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Pressure-induced superconductivity in high-pressure phases of Si

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The electrical behavior of Si was studied for pressures up to 43 GPa and temperatures down to 2 K using a sintered-diamond-compact anvil cryogenic clamp press. Two types of samples, amorphous thin-film Si and semiconductor-quality crystalline Si, were used. The superconducting transition temperatures T_c for high-pressure phases of the amorphous Si are about 3 K higher than those of the cystalline Si. The T_c decreases monotonically for pressures higher than 25 GPa. No upturn in T_c around 25 GPa as predicted theoretically for the simple-hexagonal phase was observed.

Recently, there have been many investigations on the structural phase transitions in Si under high pressure and the superconductivity in these high-pressure phases. The superconductivity in high-pressure metallic Si was reported by Wittig,[1] Il'ina and Itskevich,[2] Bundy and Dunn,[3] and recently Chang *et al.*[4] Until the x-ray diffraction work by Olijnyk, Sikka, and Holzaepfel[5] and Hu and Spain[6] in which additional sh (simple hexagonal) and hcp high-pressure Si phases were found, Si was thought to transform simply from diamond cubic to β-Sn structure. This led to the *ab initio* psuedopotential calculation by Chang and Cohen[7] which predicted a pressure-induced phase-transition sequence of diamond cubic $\rightarrow \beta$-Sn $\rightarrow$ sh $\rightarrow$ hcp for Si, and later, the theoretical prediction and experimental confirmation of superconductivity in sh Si by Chang *et al.*[4] Subsequent work by Dacorogna, Chang, and Cohen[8] predicted that the critical temperature T_c for sh Si would reach a minimum around 25 GPa and rise to above 10 K before tranforming to the hcp phase. Here, we report our measurements of the electrical resistance of Si for pressure up to 43 GPa and temperatures down to 2 K. We found that T_c decreases monotonically for pressures higher than 25 up to 43 GPa. No upturn in T_c was found.

The pressure equipment used in this investigation is the cryogenic clamp-type sintered-diamond-compact anvil apparatus. The experimental procedure and pressure calibration have been described elsewhere.[9-11] Two types of samples were used, i.e., amorphous and crystalline Si. An amorphous Si thin film of about 1 μm thick was sputtered on a 10-μm-thick mica sheet. Two rectangular strips of this mica sheet of approximately 0.13×0.6 mm^2 were cut. They were placed in the high-pressure cell with the Si-coated side facing each other and a gold electrode at each sandwiched in between the strips. Because the sintered-diamond compacts are not good electrical conductors, two 0.05-mm-diameter tungsten wires connecting the gold electrode and the carbide part of the piston were used. The resistance of the sample was monitored by sending through an exciting current of 100 μA and measuring the voltage drop across the pistons. In the case of crystalline-type Si, a semiconductor p-type Si single crystal[12] with acceptor concentration of 10^{13} cm^{-1} was crushed between two carbide pistons to form fine powder. The powder was carefully transferred into the high-pressure cell to form a thin line between the two electrodes. An exciting current of 1 mA was used in this case.

The sample was loaded in the clamp press and the pressure was increased by steps at room temperature. Then the temperature was lowered by successive cycles down to 2 K. The resistance of the sample was monitored during the slow warm up. It was averaged with the exciting current in both forward and reverse directions to remove any thermal emf. The clamp press, designed to be temperature compensated, gives nearly constant cell pressure during a temperature cycle. The uncertainty in pressure scale is estimated to be ± 2 GPa. The error in T_c due to thermal gradient in the apparatus is less than 0.1 K. Results for the amorphous and the crystalline Si are shown in Figs. 1 and 2. The error bar in T_c indicates the onset and completion of the resistance drop. The T_c is chosen at the midpoint of the resistance drop. For amorphous Si, the T_c of β-Sn phase is about 6.8 K and is relatively independent of pressure. The T_c of sh phase increases from 7.6 K at 15 GPa to a maximum around 8.4 K at about 21 GPa, then decreases monotonically up to 38 GPa. It is not clear whether the slight dip in T_c at 25 GPa was due to the increasingly dominant contribution to λ of the transverse acoustic mode as predicted by Dacorogna *et al.*[8] or just due to the experimental uncertainty. For crystalline Si, the T_c of β-Sn phase is about 3.9 K. The T_c of sh phase increases from 5 K at 15 GPa to a maximum of 5.2 K at 17 GPa, then decreases monotonically to 4.1 K at about 43 GPa. Transformation to hcp phase perhaps occurred at around 35 GPa as will be discussed later. But no change in the general decreasing trend in T_c was observed at that pressure. Notice that the T_c of high-pressure phases of amorphous Si is about 3 K higher than those of the corresponding phases of crystalline Si. Our measured value dT_c/dP of sh phase of Si is about -53 mK/GPa for amorphous Si, and about -44 mK/GPa for crystalline Si. Both of them are much more moderate than that measured by Chang and co-workers.[4] In the measurements by Chang and co-workers,[4] the T_c of the β-Sn phase is about 6.3 K at 12 GPa. Above 13.5 GPa, the β-Sn transforms to sh phase. The T_c of sh phase increases to a maximum of 8.2 K at 15 GPa and then decreases monotoni-

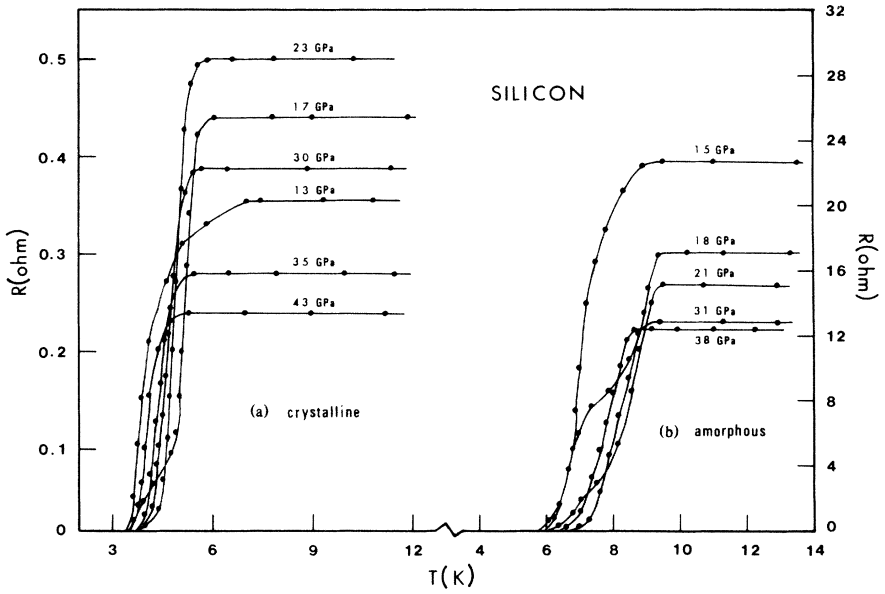

FIG. 1. Resistance vs temperature of Si at various pressures with starting sample material being (a) crystalline, (b) amorphous.

cally to 3.6 K at 25 GPa, with a dT_c/dP of -520 mK/GPa. The cause of this large difference in dT_c/dP between their results and our work is probably due to the fact that their samples were single crystals, whereas ours were powder and amorphous thin film.

Judging from the T_c behavior, we have assumed here that the high-pressure phases of amorphous Si are the same as those of crystalline Si. This assumption remains to be proved. In the experiments for crystalline Si, if we cross plot the resistance of Si of the isobaric runs at certain constant temperatures, we obtain the "synthesized" isothermal curves as shown in Fig. 3. The large dR/dP slope change at around 35 GPa indicates that Si is at a different phase for pressures from 35 to 43 GPa. The region between the two smaller arrows as shown in Fig. 3 corresponds to the sh phase of Si. This observation is consistent with the x-ray diffraction work by Olijnyk *et al.*[5] which indicates that Si transforms from β-Sn phase to sh phase at 16 GPa, to an intermediate phase (Si-VI) at 35 GPa, and to hcp phase (Si-VII) at 40 GPa. The "synthesized" isothermal curves for amorphous Si, also shown in Fig. 3, indicate a montonically decreasing behavior of resistance versus pressure

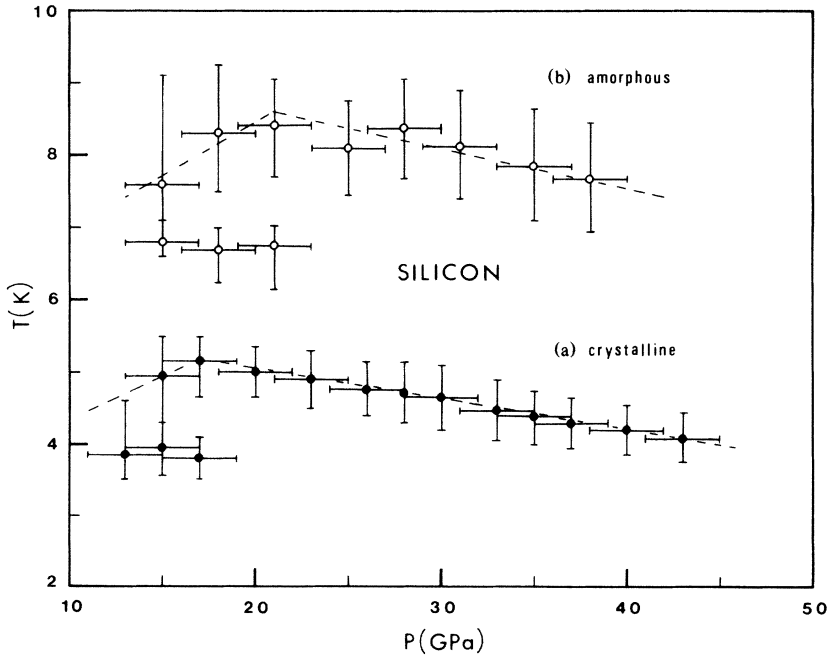

FIG. 2. T_c of Si as a function of pressure with starting-sample material being (a) crystalline, (b) amorphous Si.

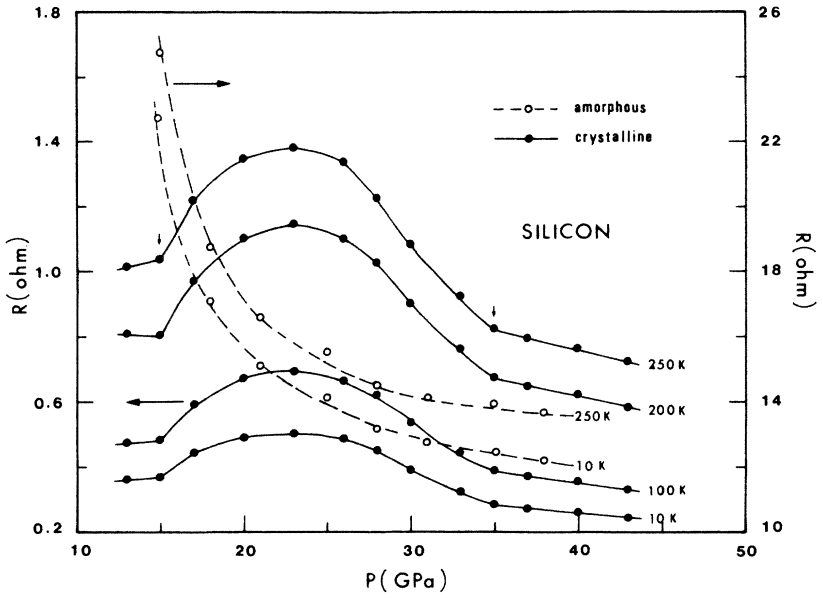

FIG. 3. "Synthesized" isothermal curves of R vs P for Si.

which is different from that of crystalline Si. The reason why they are different is not clearly understood.

Dacorogna *et al.*[8] predicted that the electron-phonon couplings for both longitudinal and transverse modes are not substantially affected by the phase transition from sh to hcp. Our observation of the T_c behavior near 35 GPa for both amorphous and crystalline Si appears to be in agreement with such a prediction. On the other hand, only the experiments with amorphous Si show a slight dip in T_c versus pressure near 25 GPa. It is not clear whether the observation of such a phenomenon of the competing contributions from the longitudinal and transverse modes in sh Si has to do with the sample size and/or its preparation. Perhaps the upturn in T_c in sh Si is not prominent as predicted due to the approximations made in the theoretical calculation, hence making it difficult to observe experimentally.

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[12]Courtesy of Professor K. L. Wang of the University of California at Los Angeles.