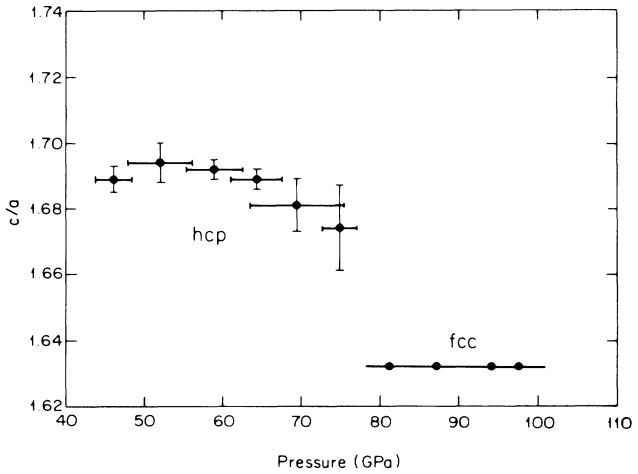

FIG. 3. The c/a ratio for hexagonal indexing for Si. The c/a ratio for fcc is the ideal $c/a = 1.633$; see text.

phase, and the ideal $c/a = 1.633$ of the fcc phase (the ratio of the interplanar spacing of closest packed planes to the atomic diameter). Within the errors of this experiment $c/a = 1.691$ remains constant at least up to 65 GPa where a systematic decrease is observed. The c/a of Olijnyk *et al.*[6] at 43 GPa is 1.698, and so we cannot rule out the possibility of a decreasing c/a throughout the 40–75 GPa pressure range.

It is interesting to point out that McMahan and Moriarty predict a further phase transition in silicon from fcc to bcc in the pressure range 250–360 GPa.[3]

From these results we may draw the following conclusions: (1) The hcp-to-fcc phase transition in Si occurs at the hcp $V/V_0 = 0.481 \pm 0.005$, and a pressure of 78 ± 3 GPa. The EOS allows the possibility of a fractional volume decrease of 0.006 ± 0.006 at the transition. In the hcp phase, c/a remains well above the ideal $c/a = 1.633$. (2) Theoretical calculations made prior to the experiment agree well with these experimental results. The GPT of McMahan and Moriarty[3] succeeds in calculating both the V/V_0 of Si at the transition and the transition pressure, while their LMTO theory succeeds with the transition pressure, but overestimates the transition volume. The AP theory of Chang and Cohen correctly predicts a transition to fcc and a reasonable volume fraction change at the transition, but the computed transition pressure is larger than our value. (3) The ability to do EDXD at megabar pressures on weak scatterers such as Si is confirmed.

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