High pressure studies on silane to 210 GPa at 300 K: optical evidence of an

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# High pressure studies on silane to 210 GPa at 300 K: optical evidence of an insulator–semiconductor transition

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**Abstract**
Silane ($SiH_4$) has been studied in a diamond anvil cell from 7–210 GPa by using optical reflection and absorption techniques at 300 K. The reflectivity and transmission measurements showed a dramatic change in the neighbourhood of 100 GPa. On the basis of reflectivity and absorption experimental data, the pressure dependence of the refractive index ($n$) of solid $SiH_4$ was derived, which was then used to determine the ratio of the molar refraction ($R$) to the molar volume ($V$). There is a large jump in the ratio $R/V$ between 92 and 109 GPa. At 109 GPa and 1.6 eV, $n^*(SiH_4) = 3.62$ (the real part of refractive index) and $R/V(SiH_4) = 0.79$, which are similar to the values for silicon at one atmosphere at the same energy. The results indicated that an insulator–semiconductor phase transition might have occurred in solid $SiH_4$ between 92 and 109 GPa. Comparing values of the real part of $n$, $n^*$, and the extinction coefficient $k^*$ with that of metals, we conclude that $SiH_4$ is not yet a metal at the maximum pressure investigated (210 GPa), suggesting that a higher pressure is needed for its metallization.

(Some figures in this article are in colour only in the electronic version)

For decades, great efforts have been made to convert hydrogen ($H_2$) into a metal by pressurizing it. It is calculated that hydrogen ($H_2$) should become a metal at multimegabar pressures [1] (1 megabar = 100 GPa = 1 million atmospheres) and will be a high-temperature superconductor [2]. However, hydrogen is still not a metal even at 342 GPa [3]. It is calculated

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that hydrogen should become a metal at 600 GPa [1]. It is difficult to achieve a static pressure that high because the hydrogen diffuses into the diamond under high pressure and damages the diamond anvils [3]. Experiments are underway to construct barriers for the hydrogen to prevent its diffusion into the diamond anvil and consequently accomplish higher pressure. In the meanwhile, it was decided to explore a few hydrogen-containing compounds, a route taken earlier with CsH [4]. As Cs itself is a metal, it was thought that perhaps the 'alloy' CsH would metallize at a lower pressure than hydrogen. However, it was found that CsH still had a band gap of 1.9 eV at 251 GPa, suggesting a much higher metallization pressure. More recently, theoretical calculations predicted that the dense hydrogen-rich compound silane ($SiH_4$) should be metallized at 91 GPa [5] and should then be a high-temperature superconductor [6]. No previous report on $SiH_4$ behaviour under such a high pressure has been made. The purpose of this study is to attempt to find metallization in the hydrogen-rich compound, $SiH_4$, through optical measurements in a diamond anvil cell at 300 K.

It is well known that a standard optical method for studying metallization of materials is to observe a plasma edge, i.e. to find that the reflectivity at a fixed pressure increases rapidly as the energy of the incident light decreases (for example, see the results on Xe [7, 8], $O_2$ [9, 10], S [11–13] and BaTe [14]). Another optical concept which helps to clarify material metallization follows. From the Mossotti equation[6] (1850),

$$R/V = (\varepsilon - 1)/(\varepsilon + 2) \tag{1}$$

where $R$ is the molar refraction, $V$ is the molar volume and $\varepsilon$ is the permittivity of the sample. For high frequencies, Maxwell (1873) notes in his classic book on electromagnetism that

$$\varepsilon = n^2 \tag{2}$$

where $n$ is the refractive index, so that for an optically isotropic sample

$$R/V = (n^2 - 1)/(n^2 + 2) \tag{3}$$

where

$$n = n^* + ik^*. \tag{4}$$

Goldhammer [15] and later Herzfeld [16] suggested that metallization occurs when

$$R/V_m \Rightarrow 1 \tag{5}$$

where $V_m$ denotes the molar volume of metallization. From the polarizability given by Lide [17], we find $R = 13.7 \text{ cm}^3 \text{ mol}^{-1}$ and hence from the above an estimate of the volume of metallization $V_m = 13.7 \text{ cm}^3 \text{ mol}^{-1}$. The liquid just above $T_m$ (the melting temperature) under a pressure of 1 atm of inert gas has a volume of about $58.2 \text{ cm}^3 \text{ mol}^{-1}$. Thus the estimated fractional volume at metallization is about 0.23, much larger than that expected for $H_2$ (less than 0.1).

The Goldhammer–Herzfeld criterion is obeyed in xenon [8] and BaTe [14]. These materials metallized, in the absence of any measurable first-order phase transition, at very close to the volume given by equation (5). In this study, we used the above criterion to describe the high-pressure behaviour of $SiH_4$.

$SiH_4$ is highly pyrophoric and must be handled accordingly. The diamond anvil cell was loaded in an ultra-dry, ultra-pure helium atmosphere in a glove box. The diamond anvils were each 1/3 carat with a 17.5 $\mu$m radius tip with an 8° bevel to a radius of 150 $\mu$m. The initial $SiH_4$ pressure in the first experiment was found to be 7 GPa, and in the second experiment it was found to be 45 GPa.

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[6] This expression was first derived by Mossotti. Further understanding was added later by Clausius and still later by Lorenz and Lorentz. Physicists often call it the Lorenz–Lorentz equation.

The optical measurements were performed using a micro-optical system equipped with a microscope and fibre optics connected to a spectrometer [18]. The measurements from Raman scattering, reflectivity and absorption for two separate experiments were recorded by a CCD detector. Reflectivity and absorption measurements were carried out on $SiH_4$ at high pressure to 210 GPa at 300 K from 1.2 to 2.9 eV. The optical studies utilized a light source with a 4 $\mu$m diameter beam on the sample over the entire pressure range. The pressure cell consisted of a diamond anvil with parallel faces, a sample in a hole in a thin metal gasket, and the second diamond whose faces were parallel to each other and to the faces of the other diamond. The spectra were referenced to a single diamond with air on each side. The intensity of the incident beam was kept constant.

The pressure determination for the $SiH_4$ sample is described as follow. Pt was deposited on the cylindrical wall of the sample hole, which is at 8.5 $\mu$m from the centre of the sample. The Pt sample was 0.5 $\mu$m thick, 2.8 $\mu$m wide, and 4.0 $\mu$m high. The lattice parameter of the Pt was measured by *in situ* x-ray diffraction under high pressure. From this, the volume was deduced, and from the known $P$–$V$ relation [19, 20] the pressure was obtained. This procedure has been analysed in detail by Chijoke *et al* for other materials [21]. In an earlier study, the Raman shift at the centre of the surface of the diamond tip was measured against the pressure of the Pt and a convenient optical pressure scale was established, as described in detail in [22]. According to the optical pressure scale, which was calibrated by Pt, the pressure of the $SiH_4$ sample was determined.

Inasmuch as the optical measurements on the silane sample were made at the axial centre of the diamond tip, we can obtain an upper bound for the pressure difference at the centre of the sample and at the edge where the Pt is located by comparison with careful measurements of the pressure profile of a rhenium (Re) sheet (Re was the sample as well as the gasket) [23]. The measured pressure at $r = 0$ was 206 GPa in the Re, and the measured pressure at $r = 4$ $\mu$m was 203 GPa. Because the pressure gradient is proportional to the yield strength, which increases as pressure increases [24], a smaller difference would be expected in silane.

The reflectivity of the sample was obtained at high pressure using [25]

$$R_{ds} = (I_{rs}/I_{ra})R_{da} \qquad (6)$$

where $R_{ds}$ and $R_{da}$ are the reflectivities of the diamond–sample and diamond–air interface, $I_{rs}$ is the reflected intensity of light at normal incidence from the diamond cell, while $I_{ra}$ is the intensity of the light reflected using only a single diamond (with air on each side). This measurement determines $R_{ds}$ at each pressure. Figure 1 shows the reflectivity versus the photon energy of the $SiH_4$ sample at three pressures. The reflectivity on the low-energy side is clearly increased at 109 GPa and becomes more distinctive as pressure increases to 210 GPa. Figure 2 shows the reflectivity versus pressure at 1.6 eV for two separate experiments. The reflectivity shows normal insulator behaviour ($\sim$5%) at pressures of 92 GPa and below. At the highest pressure reached, $P = 210$ GPa, the reflectivity of the $SiH_4$ increased to $\sim$15% at 1.6 eV and $\sim$35% at 1.4 eV. Upon downloading, the reflectivity of the sample decreased to $\sim$3% at 78 GPa, close to the value found on loading. To check if decomposition or disproportionation had occurred in $SiH_4$ at high pressure, we measured the hydrogen Raman spectrum (if decomposed, $nSiH_4 \rightarrow [SiH_2]_n + nH_2$) at each loading point to the maximum. No hydrogen vibron was observed in the pressure range investigated. Hence no measurable $SiH_4$ was decomposed under high pressure to 210 GPa. Therefore, the increase in reflectivity with pressure suggests that pressure might drive a phase transition in solid $SiH_4$.

Based on the measurements of $R_{ds}$, we interpret the refractive index ($n^*$) of solid $SiH_4$ to 210 GPa according to the following equation:

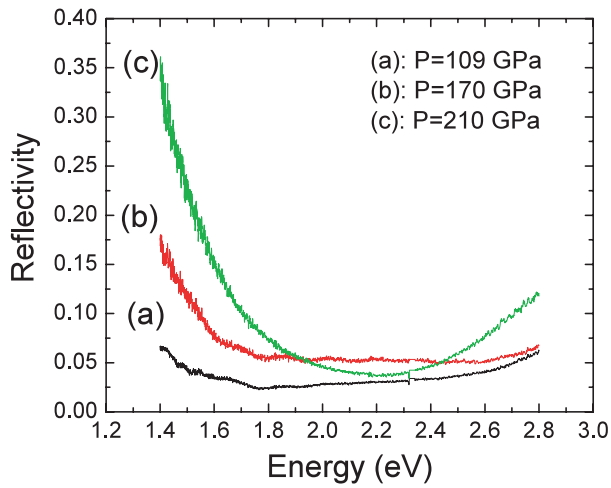**Figure 1.** Reflectivity at the SiH$_4$–diamond interface versus energy at three pressures at 300 K.
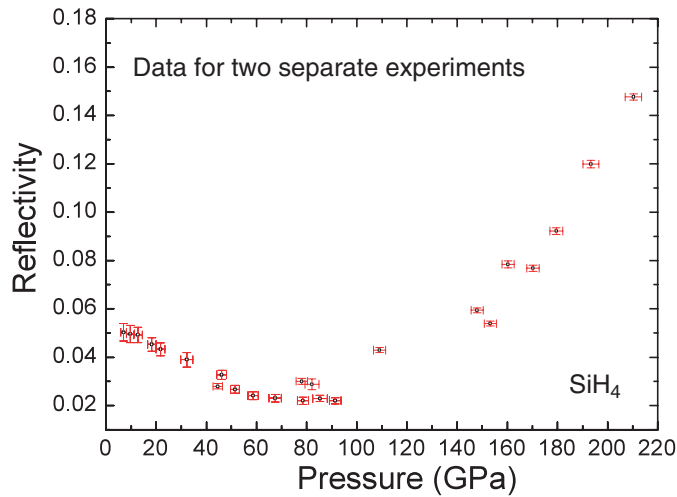


**Figure 2.** Pressure dependence of reflectivity of the SiH$_4$–diamond interface at 1.6 eV and 300 K.

$$R_{ds} = \frac{(n^* - n_d)^2 + k^{*2}}{(n^* + n_d)^2 + k^{*2}} \tag{7}$$

where $n^*$ is the real part of the refractive index of the sample, $k^*$ is the extinction coefficient of the silane sample, and $n_d$ is the refractive index of the diamond.

The centre of the loaded diamond tip is not under hydrostatic pressure, even when the sample is. In the absence of experimentally available data for the refractive index at the centre of the tip of a loaded diamond, we proceed as follows.

The computed value of the refractive index of diamond at zero stress is 0.073 less than the experimental value, while the initial slope of computed refractive index versus pressure agrees with experiment [26]. As a result, we have used the theoretical value of refractive index of diamond plus 0.073 for our value of $n_d(P)$ (to be used in our analysis of data). It should be noted that the theoretical values of refractive index of diamond are, for the case of a loaded diamond anvil tip as used in our experiments, not those for a diamond under hydrostatic pressure. It should be noted that $n_d(109) = 2.38$ compared to $n_d(0) = 2.41$.
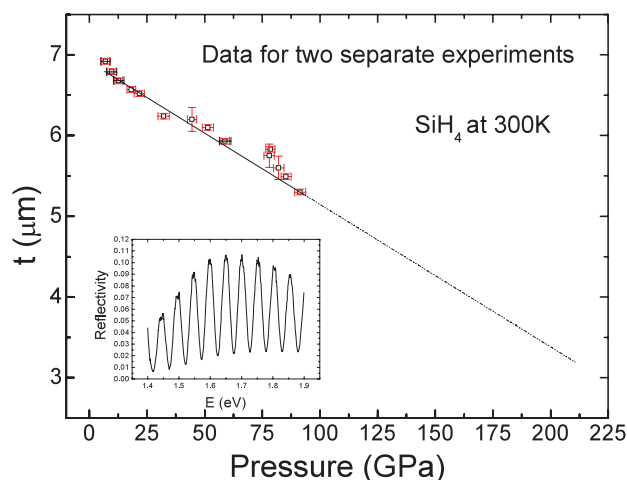
**Figure 3.** The sample thickness measured by its Fabry–Perot pattern at pressures to 92 GPa and linear fit. Error bars are for $2\sigma$. The inset of the main figure shows interference patterns of the $SiH_4$ sample at 7 GPa.

There are two cases for the $k^*$ value in general. If the sample is transparent, $k^*$ is so small that it has a negligible affect on the reflectivity in equation (7). In this case, $k^*$ can be taken as zero and $n^*$ can easily be determined assuming $k^* = 0$, given $n_d$. When the sample is not transparent, for example it turns grey or black, $k^*$ is large ($k^* \neq 0$) and hence $k^*$ must be measured. In this study, the $SiH_4$ sample was transparent in the pressure range 7–92 GPa, and we assume the parameter $k^* = 0$. However, at 109 GPa and above, the colour of the sample had turned dark grey; we take $k^*$ into account in this case, with

$$k^* = \alpha\lambda/4\pi \tag{8}$$

where $\alpha$ is the absorption coefficient and $\lambda$ is the wavelength (*in vacuo*). In order to obtain $k^*$, the absorption coefficient of the sample was measured and $\alpha$ was extracted from the equation:

$$\alpha = \frac{1}{t}\left[2\ln(1 - R_{ds}) - \ln\left(\frac{I_{ts}}{I_{ta}}\right)\right] \tag{9}$$

where $t$ is the sample thickness, $I_{ts}$ is the transmitted intensity (resulting from a beam at normal incidence) through the diamond cell (two diamonds) with the sample present in the sample hole, and $I_{ta}$ is the transmitted intensity from the single diamond referenced with air on both sides [25]. Inasmuch as $R_{ds}$ was obtained from optical measurements, then, if $t$ is known, $\alpha$ and hence $k^*$ can be calculated from equations (9) and (8).

At 92 GPa and below, the sample is transparent ($k^* = 0$), and the sample thickness $t$ can be obtained from [27]

$$t = m\lambda/2n^* \tag{10}$$

where $m$ is the order of the interference and $\lambda$ is the wavelength (*in vacuo*) of the corresponding interference minimum of the Fabry–Perot pattern, and $n^*$ is the real (and only) part of the refractive index of the sample. Therefore, we were able to obtain the thickness of the sample, $t$, at 92 GPa and below from its Fabry–Perot interferometry pattern. The sample thickness above 92 GPa was estimated by the extrapolation of the fitted curve of data points from 7 to 92 GPa. Figure 3 demonstrated the experimental data of the sample thickness and fitted curve versus pressure, while the inset of the main figure shows an interference pattern of the $SiH_4$ sample at
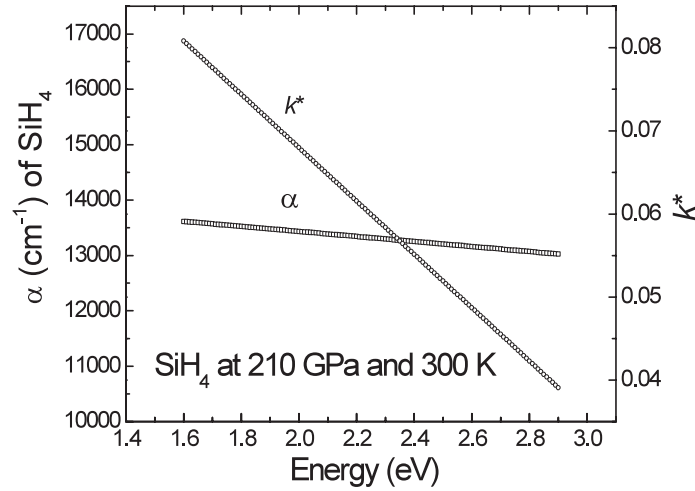
**Figure 4.** Experimental results of absorption coefficient, $\alpha$, and the extinction coefficient, $k^*$, of the SiH$_4$ as a function of photon energy at 210 GPa. The error bars of $\alpha$ and $k^*$ are both 24% ($\pm 2\sigma$).

7 GPa. Extrapolation to 210 GPa gives a sample thickness of $3.2 \pm 0.2$ $\mu$m. It is noted that, with a phase transformation, the thickness would be less. A volume change due to a phase transition of 10% could introduce a 10% error in $\alpha$ not accounted for here. Even if $\alpha$ and $k^*$ were increased by 10%, this would not suggest metallization in the SiH$_4$ sample.

At 92 GPa and below, the absorption by SiH$_4$ on the energy range 1.2–2.9 eV was very low. However, there is a significant increase in absorption at 109 GPa. The experimental results of absorption coefficient and $k^*$ of solid SiH$_4$ versus photon energy at the highest pressure 210 GPa in this study were plotted, as shown in figure 4. It is seen that $k^*$ is 0.08 at 1.6 eV, which is much less than the value of any metals at the same energy (for example, $k^* = 5.4$ for Ag, $k^* = 3.3$ for Ta). Once $R_{ds}$, $n_d$ and $k^*$ are known at a given pressure, $n$ can be obtained from equation (1). Figure 5 shows the pressure dependence of the real part of the refractive index of the SiH$_4$ sample. Below 109 GPa, the real part of the refractive index ($n^*$) of the sample increased linearly. The $n^*$ increased dramatically between 92 and 109 GPa, and the increase persisted to 210 GPa. Upon downloading the sample to 78 GPa, $n^*$ decreased to the low level found on loading. It is seen that there would be two distinct regions in figure 5, each of which could be fitted by a straight line if the point at 109 GPa is missing. We label the upper group as the *ab* line and lower group as the *cd* line. The experimental value at 109 is $3.63 \pm 0.003$, while the value of $n^*$ on the extrapolated line *ab* at 109 GPa is $n^*_{(ab)} = 2.88$. The value of $n^*$ on the extrapolated line *cd* at 109 GPa is $n^*_{(cd)} = 1.88$. To analyse the error in $n^*_{(ab)}$ and $n^*_{(cd)}$ at 109 GPa, we use $dn^* = da + P\,db + b\,dP$ based on the equation $n^* = a + bP$:

$$n^* = 1.5089(\pm 0.013) + 0.00349(\pm 2.56 \times 10^{-4})P(\pm 2.4) \qquad (7 \leqslant P \leqslant 109 \text{ GPa}) \qquad (11)$$

$$n^* = 0.339\,55(\pm 0.038) + 0.023\,32(\pm 0.0003)P(\pm 2.4) \qquad (109 \leqslant P \leqslant 210 \text{ GPa}). \qquad (12)$$

The errors of $n^*_{(ab)}(109)$ and $n^*_{(cd)}(109)$ were obtained through the equation of $\Delta n^* = \{[(da)^2 + (P\,db)^2 + (b\,dP)^2]/2\}^{1/2}$. $\Delta n^*_{(ab)} = 0.035$ and $\Delta n^*_{(cd)} = 0.022$. The difference between 3.63 (the measured value at 109 GPa) and $n^*_{(ab)}(109)$ is 0.75, about $20\sigma$. There is clearly a dramatic jump between 92 and 109 GPa. Possibly there is a first-order transition, but further studies, in which more data points are obtained in this range, need to be made to check this.
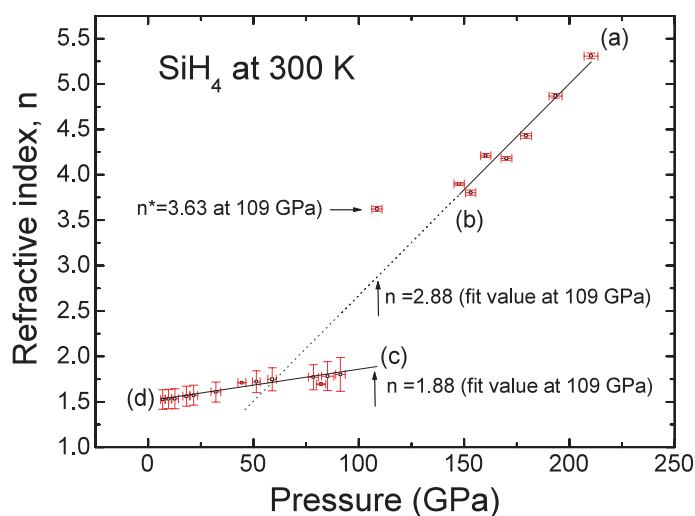
**Figure 5.** Pressure dependence of the real part of the refractive index, $n^*$, of the SiH$_4$ sample at 1.6 eV. Error bars are for $2\sigma$. Line *ab* is a fit curve (solid line) of the high-pressure data (upper group) excluding the 109 GPa point extrapolated down to the low pressure and curve (dash line). Line *cd* is a fit curve of the low-pressure data.
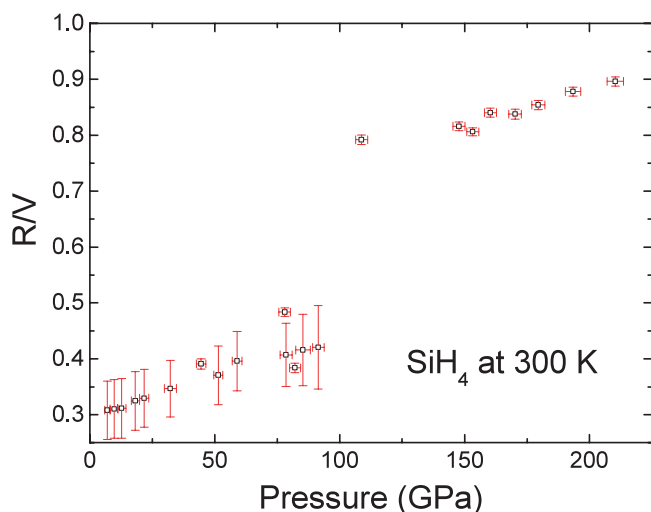


**Figure 6.** The ratio of $R/V$ obtained from experimental data versus $P$ at 1.6 eV. Solid squares represent data for the first experiment; open squares represent data for the second experiment. Error bars are for $2\sigma$.

Finally, the ratio of $R/V$ versus pressure is plotted according to equation (3), as shown in figure 6. It can be seen that there is a dramatic increase in $R/V$ between 92 and 109 GPa. The values of $n^*(\text{SiH}_4)$ and $R/V(\text{SiH}_4)$ are 3.62 and 0.79, respectively, at 109 GPa and 1.6 eV, which are very close to the values of silicon at one atmosphere at 1.6 eV, namely $n^*(\text{Si}) = 3.7$ and $R/V(\text{Si}) = 0.8$. According to our experimental results, it is likely that SiH$_4$ has changed into a semiconductor by compressing it to 109 GPa. Despite the fact that the values of $n^*(\text{SiH}_4)$ and $R/V(\text{SiH}_4)$ have increased to 5.31 and 0.9 at 210 GPa at 1.6 eV (for Ag $n^* = 0.9$ at the same energy), the value for $k^*(\text{SiH}_4)$ ($\sim$0.08) was much less than the $k^*$ value of any metal.

We hence conclude that $SiH_4$ is not metallic at the highest pressure, 210 GPa, in this study. These results also suggest that the metallization in $SiH_4$ needs a higher pressure at 300 K.

## Acknowledgments

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