# High-Pressure Synthesis, Amorphization, and Decomposition of Silane

Michael Hanfland,[1] John E. Proctor,[2] Christophe L. Guillaume,[2] Olga Degtyareva,[2] and Eugene Gregoryanz[2]

[1]*European Synchrotron Radiation Facility, BP 220, Grenoble, France*
[2]*SUPA, School of Physics and Centre for Science at Extreme Conditions, University of Edinburgh,*
*Edinburgh EH9 3JZ, United Kingdom*

By compressing elemental silicon and hydrogen in a diamond anvil cell, we have synthesized polymeric silicon tetrahydride ($SiH_4$) at 124 GPa and 300 K. *In situ* synchrotron x-ray diffraction reveals that the compound forms the insulating $I4_1/a$ structure previously proposed from *ab initio* calculations for the high-pressure phase of silane. From a series of high-pressure experiments at room and low temperature on silane itself, we find that its tetrahedral molecules break up, while silane undergoes pressure-induced amorphization at pressures above 60 GPa, recrystallizing at 90 GPa into the polymeric crystal structures.

Silane, $SiH_4$, belongs to the class of hydrides which are made up from the group IVa elements and a dominant constituent, hydrogen. Silane exists at atmospheric pressure in a gaseous form, unstable even at room temperature, but for kinetic reasons does not decompose until heated to 645 K. Because of this relatively low temperature of pyrolysis, silane is extensively used for industrial production of solar grade silicon with application to solar cells (see, for example, Ref. [1]). It also is the principal material used in the production of polysilicon and is an essential component for thin film photovoltaics, semiconductors and LCD display manufacturing [2,3]. Because of its high reactivity, $SiH_4$ also has applications as rocket and scramjet fuel [4]. Recently, silane gained prominence in the fundamental solid state physics and chemistry due to being suggested as a precursor to metallic hydrogen, and hence as a candidate for high-temperature superconductivity in its highly dense state [5,6]. The high-pressure behavior of silane was mainly studied using theoretical calculations [5–11], while, because of its pyrophoric nature, experimental studies on silane are scarce [12–15], even becoming a subject of controversy [16].

$SiH_4$ consists of isolated high-symmetry tetrahedrally bonded molecules and it has long been known to solidify on cooling in phase I below 88.5 K and phase II below 63.5 K, but the details of their crystal structure still remain unclear [17]. On compression at room temperature, silane solidifies at 4 GPa in phase III, transforming at about 6.5 GPa to phase IV, which is stable up to 10 GPa [9]. The crystal structure of these phases is as yet unknown, while the phase V stable above 10 GPa was reported to have a $SnBr_4$-type structure [12] and is observed up to approximately 40 GPa. Above 50 GPa, the formation of a metallic and superconducting phase with a hexagonal close-packed structure has been claimed for silane [14], which was later attributed to a product of a chemical reaction [16].

The aim of the present work was to elucidate the high-pressure behavior of silane above 50 GPa and investigate the possibility of producing silane from solid silicon and solidified hydrogen gas at high pressures as a nonchlorine route to make silane. The reaction $Si + 2H_2 \rightarrow SiH_4$ is endothermic, the molecule is only dynamically stable, and the elements in separated form are thermodynamically preferred at 1 atm, making silane synthesis very difficult and expensive. Therefore, we investigate the use of high pressures to synthesise silane—pressure can have a profound effect on chemical reactivity because it can induce large changes in electronic and atomic structure. Two different elements that do not react at normal conditions can form novel compounds if compressed in a diamond anvil cell with or without application of temperature. For example, metallic nitrides synthesized from elemental nitrogen and Pt, Os and Ir using laser-heated diamond anvil-cell techniques form at pressures above 50 GPa, one of the highest pressures at which synthesis has been carried out with complete recovery of the product to ambient conditions [18,19]. Compression alone without additional heating was sufficient for a synthesis of novel compounds in the K-Ag system, considerably extending the chemistry of these nonreacting elements [20]. These results show that the kinetics of the solid state reactions to form novel compounds could be greatly influenced and tuned by the application of pressure.

In this Letter, we show that polymeric silicon tetrahydride could be synthesised at 124 GPa and 300 K from elemental silicon and hydrogen, two elements that do not react with each other at ambient pressure. From separate series of experiments at room and low temperature on the silane itself, we find that its tetrahedral molecules break up, while it undergoes pressure-induced amorphization at pressures above 60 GPa, recrystallizing at 90 GPa into polymeric crystal structures identical to the ones observed on synthesis of silicon tetrahydride from elemental Si and $H_2$, and theoretically predicted to be insulating [7].

To synthesize silane, fluid hydrogen and polycrystalline silicon were loaded into a diamond anvil cell

(see supplemental material for the experimental details [21]). At above 5.5 GPa the volume ratio of Si to solid hydrogen was estimated to be 1:1. Over the period of several months pressure was increased up to 123 GPa at 300 K with no chemical reaction observed, as Raman and synchrotron x-ray diffraction measurements showed a mixture of pure $H_2$ and Si (see Fig. 1, lower panel). After 8 months at 124 GPa (Fig. 1, upper panel and inset), Raman and x-ray scattering both showed presence of a new phase. To the best of our knowledge this is the first case of the
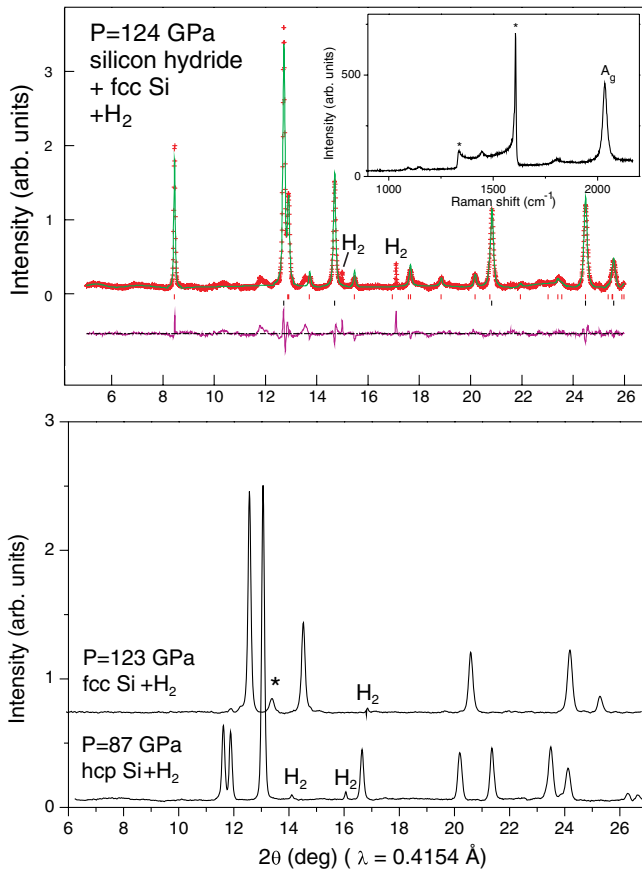


FIG. 1 (color online). Powder x-ray diffraction spectra showing synthesis of the polymeric silicon tetrahydride. (Lower panel) Powder diffraction spectra of hcp and fcc phases of pure Si with two weak diffraction peaks from hcp phase of molecular hydrogen marked as "$H_2$", before the reaction took place. "*" denotes the remaining peak from hcp Si. (Upper panel) Powder diffraction spectrum and the full structure Rietveld refinement of the synthesized silicon tetrahydride in an $I4_1/a$ phase (upper tick marks) in the presence of the remaining fcc phase of Si (lower tick marks) and hcp phase of molecular hydrogen (two strongest peaks marked on the spectrum as $H_2$). The crosses, upper solid line and lower solid line represent experimental, modeled and difference spectra, respectively. Inset in the upper panel shows a Raman spectrum of the $I4_1/a$ phase of silicon tetrahydride. The stars indicate the peaks from diamond, and the strongest Raman line from the silicon tetrahydride corresponding to the Si-H stretching mode is denoted as $A_g$.

high-pressure cold (room temperature) synthesis at such extreme pressures. The phase formed was indexed as a body-centered tetragonal structure with lattice parameters $a = 3.0864(2)$ Å, and $c = 6.957(1)$ Å. Silicon occupies $4(a)$ position of the space group $I4_1/a$, which is, quite remarkably, the same as the $4a$ position of the space group $I4_1/amd$ occupied by the Cs atoms in the Cs-IV structure [22] (as well as Rb in Rb-V structure). This tetragonal phase is a product of reaction of the face-centered cubic phase of Si with hydrogen, forming polymeric silicon tetrahydride, an insulating phase where each Si atom is bonded to 8 hydrogen atoms (Fig. 2). This tetragonal structure happens to be the same insulating phase observed on the compression of silane itself [14] and as predicted from *ab initio* calculations for silane between 50 and 260 GPa [7]. The measured volume for the synthesized silicon tetrahydride phase at 100 GPa agrees with the value predicted for silane [7]. We have attempted to recover this phase but both diamonds failed when pressure was decreased down to ~100 GPa.

In the second set of experiments we have loaded the silane gas and performed the Raman and x-ray synchrotron diffraction studies up to 130 GPa at 300 and 90 K (see Ref. [21]). Compressing $SiH_4$-V (the $SnBr_4$-type structure [12]) above 40 GPa and 90 K results in appearance of additional diffraction lines corresponding to the $SiH_4$-VI phase, identified here for the first time (Fig. 3, left panel). We note that the diffraction pattern is similar in its complexity to that observed for the orthorhombic structure known to form under pressure in elemental Si as well as Cs (phases Si-VI and Cs-V, respectively) [22]. At 65 GPa and 300 K, we observed disappearance of x-ray diffraction
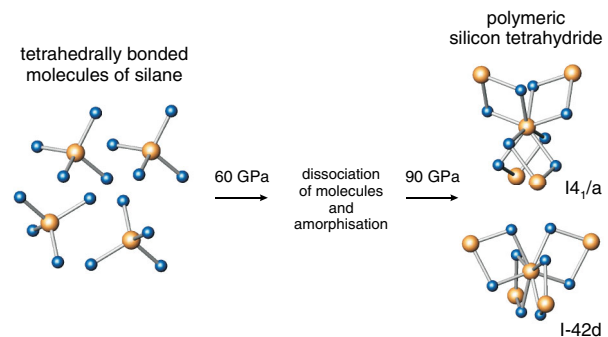


FIG. 2 (color online). Schematic illustration of the transformation of the molecular silane into a polymeric atomic arrangement. (Left) Four molecules of the phase V at 25 GPa are shown that constitute one unit cell of the $SnBr_4$-type structure. Above 60 GPa, the molecules dissociate and the sample becomes amorphous, crystallizing (right) above 90 GPa into a polymeric phase with an eight-coordinated silicon, with two different crystal structures observed (upper) $I4_1/a$ and (lower) $I\bar{4}2d$. The lattice parameters and atomic coordinates of Si are obtained in the present work from Rietveld refinement of diffraction spectra at 108 GPa with hydrogen positions taken from Ref. [7]. Bonds up to 1.8 Å are shown.
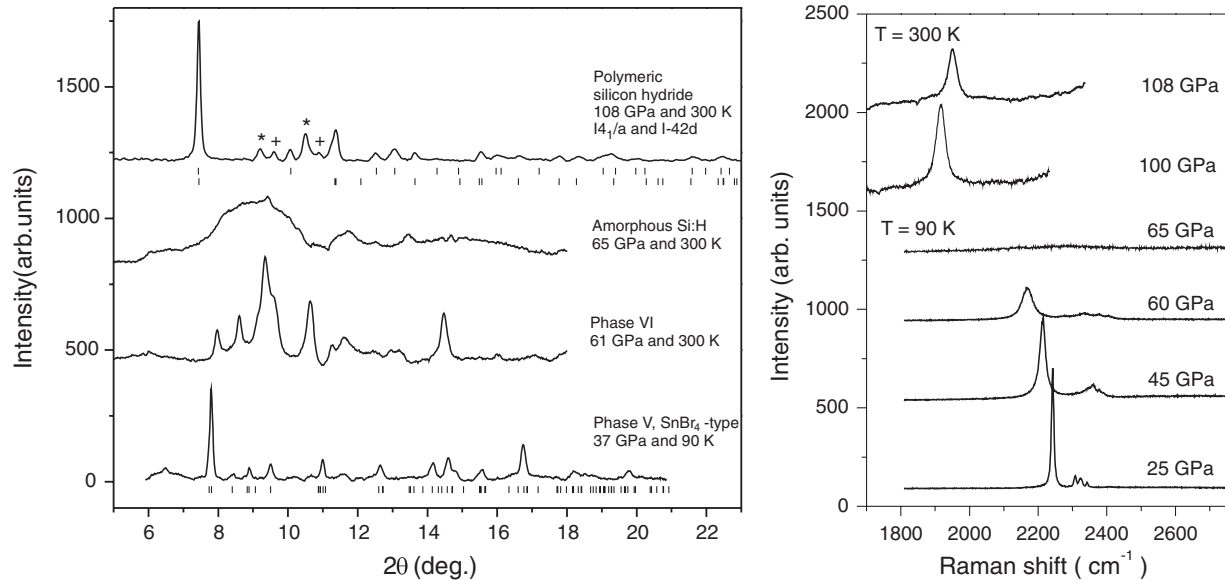
FIG. 3.   Representative Raman and x-ray powder diffraction patterns of SiH$_4$ at different pressures and temperatures. (Left) Powder x-ray diffraction spectra of silane collected on pressure increase at 90 and 300 K show transformation from phase V to phase VI, then to an amorphous state recrystallizes into a mixture of two new phases at higher pressures. The tick marks below the spectra show the calculated peak positions for the SnBr$_4$ structure for phase V and the $I4_1/a$ (lower tick marks) and $I\bar{4}2d$ (upper tick marks) structures for the upper spectrum of the mixture of two silane phases. "+" and "*" denote the two strongest peaks from Re (gasket material) and Re hydride, formed after the reaction with atomic hydrogen released due to a partial decomposition of silane at lower pressure (see also Ref. [16]). (Right) Raman spectra of silane at various pressures and temperatures, showing the absence of Raman peaks from the amorphous phase.

peaks from the crystalline SiH$_4$-VI phase (Fig. 3). The crystalline peaks in the diffraction pattern are replaced by a single broad peak at $2\theta = 9°$ with full width at half maximum of 2° (Fig. 3 left panel). Using the Scherrer formula $L = \lambda/\delta 2\theta \cos(2\theta)$, with $\lambda$ being the wavelength of 0.4127 Å, the correlation length is estimated to be approximately 12 Å which is comparable to two unit cells of the SiH$_4$-V. Raman spectra of silane at 300 and 90 K (Fig. 3) show several modes all decreasing in intensity with pressure increase and their disappearance at above 60 GPa in a good agreement with Ref. [13]. The strongest in intensity $\nu_1$ mode (at $\sim 2200$ cm$^{-1}$ at 45 GPa) shows pressure-induced softening (see Fig. 3, right panel). The softening of this Si-H stretching mode is indicative of the instability of the tetrahedral SiH$_4$ molecule at these pressures, marking its dissociation and a formation of a new atomic arrangement which possibly resembles the subsequent polymeric $I4_1/a$ structure where each Si atom is bonded to 8 hydrogen atoms. The transformation of SiH$_4$ to an amorphous state is analogous to the known pressure-induced amorphization of the isoelectronic molecular crystals SnBr$_4$, SnI$_4$ and GeI$_4$ [23–25].

Further compression of the amorphous silane above 90 GPa leads to a recrystallization of the SiH$_4$ into 2 different phases, that can be indexed with tetragonal symmetry and space groups $I\bar{4}2d$ and $I4_1/a$, respectively, (Fig. 3). This transition is reminiscent of recrystallization taking place in molecular sulphur at very similar $P - T$

conditions [26]. The refined lattice parameters for the $I\bar{4}2d$ phase are $a = 4.255(3)$ and $c = 3.923(3)$ and for the $I4_1/a$ phase they are $a = 3.147(1)$ Å, and $c = 7.097(5)$ Å at 108 GPa and 300 K. The volume of the $I4_1/a$ phase is 1% smaller than that of $I\bar{4}2d$, indicating that the $I\bar{4}2d$ phase is likely to be present in a metastable form. On further compression the $I\bar{4}2d$ phase decreases in intensity and the $I41/a$ phase appears to be stable. These two phases are identical to those predicted theoretically [7] and the $I4_1/a$ phase is the phase pure silicon and hydrogen form at 124 GPa and 300 K (see above). Figure 2 shows the atomic arrangement of Si and H atoms in the $I\bar{4}2d$ and $I4_1/a$ phases, with the lattice parameters and atomic positions of Si atoms refined from the diffraction data in the present work. In both structures, each Si atom is bonded to 8 H atoms. As noted above, the Si atomic positions in the $I4_1/a$ phase are the same as in the Cs-IV structure, while those in the $I\bar{4}2d$ phase resemble those in the $\beta$-Sn structure type that appears in pure Si under pressure [22]. In our Raman measurements, the Raman vibron reappeared at 100 GPa at room temperature, confirming the recrystallization observed in the x-ray diffraction experiments (Fig. 3). The observed Raman vibron at 1940 cm$^{-1}$ and 100 GPa corresponds to the strongest mode of the $I4_1/a$ phase, with the frequency close to the vibron that disappeared above 65 GPa, and now hardening with pressure. This is in accordance with an earlier observation of the $I4_1/a$ phase in silane in the x-ray diffraction experiment in Ref. [14]
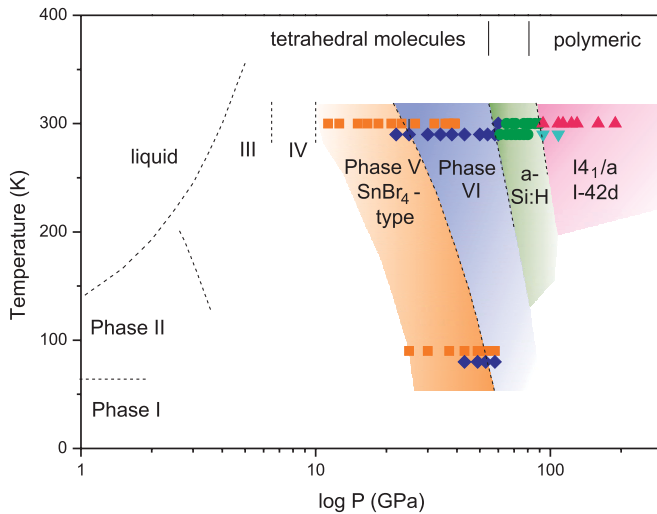
FIG. 4 (color online). Proposed phase diagram of silane (pressure logarithmic scale) in a wide pressure and temperature range. The data points are shown from the present study, that reveal the existence of phases V and VI (tetrahedral molecular phases), an amorphous state and the $I4_1/a$ and $I\bar{4}2d$ (polymeric) phases.

above 100 GPa, with the Raman spectrum giving the strongest mode of 2083 cm$^{-1}$ at 151 GPa assigned to an $A_g$ Si-H stretching mode.

From present observations we propose the following phase diagram of silane (Fig. 4). Although the structure symmetry of the ambient pressure phases I and II has been revisited two years ago [17], the details of the crystal structure and phase boundaries of these phases as well as of the phases III and IV remain unknown. Above 10 GPa at room temperature lies the stability range of the phase V with the SnBr$_4$ structure (Ref. [9] and present work), whereas above approx. 30 GPa at room temperature and 40 GPa at 90 K phase VI is formed with a crystal structure that is unresolved. We find that silane does not, as previously reported [13,14], metallize at 60 GPa. Instead, it amorphizes at above 60 GPa marking dissociation of tetrahedral molecules. This is followed by a recrystallization into 2 phases at pressures of about 90 GPa (one stable and one metastable phase), the polymeric crystal structures of which are the same as predicted by Pickard and Needs [7]. Thus silane remains nonmetallic up to at least 130 GPa, the maximum pressure reached in the present study in excellent agreement with recent infrared measurements up to 150 GPa [27]. The metallic P6$_3$ phase previously claimed in SiH$_4$ above 50 GPa [14] is attributed to the formation of PtH [16].

In conclusion, we have synthesized polymeric silicon tetrahydride by compressing elemental silicon and hydrogen at room temperature. The high-pressure synthesis of SiH$_4$ from pure elements as well as the formation of the amorphous Si:H under pressure observed in the present work show the possibility of such reactions which is of great interest to the solar cell and other industries.

The rather high pressures of formation obviously lie outside the limit for the immediate industrial application. However, we propose that the pressure and time required for this reaction to take place could be substantially reduced by varying temperature and adding catalysts to find the optimum conditions for the reaction to take place.

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