Optical Properties of Silane to 218 GPa: Black Silane

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Silane, a pyrophoric compound, was loaded at cryogenic temperatures into a diamond anvil cell using a special apparatus. Reflectivity and absorption studies were made to 218 GPa. From these the real refractive index n* and the extinction coefficient k* were obtained. At 1.6 eV the refractive index shows a large jump at about 100 GPa and increases further to n* = 5.3 at 218 GPa. The extinction coefficient varies smoothly with pressure reaching a value of k* = 0.07 at 218 GPa.

It has been suggested by Ashcroft (2004) that the Group IVb hydrides will metallize at much lower pressures than hydrogen and being alloys with 80% hydrogen they will be high Tc superconductors. It is known that hydrogen is not yet a metal at 340 GPa (Narayana et al., 1998 and Loubeyre et al., 2002) and is calculated by Natolie et al. (1993) to be a metal at 600 GPa. It has been found that high Z (atomic number) materials (Xe, Reichlin et al. 1989, BaTe,

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Grzbowski and Ruoff 1984a, BaSe, Grzybowski and Ruoff 1984b) metallize at the pressure calculated by the Goldhammer (1913) criterion, i.e., when the molar volume $V_m = R$ where R is the molar polarization. This suggests for silane $V_m = 13.7$ cm^3/mole, (Lide 1992) whereas the molar volume for the solid phase at 1 atm at low temperature is about 53 cm^3/mole. The expected compression ratio is therefore less than four.

The diamond anvils had tips of 35 microns with an 8° bevel. The sample was loaded in an especially dry glove box with the piston cylinder held at cryogenic temperatures. Loading and clamping took 1 ½ minutes. Pressure was measured using the diamond-tip scale (Sun et al. 2005). Optical studies were made with a focused beam 4 microns in diameter (Zha and Bassett 2003).

The measured reflectivity at normal incidence is given by

$$R_{ds}(\omega) = \left[\frac{I_s(\omega)}{I_o(\omega)R_{da}}\right]\left[\frac{R_{da}}{(1-R_{da})^2}\right] \tag{1}$$

where $\hbar\omega$ = photon energy, $R_{ds}(\omega)$ = diamond-sample interface reflectivity, $I_s(\omega)$ = intensity of the light reflected by the sample, $I_o(\omega)R_{da}$ = intensity of the light reflected by the air-diamond interface, R_{da} = room-pressure air-diamond interface reflectivity whose weak energy dependence is neglected.

The absorption coefficient is given by

$$\alpha = \frac{1}{\ell}\left[2\ln\left(\frac{1-R_{ds}}{1-R_{da}}\right) - \ln\left(\frac{I_s}{I_d}\right)\right] \tag{2}$$

where ℓ is the sample thickness, R_{da} is the reflectivity of diamond-air interface, and I_s and I_d are the intensities of the light transmitted at normal incidence through the diamond-sample and diamond-air interface respectively. Both I_s and I_d have I_o (the incident intensity) as a factor. As

I_0 was kept constant the I_0 cancelled. The thickness ℓ was obtained to 177 GPa from the Fabry-Perot interference pattern using the equation $2n^*\ell = m\lambda$ where n^* is the real part of the refractive index, m is the order of the interference and λ is the wavelength of the corresponding interference maximum. The function $\ell(P)$ was fitted and extrapolated to get values at higher pressure. An absorption versus pressure curve at 1.6eV is shown in Figure 1.

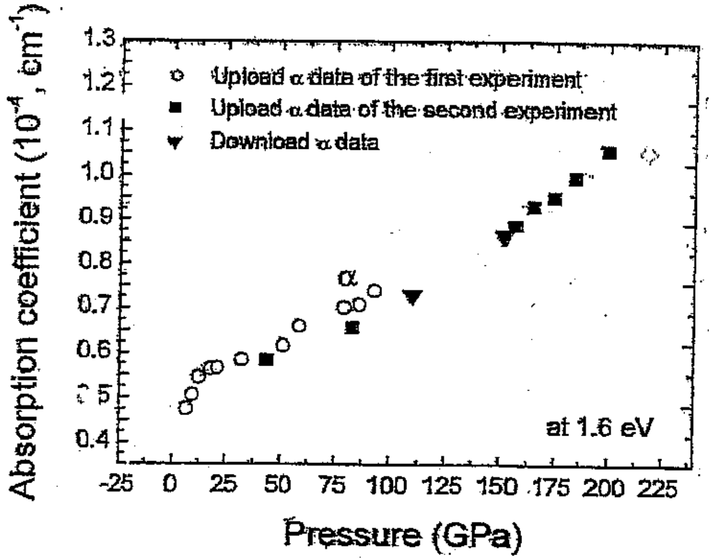

Figure 1. Absorption versus pressure.

The extinction coefficient k^* is obtained from

$$k^* = \alpha\lambda/4\pi \tag{3}$$

The reflection is related to the refractive index by

$$R_{ds} = \left(\frac{n^* + ik^* - n_D}{n^* + ik^* + n_D}\right)^2 \tag{4}$$

where n_D is the refractive index of diamond at the air interface. Examples of reflectivity vs energy curves at different pressures are shown in Figure 2.

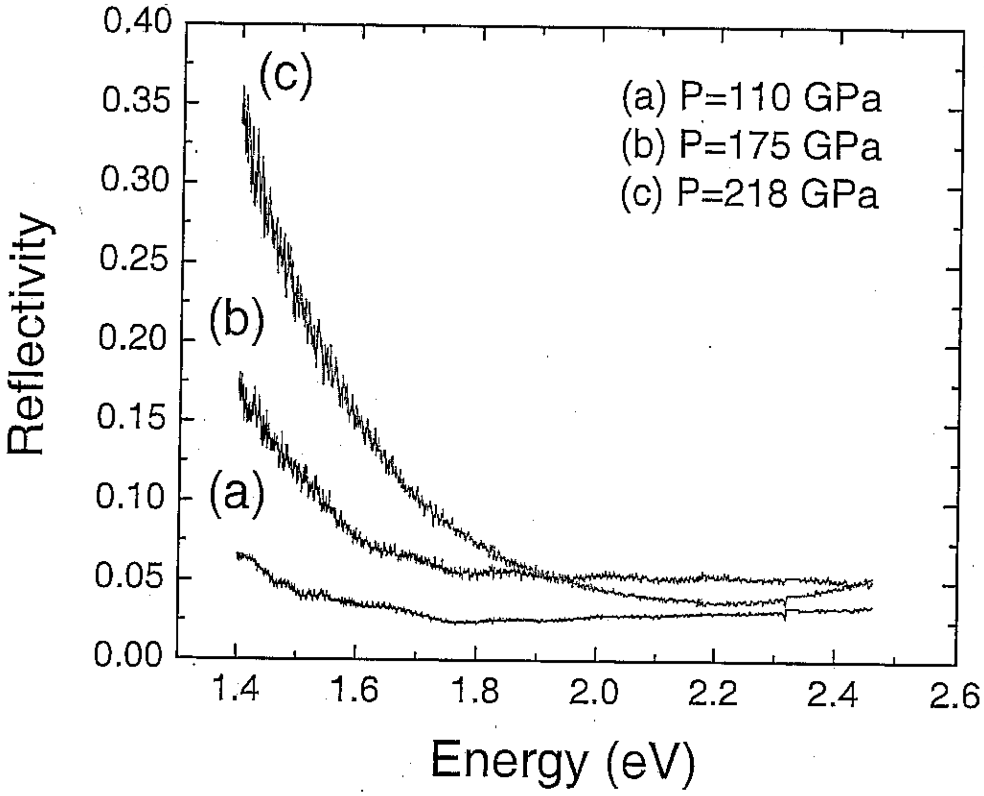

Figure 2. Reflectivity vs energy at three pressures.

The refractive index of diamond, n_D, was obtained as follows. The values of n_D were computed as a function of pressure by Surh et al. (1992). The initial slope dn_D/dP agreed with the experiment while $n_D(0)$ was low by 0.06. We, therefore, added 0.06 to the computed value $n_D(P)$ at all pressures. With n_D, k^* and R known at a given pressure, n^* of the silance is calculated. Results from n^* and k^* at $E = 1.6$eV are shown in Figure 3.

The values of k^* increase monotonically. It is conceivable that the absorption is only apparent and is in fact due to multiple internal scattering from birefringent noncubic crystals. The sample is back at 218 GPa. The real part of the refractive index increase slowly to $n^* = 1.8$

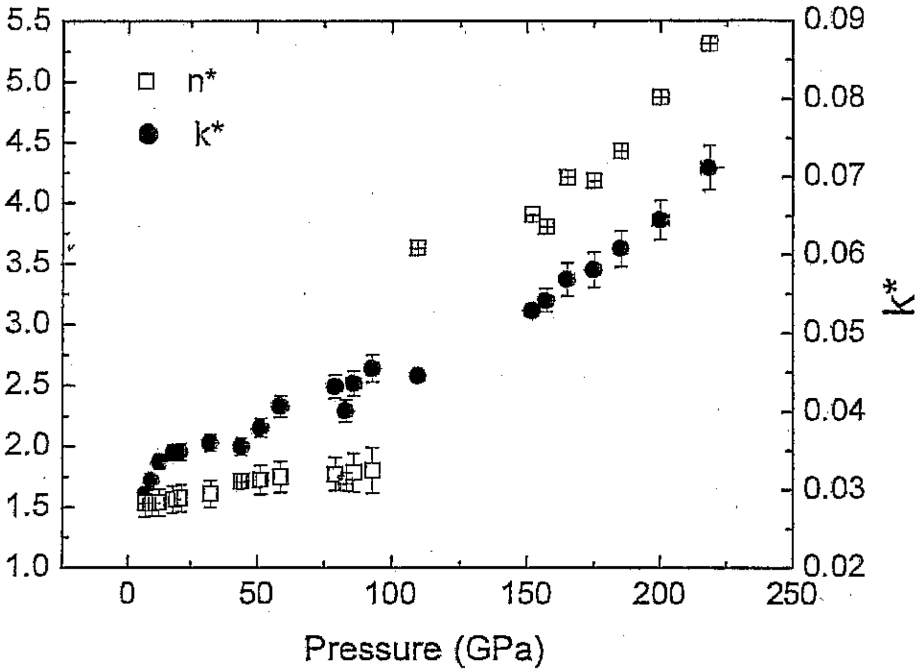

Figure 3. Absorption coefficient vs pressure at 1.6eV.

at 90 GPa but then jumps abruptly to a value of 3.7 at 115 GPa and increases at a rapid rate to 5.3 at 218 GPa.

It should be noted that Raman studies were made to 45 GPa. At lower pressures the shifts agreed with earlier data for silane by Nucara et al. (1997). The signals were too weak to measure at higher pressures. The Raman studies will be described elsewhere.

The molar refraction divided by the molar volume is given by

$$R/V = (n^{*2} - 1)/n^{*2} + 2) \qquad (5)$$

Goldhammer (1913) criterion for metallization is that metallization occurs when $V_m = R$. Strictly this holds only in the long wavelength limit. Thus for Ag, R/V = 0.9996 at 0.1eV but at 1keV, R/V = 0.901 (Lide 1992). The pressure dependence of R/V at E = 1.6eV for silane is shown in Figure 4. The value at 218 GPa and E = 1.6eV is R/V = 0.90 for silane.

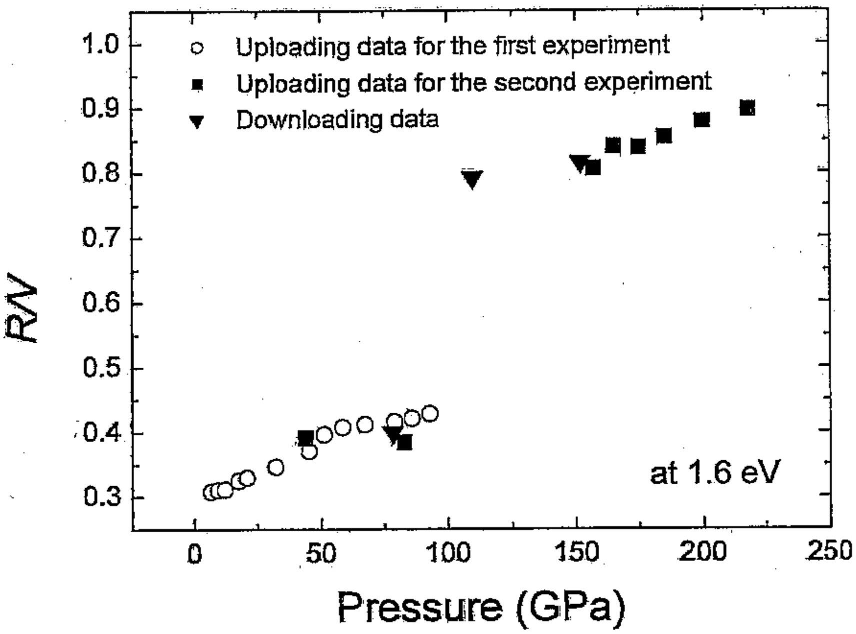

Figure 4. R/V versus P at 1.6eV (error bars are for 2σ.)

The sample was studied during unloading and behaved reversibly. This also proves that the blackness was due to the sample and not due to the plastic deformation of the diamond as observed by Dunn et al. (1982).

Silane is clearly not a normal metal at 218 GPa (the value of k* is too small). It has been noted by Ruoff (1983) that for the alkali halides and the alkaline calcogenides the relation $n^{*2}\,E_g(\mathrm{eV}) = 21$ holds closely. Using this only as a crude approximation here, we obtain $E_g \approx 0.7\mathrm{eV}$ (which does not exclude zero). Inasmuch as the absorption is very low, silane could be an indirect band-gap semiconductor or a transparent metal at 218 GPa. While further work is needed the results should be useful to scientists studying the behavior of Group IVb Hydrides.

Acknowledgements

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