

Infrared vibration spectra of hydrogenated, deuterated, and tritiated amorphous silicon

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This article presents infrared absorption data of amorphous silicon alloys in which the hydrogen isotopes deuterium and tritium have been substituted for hydrogen. Silicon–deuterium and silicon–tritium vibration frequencies are related to silicon–hydrogen vibration frequencies by simple mass relationships. The silicon–deuterium wagging vibration is broadened and blueshifted due to strong coupling to the amorphous silicon network vibrations. © 1999 American Institute of Physics. [S0021-8979(99)08304-8]

I. INTRODUCTION

Hydrogenated amorphous silicon is both fundamentally and technologically important. Fundamentally, it represents one of the simplest examples of an amorphous solid, and therefore, forms the basis for the study of more complex systems. Technologically, there are many useful applications for this material, such as solar cell power generation and flat panel displays.

While much has been done, there are still many aspects of this material that are not well understood. In particular, an unambiguous identification of the local bonding environment of the hydrogen atom is important for the development of quantitative models for the electronic density of states, and so of all the optical, electrical, and device properties. In this study, we investigate the vibrational spectra of hydrogenated amorphous silicon alloys in which deuterium (D) and tritium (T) substitutions were made. Tritium is a radioactive isotope of hydrogen that should readily substitute hydrogen in the amorphous network. It decays into a ${}^3\text{He}^+$ by emitting a β particle, and an antineutrino.¹ In this article we present new infrared (IR) data, and show that there exists strong coupling between localized vibrational modes and the transverse optic (TO)-like band of the amorphous silicon network.

II. EXPERIMENT

To deposit films, silane and molecular hydrogen, or deuterium or tritium, were allowed to flow through the growth chamber, each at a constant rate of 2.5 sccm. These gases were dissociated in a dc glow discharge excited using the saddle-field electrode configuration.² The chamber pressure was maintained at 50 mTorr. Films were deposited on 10 Ω cm, *p*-type, boron doped, crystalline silicon wafers [Czo-chralski grown, (100) orientation, with both sides polished] which were mounted on a heated (150 °C) substrate holder that was electrically grounded or floating. Films deposited

under electrically grounded substrate conditions were about 1 μm in thickness, and films deposited under floating conditions had thicknesses near 0.2 μm , as determined using a surface profiler. Differences in growth rate are attributed to ion bombardment effects during film deposition.³ Table I summarizes the deposition conditions of our samples.

IR spectra of samples were taken in the range 30–5200 cm^{-1} , using a Perkin Elmer 2000 Fourier transform IR (FTIR) spectrometer, purged with dry air. Measurements were made in the single-beam mode, in which the transmittances of the amorphous silicon film and a reference crystalline silicon substrate were measured and ratioed in rapid succession. Twenty ratios were accumulated and averaged to obtain the film transmittance spectrum. The resolution of the measurements was $\pm 2 \text{ cm}^{-1}$.

III. RESULTS AND DISCUSSION

Figures 1(a) and 1(b) display the spectral range of the high frequency vibrations occurring in the IR spectra of hydrogenated, deuterated, and tritiated amorphous silicon films [the grounded samples' spectra, displayed in Fig. 1(b) exhibit interference effects]. The individual curves have been shifted vertically with respect to each other by approximately 500 cm^{-1} for clarity. These vibrations are attributed to stretching modes. The vibrations near 2100 cm^{-1} in the hydrogenated films indicate the dominance of SiH_2 complexes.⁴ Very similar hydrogen peaks are observed in the deuterated and tritiated spectra, the hydrogen originating from the silane gas. Consequently, it is expected that bonded deuterium and tritium will exist in dihydride-like complexes, that is, combinations of HD, DD, HT, and TT will be bonded to silicon. The deuterated and tritiated spectra show additional peaks near 1500 and 1200 cm^{-1} , respectively. These peaks are attributed to Si–D and Si–T stretching vibrations. The greater reduced mass of the Si–D and Si–T oscillators relative to that of the Si–H oscillator, is responsible for the shift to lower frequencies. Differences in the nuclear mass of the bonded atoms have very little effect on the bonding

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TABLE I. Deposition parameters of tritiated, deuterated, and hydrogenated films. Substrate temperature: 150 °C, chamber pressure: 50 mTorr, silane flow rate: 2.5 sccm, and isotope gas flow rate: 2.5 sccm.

Sample	Isotope gas	Substrate current (mA)	Substrate voltage (V)	Anode current (mA)
T2	T ₂	7	0	30
T1	T ₂	—	≈300	≈27
D2	D ₂	5	0	28
D1	D ₂	—	110	30
H2	H ₂	5	0	30
H1	H ₂	—	125	30

strengths, and thus different isotopic species of the same molecule or complex will have the same force constants. Thus, the frequency of vibration of isotopically substituted complexes can be modeled on the mass of the atoms com-

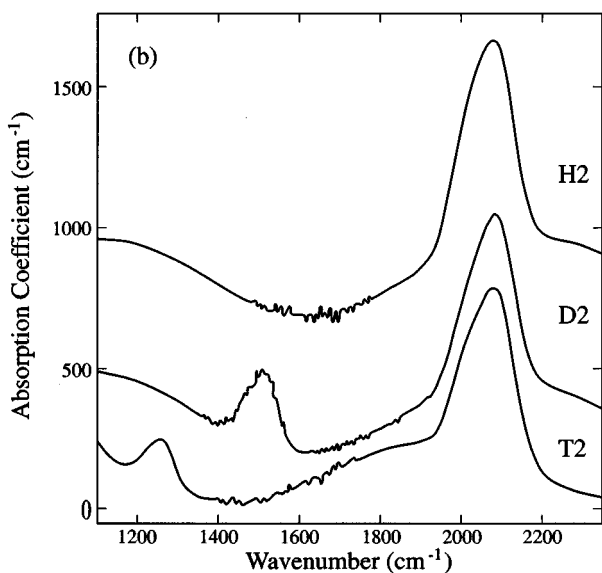
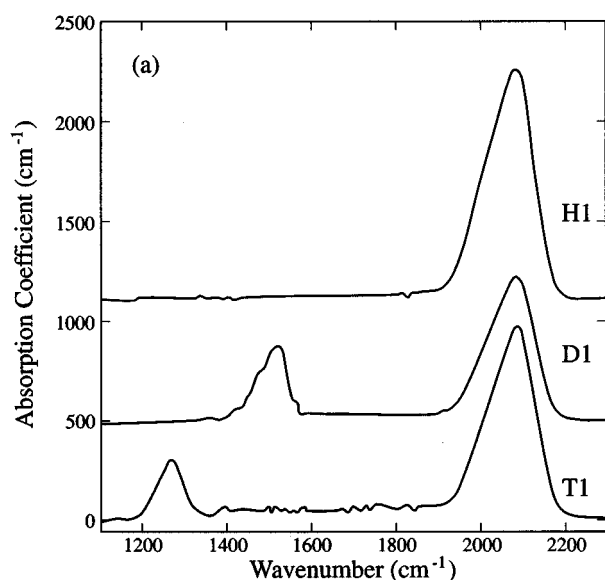


FIG. 1. (a) High frequency IR vibrations of samples: H1, D1, and T1. Both D1 and H1 have been shifted up with respect to T1 by about 500 and 1100 cm⁻¹, respectively. (b) High frequency IR vibrations of samples: H2, D2, and T2. Both D2 and H2 have been shifted up with respect to T2 by about 250 and 750 cm⁻¹, respectively.

TABLE II. Ratio of stretching frequency of Si–D and Si–T bonds with respect to Si–H bonds.

Ratio of frequencies	Experimental	Calculated
$\omega_{\text{Si-D}}/\omega_{\text{Si-H}}$	0.73	0.72
$\omega_{\text{Si-T}}/\omega_{\text{Si-H}}$	0.61	0.60

prising the complex. It should be noted that all of the peaks indicate underlying structure, i.e., splitting of the stretching modes and induction effects. We have not carried out deconvolution of these peaks.

Using the harmonic potential approximation the stretching frequencies of the Si–D(T) bonds can be calculated with respect to the Si–H bond stretching frequency, i.e.,

$$\frac{\omega_{\text{Si-D(T)}}}{\omega_{\text{Si-H}}} = \sqrt{\frac{m_{\text{H}}(m_{\text{D(T)}} + M_{\text{Si}})}{m_{\text{D(T)}}(m_{\text{H}} + M_{\text{Si}})}}, \quad (1)$$

where, $\omega_{\text{Si-H(D,T)}}$ is the stretching frequency of the Si–H(D,T) bond, $m_{\text{H(D,T)}}$ denotes the mass of the hydrogen (deuterium, tritium), and M_{Si} represents the mass of silicon. The calculated Si–D, and Si–T stretching frequencies are in agreement with measurement. Table II tabulates the experimental and calculated ratios.

The weak integrated intensity of the deuterium and tritium related vibration relative to that of the hydrogen absorption bands is expected, as integrated intensity is inversely proportional to the reduced mass of the oscillator.

Figure 2 displays the mid and far IR spectra of the samples deposited on electrically floating substrates. The individual curves have been shifted vertically with respect to each other for clarity. The vibrations occurring in the frequency range 700–900 cm⁻¹ are suggestive of bending (scissor) mode vibrations. In the literature the hydrogen related vibrations show a double peak near 886 and 844 cm⁻¹.⁴ The

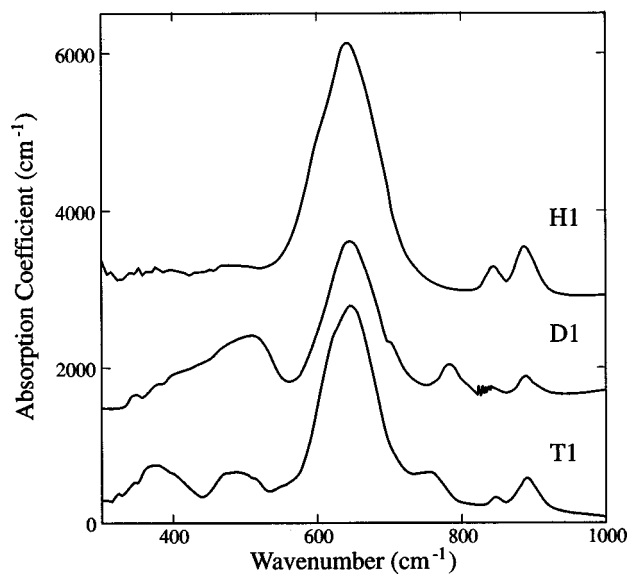


FIG. 2. Mid and far IR vibrations of samples: H1, D1, and T1. H1 and D1 have been shifted up with respect to T1 for clarity.

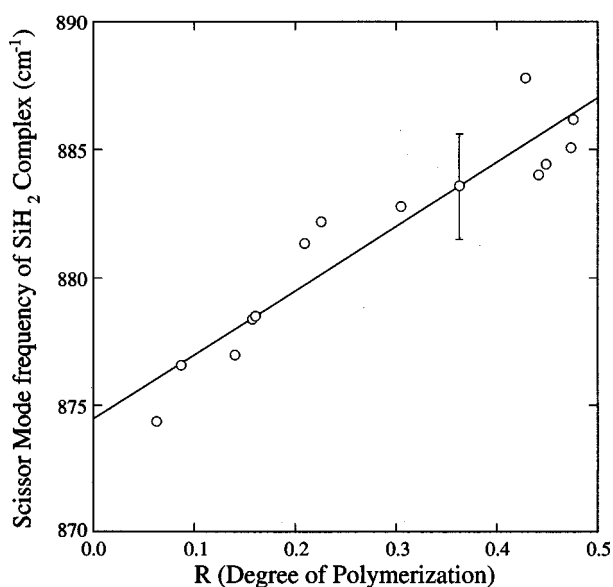


FIG. 3. Dependence of scissor mode frequency on polymerization.

low frequency peak near 844 cm^{-1} is identified as the splitting of scissor modes due to interactions between neighboring SiH_2 groups in $(\text{SiH}_2)_n$ polyhydrides,⁵ where the high frequency peak is attributed to the SiH_2 scissor mode. From Fig. 2 it can be seen that polyhydrides exist in all the films and we can expect the SiH_2 scissor mode frequency to be blueshifted due to the increased electronegativity sum of the neighboring environment. All SiH_2 groups contribute to the relatively strong absorption near 890 cm^{-1} , whereas only near-neighbor pairs of SiH_2 groups or large chain segments $[(\text{SiH}_2)_n]$ contribute to a strong absorption near 845 cm^{-1} . Therefore, the ratio of the integrated absorption of the 845 cm^{-1} absorption band to that of the 890 cm^{-1} absorption band can be considered to be a measure of the $(\text{SiH}_2)_n$ chain formation.

For the analysis of the deuterated and tritiated IR spectra, it was necessary to determine the scissor mode vibration of a single SiH_2 complex. A series of hydrogenated films were deposited with varying degrees of polymerization as determined by deconvolving the doublet near 845 and 890 cm^{-1} and taking their integrated ratios R . In Fig. 3 is plotted the scissor mode frequency as a function of polysilane formation R . As the degree of polymerization increases the scissor mode frequency increases. Extrapolating to $R=0$ for the case of no polymeric bonding in a film, the scissor mode frequency of an isolated SiH_2 complex was determined to be $875 \pm 2\text{ cm}^{-1}$. This value will be used in calculating the corresponding scissor mode frequencies in deuterated and tritiated films.

For a SiH_2 complex the force constants determining the scissor mode vibration are the H–Si–H angular force constant and the H–Si–Si force constant. The SiH_2 scissor mode vibration was modeled as a diatomic molecule. For this system the reduced mass of the oscillator is the reduced mass of the vibrating H–H pair.

The IR spectra show that hydrogen bonds in both SiH_2 and $(\text{SiH}_2)_n$ form. The deuterated and tritiated films do not

TABLE III. Scissor mode vibrations in hydrogenated, deuterated and tritiated amorphous silicon.

Scissor mode	Experiment (cm^{-1})	Calculated (cm^{-1})
ω_{HH}	875	—
ω_{HD}	782	758
ω_{HT}	755	714
ω_{DD}	650 ^a	619
ω_{TT}	490	505

^aSee Refs. 6–8.

display doublets indicative of polymeric bonding, therefore it is expected that in the deuterated and tritiated samples the following complexes are also present: SiHD , SiD_2 , and SiHT , SiT_2 , respectively. The isotopic bonding suggests that the $(\text{SiH}_2)_n$ structures in the film arise from clustering of silane radicals in the plasma which are incorporated into the film. We use Eq. (2) to model the scissor mode vibration frequency of these complexes:

$$\frac{\omega_{XY}}{\omega_{\text{HH}}} = \sqrt{\frac{m_X + m_Y}{m_X m_Y} \frac{m_{\text{H}}}{2}}, \quad (2)$$

where ω_{XY} is the scissor mode frequency of an X–Y vibrating pair, X, Y, can represent H, D, or T. Table III lists the experimental and calculated frequencies for the three films. Our calculated values were determined using the extrapolated SiH_2 scissor mode frequency at 875 cm^{-1} . The SiD_2 scissor mode has been observed near 650 cm^{-1} ^{6–8} but in Fig. 2 it is hidden by the strong silicon–hydrogen wagging vibration near 640 cm^{-1} . The calculation predicts a low frequency SiT_2 scissor mode at 505 cm^{-1} , and the IR spectrum of the tritiated film shows a peak at 490 cm^{-1} . This peak we assign to a SiT_2 scissor mode. The calculated frequencies are in agreement with the experimental values. Further evidence indicating that the vibration at 490 cm^{-1} is a SiT_2 scissor mode and not one of the silicon matrix's vibration modes (the TO-like vibration near 480 cm^{-1})⁹ can be seen from the intensity of the peak near 200 cm^{-1} in all three IR spectra of the grounded samples in Fig. 4. This peak is identified as the transverse acoustic (TA)-like vibration mode of the silicon matrix⁹ and has a similar intensity in all three spectra. The high frequency peaks superimposed on the broad TA-like peak are due to water vapor absorption inside the FTIR. If the absorption at 490 cm^{-1} was due to tritium decay induced silicon–silicon vibrations, the absorption near 200 cm^{-1} in the tritiated film T2 should be enhanced relative to that observed in the other films H2 and D2. The similar intensities indicate that there is no enhanced tritium decay induced absorption of the silicon matrix.

The Si–H wagging frequency ω was used to approximate the wagging frequencies of the Si–D and Si–T bonds using

$$\frac{\omega_X}{\omega_{\text{H}}} = \sqrt{\frac{m_{\text{H}}}{m_X}}, \quad (3)$$

where ω_X is the wagging frequency of a Si–D or Si–T bond, m_X is the mass of a deuterium or tritium atom, and m_{H} is the mass of a hydrogen atom. Table IV lists the experimental

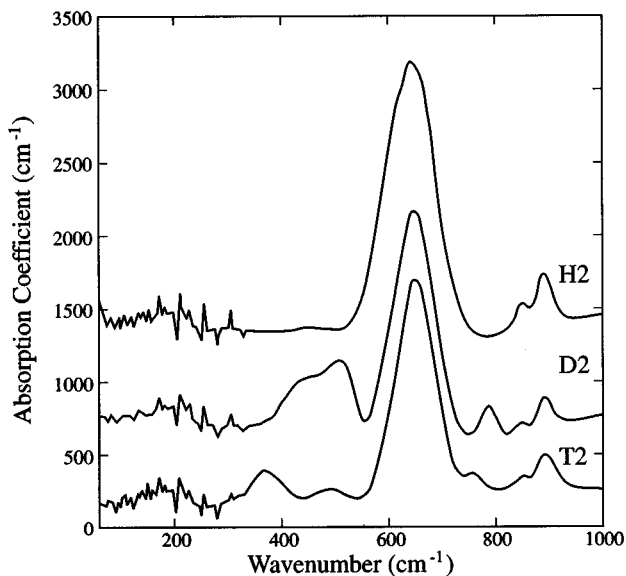


FIG. 4. Mid and far IR vibrations of samples: H2, D2, and T2. H2 and D2 have been shifted up with respect to T2 for clarity.

and calculated frequencies. The experimental Si–T wagging vibration is quite accurately predicted by Eq. (3), however, the experimental Si–D wagging vibration is underestimated. This is explained by noting that the Si–D wagging vibration falls very close to the TO-like vibrational band ($\sim 480\text{ cm}^{-1}$) of the silicon matrix. The IR absorption spectra of pure amorphous silicon and the vibrational density of states of crystalline silicon are quite similar.¹⁰ The conservation of crystal momentum and symmetry selection rules lead to zero first-order IR activity in crystalline silicon. The introduction of distortions and subsequent loss of long-range order in the amorphous phase relaxes these restrictions and permits all phonons to contribute to the IR absorption. The first-order IR spectrum should then consist of the phonon density of states modified by transition matrix elements.¹⁰ The Si–D wagging vibration and the TO-like vibration of the amorphous network occur at similar frequencies. Depending on the degree of coupling between these vibrations a broadening of the line shape and a blueshift in the Si–D wagging frequency is expected.¹¹ Another vibration that falls on the TO-like band is the SiT₂ scissor mode. It too displays a broadened line shape compared to the other scissor modes. However, the expected blueshift is not easily observed, due to the broadness of the peak.

Further investigation of the Si–D wagging vibration in Fig. 2 suggests the presence of a shoulder near 450 cm^{-1} . In Fig. 4, this shoulder is clearly seen for sample D2. Lucovsky *et al.*¹² have attributed this shoulder to a wagging-like mo-

TABLE IV. Wagging mode vibrations in hydrogenated, deuterated, and tritiated amorphous silicon.

Wagging mode	Experiment (cm^{-1})	Calculated (cm^{-1})
ω_{H}	645	—
ω_{D}	515	456
ω_{T}	373	372

TABLE V. Bonded hydrogen, deuterium, and tritium content in films determined from IR analysis.

Sample	Hydrogen content (at. %)	Deuterium content (at. %)	Tritium content (at. %)
H1	16	—	—
H2	12	—	—
D1	10	6	—
D2	8	4	—
T1	12	—	6
T2	9	—	4

tion of the Si–D oscillator, where both the deuterium and silicon atom that bonds to it move in phase. The corresponding Si–H wagging-like vibration is expected to occur near 480 cm^{-1} , and there does exist a very weak peak in both the IR spectra of H2 and H1. However, the tritiated samples show only the symmetric Si–T wagging vibration and no additional peak. We propose the following explanation. In hydrogenated amorphous silicon, the wagging vibration is expected to occur near 640 cm^{-1} . The weak peak near 480 cm^{-1} is due to the weakly IR active amorphous silicon matrix. In deuterated amorphous silicon, the Si–D wagging vibration couples to the amorphous silicon network vibration. As a result it becomes blueshifted and the weak shoulder near 450 cm^{-1} is the corresponding shifted silicon–silicon vibrations that exist in the vicinity of the Si–D oscillator. Finally, in tritiated amorphous silicon, the Si–T wagging vibration lies in that region of the host network’s vibrational density of states which is a minimum.⁹ Consequently, there is weak coupling between the oscillator and the silicon network leading to no peak shift in the Si–T oscillators’s position (see Table IV) and little observable broadening in its line shape.

The bonded hydrogen content $N_{\text{Si-H}}(\text{cm}^{-3})$ was obtained from the integrated intensity of the silicon–hydrogen IR stretching band centered near 2000 cm^{-1} , according to Kruzelecky *et al.*¹³

$$N_{\text{Si-H}} = C_{\text{Si-H}} \int \frac{\alpha(\omega)}{\omega} d\omega, \tag{4}$$

where $C_{\text{Si-H}} = (1.1 \pm 0.1) \times 10^{20}\text{ cm}^{-2}$ is the proportionality factor for this band, and $\alpha(\omega)$ is the absorption coefficient at wave number ω . To determine the bonded deuterium and tritium contents the coefficient in Eq. (4) had to be modified by the square root of the reduced mass of the Si–D or Si–T oscillator.⁶ Therefore, $C_{\text{Si-D}} \approx \sqrt{2} \times C_{\text{Si-H}} = \sqrt{2}(1.1 \pm 0.1) \times 10^{20}\text{ cm}^{-2}$, and $C_{\text{Si-T}} \approx \sqrt{3} C_{\text{Si-H}} = \sqrt{3}(1.1 \pm 0.1) \times 10^{20}\text{ cm}^{-2}$. In Table V are listed the bonded hydrogen, deuterium, and tritium concentrations in the films. From the concentrations it can be seen that the deuterium and tritium are substituting hydrogen in the amorphous network.

IV. CONCLUSIONS

Bonded deuterium and tritium behave as heavy hydrogen atoms in the amorphous silicon network. IR data show

that the silicon–deuterium wagging vibration couples strongly to the TO-like vibrations of the silicon matrix.

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