Electrical Properties of Semimetallic Silicon III and Semiconductive Silicon IV at Ambient Pressure

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Microcrystalline samples of $BC8$ silicon III and hexagonal silicon IV, grown under high pressure in the diamond anvil cell, remain metastable at ambient pressure. Hall-effect and low-temperature resistivity measurements show Si III to be a hole semimetal with $p \approx 5 \times 10^{20}$ cm^{-3}. Photoconductivity data show that Si IV, like Si I, is an intermediate-gap semiconductor. The observed behavior confirms theoretical predictions on these two new elemental materials.

Seven forms of silicon, at least, have been found to exist between room pressure and 50 GPa. Four of them are stable or metastable at ambient: Si I, a-Si, Si III, and Si IV, the first two being classical device materials.

Si III is obtained[1] from diamond cubic Si I, or amorphous a-Si, by pressurizing above 10 GPa, at 300 K, to β-Sn silicon II, which reverts to face-centered cubic ($BC8$) silicon III at room pressure. Powder samples are usually found to be mixed with remaining Si I. Up to the present, only its structure and density have been measured,[2] by x rays, along with its Raman spectrum.[3] Calculations predict that it should be a semimetal with indirect[4] or direct[5] band overlap.

Silicon IV is obtained[1] from Si III by heating above 470 K. It is stable up to some 800 K. Its structure is hexagonal diamond[6] (lonsdaleite, $P6_3/mmc$), which is derived from cubic diamond in the same way as wurtzite from blende ZnS. Only its c and a parameters have been published up to now.[6] One calculation[7] predicts that it should be a semiconductor, rather similar to Si I.

In this Letter, we report methods to obtain pure polycrystalline slabs of both varieties, by high-pressure synthesis in the diamond anvil cell. Ohmic contacts can be attached to the samples and thus electrical properties, Hall effect, and photoconductivity can be measured at variable temperature. Hall effect, and resistivity down to 1.2 K, show Si III to be a hole semimetal. The photoconductivity spectrum of Si IV points to its being a semiconductor with a band gap that compares with that of Si I.

Starting material was monocrystalline 1-Ω-cm p-type silicon ($p = 3 \times 10^{16}$ cm^{-3}), cut in parallelepipeds $150 \times 150 \times 30$ μm^3 in dimensions. Four electrical contacts were deposited on each sample, in the standard Al-Ti-Pt-Au film sequence. They were found to remain mechanically stable and Ohmic through the Si I $\rightarrow$ II $\rightarrow$ III transitions,[8] that is, up to 12 GPa, on the ruby scale, and back to room pressure. The pressure medium is silicone oil which vitrifies between 6 and 8 GPa. The samples are therefore enclosed in a highly rigid environment, at the transition pressures, and thus

come back in the form of isostatically sintered material. They can be handled like bulk material, although, after pressurization, the slabs are somewhat strained by the nonhydrostatic stresses and pressure gradients. Debye-Scherrer diagrams at room pressure showed well-defined powder patterns, and up to fourteen lines could be indexed[2] for the Si III ($BC8$) structure. A pressure of 18 GPa was necessary to transform Si I completely. Samples subjected to pressures of only 12 to 14.5 GPa still had diagrams with the characteristic spots of the original Si I monocrystal. No influence of the pressurization or depressurization rates[9] could be observed: The final product only showed the Si III diffraction lines.

Completely transformed Si III samples were heated at 470 K for 2 h, to obtain Si IV. The positions of lines which have not been published before are given in Table I. The corresponding c/a ratio is 1.646 ± 0.012, which fits with the previous result.[6]

Electrical measurements on Si III were done by the four-probe van der Pauw method.[10] Residual internal stresses often brought about random failure (open circuit), so that several samples had to be used to cover the whole temperature range (1.2 to 300 K). No significant difference was found between completely ($P_{max} = 18$ GPa) and partly ($12 < P_{max} < 14.5$ GPa) transformed samples, which is expected in view of the large difference in conductivity between Si I and Si III, especially at $T < 300$ K, the transformed (conductive) fraction always

TABLE I. Diffraction data for Si IV (space group $P6_3/mmc$). Lattice parameters are $a = 3.837$ Å, $c = 6.317 \pm 0.012$ Å, $c/a = 1.646 \pm 0.008$.

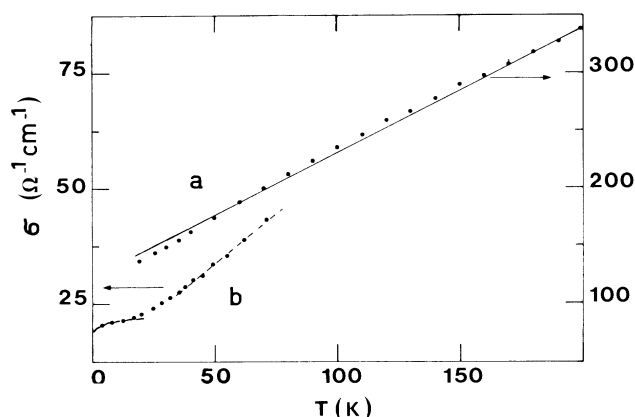| hkl	d (Å)
100	3.281
002	3.189
101	2.945
110	1.912
103	1.786
112	1.640

FIG. 1. Conductivity vs temperature of Si III samples. Curve a: linear high-temperature dependence of a high-conductivity sample (right scale). Curve b: transition from the T^1 dependence above 30 K to the $T^{1/2}$ dependence below 15 K in a lower-conductivity sample. Dashed lines only qualitatively indicate both behaviors.

FIG. 2. Low-temperature $T^{1/2}$ behavior for one sample which could be studied down to 1.3 K.

being much more than 50% of the sample. Hall effect was measured in a field of 1 T. The apparent number of carriers at 300 K is $p = (5 \pm 2) \times 10^{20}$ cm^{-3} and the apparent mobility $\mu = 4 \pm 2$ cm^2/V·sec. The errors represent both the experimental uncertainty and the dispersion of results from sample to sample. Those values are only orders of magnitude, since we used the Hall relations for one kind of carrier, whereas both electron and hole conductivity may exist. This is strongly suggested by measurements at 200 K, the lowest temperature where Hall measurements could be made, which showed a decrease of p by 50% and an increase of μ by the same ratio. Moreover, the three transitions to Si II, Si V, and back to Si III bring about a high degree of structural disorder to the original monocrystal. To appreciate its influence, two extreme cases may be considered: (i) compacted microcrystals of Si III (some 100 nm in dimension, for argument's sake) with disordered material (amorphous a-Si?) in the grain boundaries; (ii) material that is sufficiently ordered at short distance (10–20 nm) to give clear Debye-Scherrer patterns, but disordered enough for localization models to apply (next paragraph). In both cases, the observed apparent carrier density should be somewhat higher than that of the monocrystal. The mobility is a much more sensitive parameter[11] and the actual mobility of Si III must be definitely higher than that deduced from Hall effect on disordered samples.

Resistivity also was measured with a four-probe setup in a pumped ^{4}He cryostat.[12] At room temperature, resistivities were found to be vary between 3 and 20 mΩ-cm from sample to sample, and no correlation of this property with P_{max} has yet been found. Nevertheless, the relative variation with temperature was found to
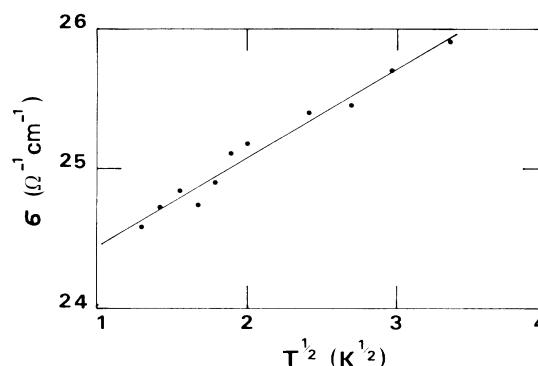
be quite similar over more than ten samples studied. Figure 1 is representative of the variation of conductivity with temperature for samples with high (curve a) and low (curve b) conductivities. This behavior is different from that of any known monocrystal, and thus must be related to the structural disorder of the sample. In the case of a mosaic crystal, (i) (above), the variation of resistance will be dominated[11] by that of the interstitial material which should decrease with temperature, especially if it were a-Si. Hall effect, in contrast, will be more sensitive to the high-mobility Si III domains. Amorphous silicon transforms to Si II under pressure[13]; we mention it here for the sake of thoroughness only: It does not show on the x-ray patterns and its lower density would make it less stable than crystalline silicons, anyway. The second hypothesis, (ii), allows a semiquantitative analysis: In Fig. 1, curve a shows a linear dependence of the conductivity σ with temperature between 25 and 200 K. The localization theory of disordered systems[14] indeed predicts this behavior due to electron-electron scattering, at least[15] up to one-third of the Debye temperature, that is,[3] around 200 K, for Si III. At lower temperature (Fig. 1, curve b), this no longer holds, and below some 15 K, the conductivity may be fitted with a $T^{1/2}$ law (Fig. 2), which has indeed been predicted[14] and observed[15-17] in disordered systems, at low temperature, when diffusion (interaction) effects dominate. As shown in curve b (Fig. 1), a crossover region occurs between the $T^{1/2}$ and T dependences in the region of 15 to 30 K. At this point it must be noted that the region between 10 and 80 K might equally be fitted by semiempirical power laws,[8] as was done in other disordered systems.[18] Nevertheless, this somewhat lacks physical bases, and moreover does not correctly represent experimental data below 10 K and above 100 K. The above discussion is, of course, no claim to testing of localization theories: The point is that the observed temperature variation of conductivity in our Si III samples precisely agrees with the expected behavior of a highly disordered microcrystalline conductor. Down to 1.2 K, no indica-
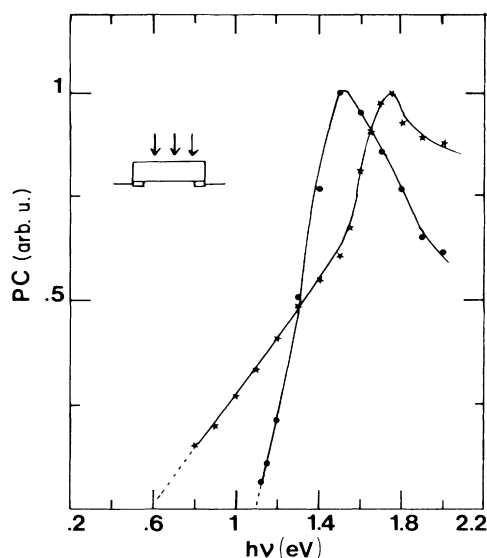
FIG. 3. Photoresponse of a Si IV sample at constant incident photon density (stars). Thickness=25 μm. Photoresponse of an identical Si I slab (dots), under the same conditions. Scaled down by a factor of 10^2 to normalize both curves at maximum value.

tion of superconductivity could be found on our samples, which is not too surprising in view of the small ($< 10^{21}$ cm^{-3}) charge-carrier density. On the other hand, it does not preclude this possibility, in monocrystalline Si III.

The observed properties of Si III, as a semimetal with dominant hole conductivity at 300 K, confirm existing calculations on its band structure. The apparent number of carriers would fit better with a material with 5×10^{-2} charge carriers per site[4] and an indirect overlap of about 0.3 eV than with 10^{-3} charge carriers per silicon atom.[5]

Silicon IV samples exhibit completely different behavior. The apparent resistivity, measured on the same size samples, is 10^4 Ω-cm, at room temperature. Hall effect being impractical in this case we used photoconductivity to characterize the material. Crystals were illuminated in the "back surface" geometry by monochromatic radiation, modulated at low (50 to 200 Hz) frequencies. Spectra are at constant incident photon number. The photoconductivity response is compared in Fig. 3 with that of the original Si I monocrystal. Although the absolute value of the signal is 10^2 times smaller in disordered Si IV than in crystalline Si I, it is a good indication of a semiconductor material. A rough extrapolation (dashed line) of the photoresponse to zero intercepts the abscissa around 0.6 eV, but this may be misleading: The low-energy part of the spectrum should be dominated by a defect density of states which will smear out the photoconductivity edge.

Nevertheless, these data definitely point to Si IV being

a semiconductor with a gap close to that of Si I. Predictions[7] of an indirect gap ≈ 0.8 eV are thus in accordance with the observed behavior. An alternative would be to assign photoconductivity to amorphous silicon, as discussed above. Comparison with existing data[19] on the photoconductivity of a-Si does not show any significant analogy, and, at the present stage, this assignment would not be legitimate. The large increase in the resistance of the samples when going from Si I to Si IV (from 1 to about 10^4 Ω-cm) may be related to variation of the impurity-ionization energy in Si IV, or of the diffusion parameters with structural disorder since the band structures of Si IV and Si I should be qualitatively similar (cf. cubic and hexagonal diamond).

The conclusions of this work may be summed up as follows: (1) Body-centered cubic Si III and hexagonal Si IV can be grown under pressure as bulk microcrystalline samples suitable for electrical measurements. (2) Si III is a hole-conduction semimetal at room temperature, which confirms recent predictions.[4] It does not exhibit superconductivity above 1.2 K. (3) Indexation of the Debye-Scherrer lines confirms that Si IV is hexagonal[20] and that the c/a ratio is the same as in lonsdaleite carbon. It behaves like a semiconductor with an intermediate (≤ 1 eV) band gap.[7]

The possibility of obtaining large crystalline samples of Si III, and possibly Si IV, is all but excluded in the near future: In one experiment, we completely transformed a Si I sample under only 12 GPa by uncontrolled (2000 K $< T <$ 4000 K) heating from an yttrium aluminum garnet laser,[19] in an NaCl-LiCl matrix. The final sample was polluted by the molten salts, but otherwise was pure Si III, with no trace of Si I. Even this pressure is certainly not necessary to induce the Si I → Si II transition at high temperature. In a separate set of experiments to be reported later, we could show by resistivity measurements under pressure[21] that the Si I → Si II actually starts below 9 GPa. It is now possible to generate high temperatures in this pressure range[22] over large volumes (≈ 1000 cm^3), and therefore large samples of Si III and Si IV can be grown, possibly in (mono)crystalline form, if an adequate pressure-temperature path exists. Apart from the evident interest of a fundamental study of those two new elemental systems, the possibility of directly transforming a semimetal to a semiconductor by moderate heating may not be without potential applications.

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