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Infrared vibrational spectra of rf-sputtered hydrogenated amorphous silicon

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We report the vibrational absorption spectra between 200 and 4000 cm^{-1} of a series of amorphous sputtered $Si_{1-x}H_x$ alloys prepared under different conditions of substrate temperature, and hydrogen, oxygen, and argon partial pressures. The spectra show stretching and wagging vibrational modes of the Si–H bond, and bending modes attributable to Si–H_2 configurations. Multiple features in the stretching vibrational spectrum are interpreted in terms of two different configurations of a single H atom. The integrated stretching vibrational absorption is correlated with the H content estimated from experiments on gas evolution upon heating. Finally, it is shown that different preparation conditions can lead to the same total H content but different vibrational spectra.

I. INTRODUCTION

The deliberate incorporation of hydrogen into tetrahedrally coordinated amorphous semiconductors during their production by sputtering has been shown to lead to dramatic differences in properties from those of the unhydrogenated material.[1-3] For example, the spin density and the electrical conductivity at a fixed temperature are both decreased by several orders of magnitude and the absorption edge is shifted to higher energy by several tenths of an electron volt. These and other results on phototransport[4] and photoluminescence[5] are in satisfactory semiquantitative accord with the expectation that the H electron forms a covalent bond with orbitals of the parent matrix which would otherwise be left "dangling" or, more likely, would form weak bonds over a distance considerably larger than the smallest interatomic distance. Since the energy of the H covalent bond formed lies deep in the valence band,[6] the state density in the gap attributable to dangling bonds and to the weak (sometimes referred to as "reconstructed") bonds is very much reduced and the changes in property enumerated above are a natural consequence. The discovery that amorphous silicon (a-Si) produced by glow-discharge decomposition of silane, which had also long displayed properties corresponding to a very low density of gap states,[7] normally contained a large atomic percentage of hydrogen[8] has led to a certain degree of confluence in the investigations of the sputtered and the glow-discharge-decomposed materials.

One of the most direct identifications of the role of H in the a-Si matrix comes from studies of the optical absorption in the infrared attributable to vibrations of the Si–H unit. The first study of rf sputtered hydrogenated a-Si found two absorption bands,[9] the first a partially resolved doublet near 2000 cm^{-1} and the second a broader absorption near 650 cm^{-1}. These were identified, following the reasoning of an earlier study on amorphous hydrogenated Ge,[9] as caused by stretching and wagging vibrations of a single H covalently bonded to a Si atom in two different local environments. Later, however, additional bands were reported[10] at 850 and 890 cm^{-1}. Brodsky, Cardona, and Cuomo[10] analyzed a combination of infrared-absorption and Raman scattering results on sputtered and glow-discharge Si to suggest a detailed attribution of the several features in these spectra to stretching, bending, and wagging vibrations of SiH, SiH_2, and SiH_3 complexes. Some of the details of this attribution have been contested by Knights *et al.*,[11] who prefer $(SiH_2)_n$ complexes to SiH_3. These two detailed models agree, however, in explaining the different peak energies found near 2000, 890, and 650 cm^{-1} as due to more than one H atom attached to an atom of Si.

Identification of the local environment of the H atom and, in particular, examination of the possibility of different environments for a singly bonded H 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 have measured the vibrational absorption spectra of samples rf sputtered in argon at different substrate temperatures and partial pressures of hydrogen. Our purposes were (i) to determine the relative amounts of H incorporated under the different sputtering conditions; (ii) to exploit the control on the amount of H incorporated, afforded by the sputtering process, to examine the finer details of the spectra and, in particular, to examine the possibility of the existence of identifiably different environments for single Si–H bonds; and (iii) to contribute to an integrated

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program of measurement and correlation of optical, spin resonance, photoluminescence, and transport properties of a-$Si_{1-x}H_x$ alloys.[12] The experimental methods are described in Sec. II, the results in Sec. III, and the interpretation of the results in Sec. IV.

II. EXPERIMENTAL METHODS

A. Material preparation

Films of a-$Si_{1-x}H_x$ and a-$Si_{1-x}D_x$ were prepared by rf sputtering in a Vacuum Industries 2305 diode sputtering system.[13] The base pressure was reduced by a turbomolecular pump to 5×10^{-7} Torr (mostly water vapor by residual gas analysis) before 5×10^{-3} Torr of 99.9995% pure argon (Ar) was introduced into the system. Hydrogen or deuterium incorporation was achieved by adding a partial pressure, p_H or p_D, respectively, of between 0 and 5×10^{-3} Torr of 99.999% pure H_2 or D_2 to the Ar. The gas pressures measured with a capacitance manometer[14] were stable to within ±10% during the period of a typical run, roughly 24 h for a sample thickness of about 10 μm. This corresponds to a deposition rate of approximately 1 Å/sec.

Optical grade polycrystalline Si targets 5 in. in diameter were used, and were cleaned *in situ* by sputtering at 2 W/cm^2 for 5 min with all substrates shielded. The substrates used in this investigation included KBr, CaF_2, BaF_2, Al_2O_3, Corning 7059 glass, and crystalline Si (c-Si). All of these substrates, except glass, were suitable in terms of their transparency in the infrared, but all except Al_2O_3, glass, and c-Si presented the difficulty that thick a-Si films frequently exploded off them. The reason presumably is the very different coefficients of thermal expansion of a-Si and these ionic crystals: if a-Si is similar to c-Si, it will have a thermal expansion coefficient near the value for the crystal of $(4.2\times10^{-6})/°C$; by contrast, the ionic crystals have coefficients greater than $(15\times10^{-6})/°C$.[15] Crystalline Si has the additional advantage of having an index of refraction close to that of a-Si,[16] which diminishes the amplitude of interference fringes produced by the film and facilitates the analysis of the vibrational absorption bands.[17] The Si was lapped on both sides, but polished to an optical finish on only one side to further lessen the magnitude of the fringes. The substrates were ultrasonically cleaned and degreased before insertion into the sputtering chamber, and then further cleaned by reverse sputtering at 0.5 W/cm^2 for 20 sec. It is estimated that this procedure removes the last of surface contaminant and damage, without running the risk of deteriorating the flatness of the surface by uneven off-sputtering. The substrate temperature T_s was controlled at temperatures between 25 and 450 °C, although the preferred T_s lies between 200 and 250 °C; lower T_s seems to give films with more unhealed defects and higher T_s films with less incorporated H for a given p_H. After completion of a run, the films were either left to cool and equilibrate in the sputtering apparatus for several hours (usually overnight) at the base pressure, or they were "annealed" at a temperature of ~100 °C for several hours before all power was removed.

The effect of hydrogen desorption was studied by measuring the optical absorption spectra after the samples had been heated at a rate of 100 °C/h in a vacuum of 10^{-6} to 10^{-5} Torr. The temperature was measured by a chromel-alumel thermocouple placed in contact with the sample, which implies that the real temperature of anneal of the sample may be different from the nominal one by as much as 10 °C. When the desired temperature was reached, the heat was immediately turned off and the sample cooled by radiation in the vacuum to room temperature.[18]

B. Structural measurements

X-ray diffraction studies on unsupported films and films on Be were done to verify the fact that the films were amorphous. The criterion for amorphousness we used was the absence of spots or sharp rings in the diffraction pattern. Even when such films did indicate some crystallinity, it was often the case that films on other substrates, deposited under the same conditions, showed none.[19] This is attributed to differences in the real temperature at the growth surface of the film, which depends not only on the nominal platform temperature T_s, but also on the quality of the thermal contact between substrate platform and substrates and on the thermal conductivity of the substrate.

Film thicknesses were measured with a Sloan Dektak,[20] which has a nominal accuracy of ±2%. The actual accuracy of estimation of thickness depends not only on film flatness and uniformity, but also on the flatness of the substrate near the edges of the film. For our substrates and films of about 10-μm thickness, the overall accuracy is estimated at ±4%.

The mass density of the films was measured by determining the density of solutions of $ZnBr_2$ in water in which unsupported samples of a-Si (off Be or Al) have zero buoyancy. Care was taken to ensure that no air bubbles attached to the film, through pumping with a mechanical pump. The density of the solution was determined by pipeting off a precise volume of 1 ml using special pipets[21] and mass measurement with a Met-

tler H16 scale.

The films are known to contain about 1–2 at.% of Ar, which is presumed to inhabit the microvoids.[22] Accidentally incorporated impurities are believed, from electron microprobe analysis and mass spectrometer analysis after Ar^+ off-sputtering of samples produced in our earlier work, to be in the ppm range.[22]

C. Optical measurements

Optical transmission and reflection data were obtained for photon energies between 0.03 and 0.5 eV using a Perkin-Elmer model 567 double beam spectrometer with two spectular reflectance accessories.

The index of refraction n was calculated by examining the interference fringe minima in reflection and determining their order numbers m. Samples on glass substrates were employed, because the low refractive index of the glass relative to the a-Si led to sharp interference fringes. Also, the reflection mode was used, since absorption in the film reduced the sharpness of the interference fringes less than for the transmission mode. Then, $n = m\lambda_m/2t$, where λ_m is the wavelength in air at the mth minimum and t is the known thickness determined by the Sloan Dektak.

Since m is a small integer, it could be determined without any error. Although there could be a small uncertainty in the value of λ_m, it is so much smaller than the error in t that we can say that the error in n is equal to the error in t.

The absorption coefficient α is[23]

$$\alpha = -(1/t)\ln|(1/B)\{A+[A^2+2BT(1-R_2R_3)]^{1/2}\}| ,$$

where $A = -(1-R_1)(1-R_2)(1-R_3)$, $B = 2T(R_1R_2 + R_1R_3 - 2R_1R_2R_3)$, T is the transmittance, and R_1, R_2, and R_3 are the reflectances of the air-film, film-substrate, and substrate-air interfaces, respectively.

Since the imaginary part of the index of refraction is always less than 0.1, it is valid to calculate the reflectance of a surface between media a and b, refractive indices n_a and n_b, using

$$R_{ab} = [(n_b - n_a)/(n_b + n_a)]^2 .$$

Thus, we can find R_1, R_2, and R_3 from n and the refractive index of the substrate.

III. RESULTS

Figure 1 shows a typical transmission spectrum between 200 and 4000 cm^{-1} of a film 9.5 μm thick on c-Si, which, as will be shown, contains approximately 15-at.% H. The side of the c-Si on which the film was deposited has been roughened slightly in order to reduce the amplitude of the interference fringes.

Several features are notable. (a) There is a broad absorption displaying two peaks which occurs between 200 and 550 cm^{-1}. Although these peaks look like interference fringes in this figure, their position never changes. This is attributed to absorption in the a-Si matrix, and its shape is in reasonable agreement with earlier measurements on unhydrogenated sputtered a-Si.[24] We shall not consider this absorption further in this paper, except to remark that as the H content is increased, there appears to be a tendency for the spectrum to change. This is reasonable, in view of the considerable change in network connectivity and mass density[25] for H contents of the order of 20 at.% or more, but our data are not systematic or quantitative enough for any extended comment.

(b) There is a second absorption at 650 cm^{-1}. This is attributed to a wagging vibration of H atoms roughly normal to the direction of the Si–H bond.[26] This absorption always has the greatest oscillator strength of all the Si–H modes. It is always a single peak. The structure of the absorption is never sufficiently distinct that it can be deconvoluted into separate overlapping peaks.

(c) There is a doublet which peaks at 850 and 890 cm^{-1}. The strength and, importantly, the *occurrence* of this doublet are critically dependent on the conditions (p_H, T_s) of the deposition. This mode has been identified as a bending vibration.[26] In our films the 890-cm^{-1} absorption is always greater than the one at 850 cm^{-1}.

(d) A background absorption sometimes occurs (see, for example, Figs. 2 and 3) with a broad shape extending from 800 to 1050 cm^{-1}. The strength and occurrence of this background are also critically dependent on the preparation conditions. There is a natural suspicion that this absorption is associated with the presence of oxygen,[27] since the frequency of the Si–O stretch-

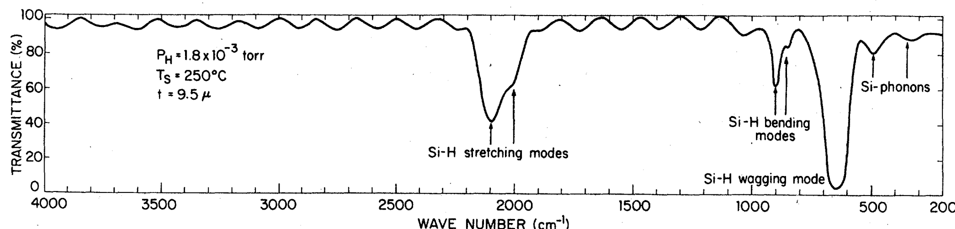

FIG. 1. Typical spectrum of Si–H vibrational absorption modes.

ing vibration in silane-deposited c-Si is 995 cm^{-1},[28] and since air or water vapor contamination are always a possibility. We shall pursue this question below.

(e) A doublet occurs with peaks at 2000 and 2090 cm^{-1} which has been identified as a stretching vibration.[9] Again, the relative strength and, indeed, the frequency, depend on the preparation conditions.

Spectra similar to Fig. 1 were measured on a matrix of samples for T_s = 25, 200, 250, and 350 °C and p_H = 0, 0.05, 0.1, 0.4, 0.9, 1.2, 1.5, 3.6, and 5.0 μm. The changes observed were complex and often not systematic, and we shall first describe them with a minimum of interpretation.

Figure 2 illustrates the effect on the vibrational absorption spectra of changing T_s at a fixed $p_H = 4\times 10^{-4}$ Torr. There is a reduction in the intensity of the absorption for T_s greater than about 200 °C, but the changes in shape of the spectrum are not systematic in T_s.

Next we examine the effect of incorporating very little hydrogen. Figure 3 shows the transmission spectrum for a very low p_H of 7×10^{-5} Torr, which, it will turn out, corresponds to 2-at.% incorporated H. The stretching vibration gives a doublet absorption with a weak peak at 2000 cm^{-1} and a much stronger one at 2140 cm^{-1}, which is further illustrated in Fig. 4. There is not clear evidence for a peak in absorption near 890 cm^{-1}, which would correspond to the bending vibration, but this conclusion is somewhat vitiated by the presence of the broad absorption background referred to earlier. It should be noted, parenthetically, that this film was 20 μm thick, produced in a 48-h sputtering run, so that any (oxygen?) contaminant might be more easily observed. We made several films at low values of p_H and all showed the same stretching vibrational doublet with unequal peaks at 2000 and 2140 cm^{-1}. None showed a definite peak in absorption near 890 cm^{-1}, but the difficulty of background absorption again prevented our drawing a final conclusion about the existence of bending vibrations.

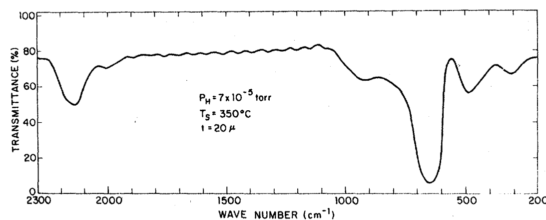

FIG. 3. Vibrational spectrum of Si–H bonds for a low partial pressure of H in the sputtering gas.

A film was also prepared at a low deuterium partial pressure $p_D = 5\times 10^{-5}$ Torr and a substrate temperature of 350 °C. The spectrum is shown in Fig. 5. It shows absorption peaks at 1560 and 1460 cm^{-1}, which both scale as 1/1.37 of the frequency of the peaks in Fig. 4. The shape of this absorption informs us that the H and D are similarly incorporated, whatever the precise local configuration. Again there is a broad background absorption between 800 and 1050 cm^{-1}. The transmission minimum at 650 cm^{-1} scales as 1/1.37 of the expected bending vibration frequency of SiH_2 of 890 cm^{-1}. The asymmetric minimum near 500 cm^{-1}, different in shape from that near 650 cm^{-1} in Fig. 3, is probably a superposition of one of the Si matrix modes at 480 cm^{-1} (Fig. 1) and a Si–D wagging mode.

In Fig. 6 we illustrate the spectrum for a film prepared at a very high value of p_H, 3.5×10^{-3} Torr, and a T_s of 200 °C. Although we have been unable to discern any systematic trend in the changes of absolute intensity of the several absorption peaks with p_H, it seems clear that there is an increasing dominance of the 2090-cm^{-1} peak over those at 2140 and 2000 cm^{-1} and a growth of the doublet at 850 and 890 cm^{-1}. Figure 7 shows the spectrum for a film prepared at a very high partial pressure of deuterium, 3.5×10^{-3} Torr, and a T_s of 200 °C. There is a doublet with a strong minimum at 1525 cm^{-1}, which scales as 1/1.37 of 2090 cm^{-1}, and a smaller shoulder at 1460 cm^{-1}, which scales as 1/1.37 of 2000 cm^{-1}.

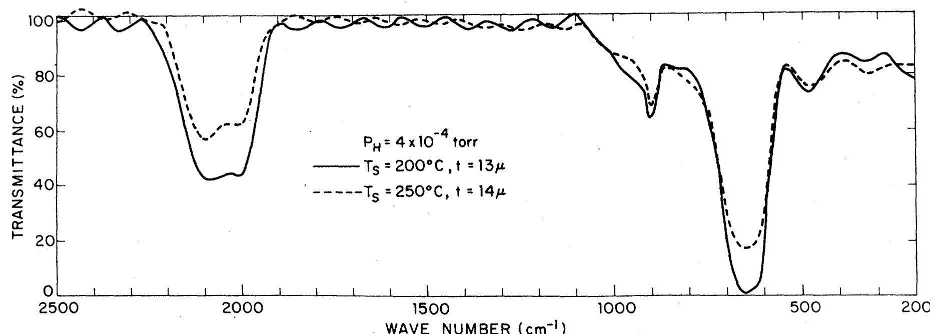

FIG. 2. Dependence of Si–H vibrational spectrum on the temperature of the substrate during preparation.

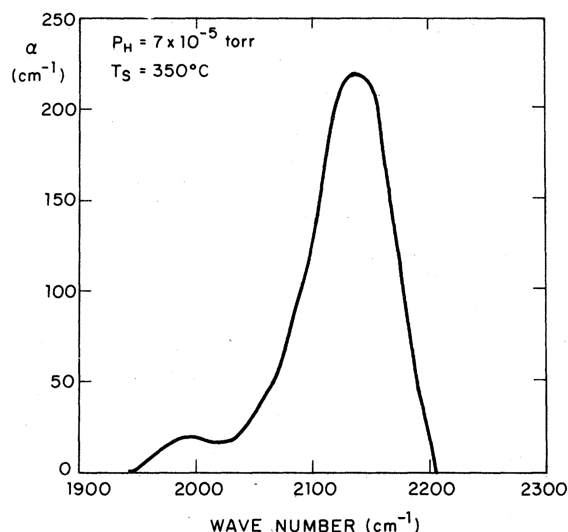

FIG. 4. Absorption coefficient versus photon energy for the stretching absorption of the film in Fig. 3.

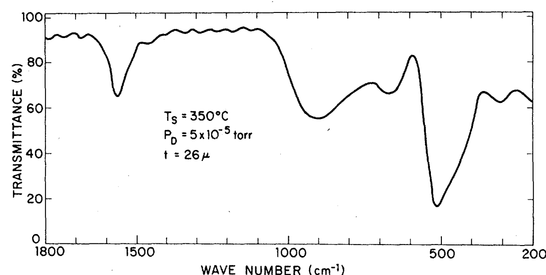

FIG. 5. Vibrational spectrum of a film produced under the same conditions as Fig. 3, but with D substituted for H.

The minimum at 650 cm^{-1} scales as 1/1.37 of 890 cm^{-1}. There is no discernible feature at 1/1.37 of 850 or 620 cm^{-1}. The shape of the transmission minimum near 500 cm^{-1} is essentially the same as that for the film produced at low p_D.

Figure 8 shows the spectrum for a film produced at a T_s of 200°C and equal partial pressures, 1.5×10^{-3} Torr, of hydrogen and deuterium very noticeable, on examination of this spectrum, is a new mode at 790 cm^{-1}, which is additional to the superposed spectra of Si–H and Si–D in Figs. 6 and 7.

A film was also prepared with no H, but at a low partial pressure of oxygen. Its spectrum is shown in Fig. 9. The most remarkable feature is a broad absorption between 800 and 1050 cm^{-1}, peaking at 920 cm^{-1}, which seems to replicate quantitatively the broad, unattributed background absorption in this range reported above. For comparison, the absorption frequency of O in bulk crystalline Si pulled from the melt[28] is 1100 cm^{-1}; in thin crystalline films produced from SiH_4 decomposition,[29] it is 995 cm^{-1}.

As oxygen is highly electronegative, it is possible that the Si–H vibrational absorption line shapes could be altered by the presence of oxygen.[27] To investigate this, we prepared the two films whose stretching absorption spectra are shown in Fig. 10. The film without deliberately incorporated oxygen had no measurable absorption due to Si–O vibrations. The shapes of the stretching absorption spectra do not differ in any significant way.

When films of a-Si containing H are heated above 300°C, the H is evolved. The kinetics of this process, which may be informative about the way in which the H is incorporated, do not concern us here; what does is that a knowledge of the pressure produced in a closed known volume by the gas evolved from a known mass of film which is heated to crystallization gives an estimate of the atomic fraction of gas atoms in the film. A residual gas analyzer mass spectrometer may be used to identify the gas producing the pressure. Measurements in our laboratory have shown that our films contain 1–2 at.% of argon and have also determined the atomic fraction C_H versus the H partial pressure p_H.[30]

Figure 11 illustrates the changes in the infrared spectrum produced by heating. The sample was prepared at T_s = 200°C. Heating to 260 and then to

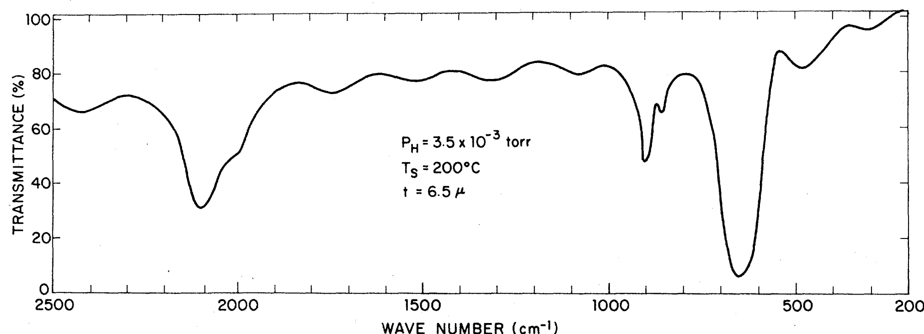

FIG. 6. Vibrational spectrum of Si–H for a high partial pressure of H in the sputtering gas.

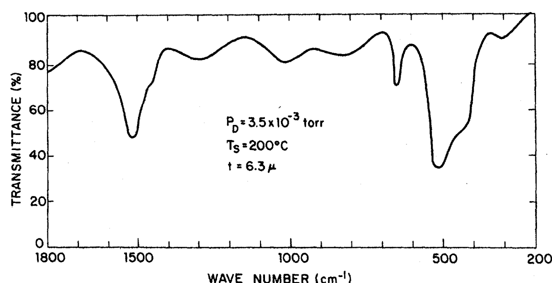

FIG. 7. Vibrational spectrum of a film produced under the same conditions as Fig. 6, but with D substituted for H.

300 °C caused no noticeable change. After anneal to 330 °C, however, the intensity of the absorption decreased to 65% of its original value, while the shape of all of the absorption bands remained unchanged. It was not feasible to heat above 350 °C the thick (10-μm) films necessary to measure the vibrational absorption, as they either exploded off the substrate or the surface of the film became very rough.

Two additional pieces of information, which were not followed up, are presented here for completeness. Films produced at $T_s = 250\,°C$ and $p_H = 4\times 10^{-4}$ Torr in the same manner as described earlier, but on polished KBr substrates, showed significantly different spectra, illustrated in Fig. 12. The cause of the differences is not known, but it is speculated that a difference in actual growth temperature or internal strain may be possible.

The second item involved a major change over time (5 months) in the absorption spectrum of a film produced at a high Ar pressure of 5×10^{-2} Torr, compared with the stable characteristics of films produced at our usual Ar pressure of 5×10^{-3} Torr. This is illustrated in Fig. 13. It is of interest that the transmission minima correspond very closely to those expected for N, O, and C reacting with Si or H. It is speculated that this

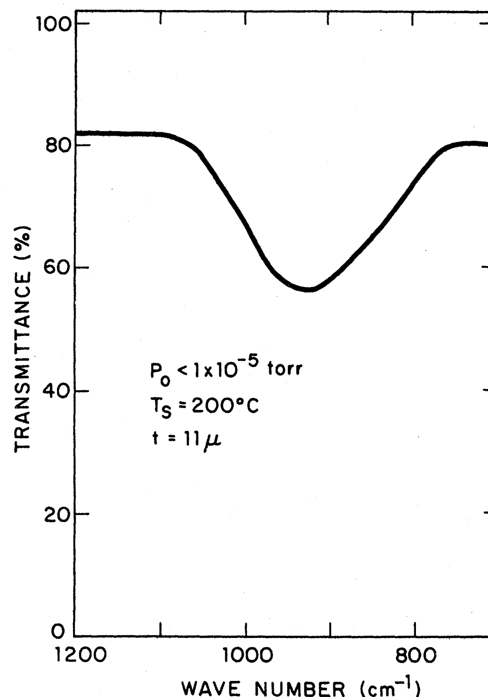

FIG. 9. Stretching vibrational spectrum of a film produced with oxygen and no H in the sputtering gas.

film is more porous to air, but we have no corroborative evidence of this.

IV. DISCUSSION

A. Details of the spectra

First we shall compare the details of our spectra, summarized in Table I, with those already published. By and large, our spectra and interpretation agree with those in the literature,[10,11] so we confine our remarks to the remaining discrepancies. In principle, our measurements on the frequency of the bending vibrations in $Si_{1-x-y}H_xD_y$ films should resolve the disagreement between the IBM and the Xerox groups on the

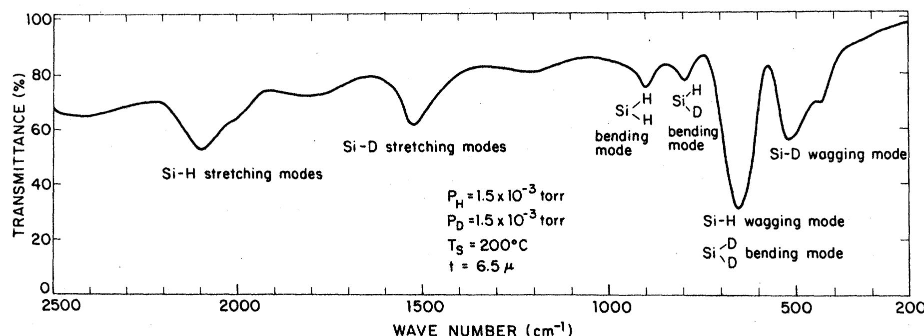

FIG. 8. Vibrational spectrum of a film produced with high and equal partial pressures of H and D.

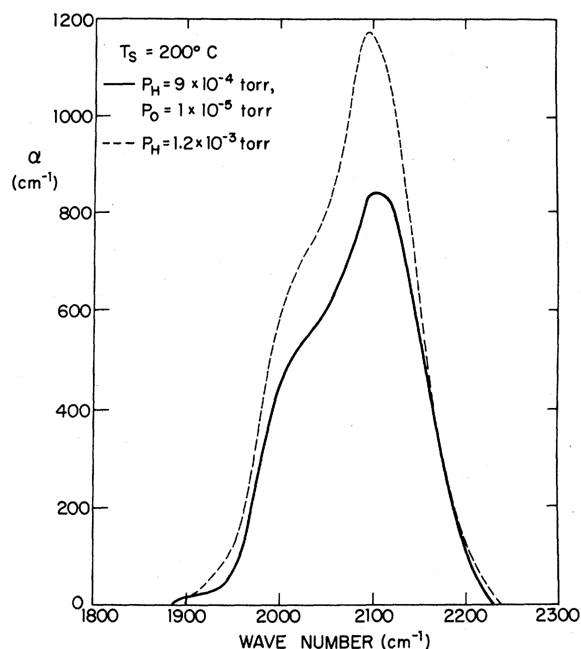

FIG. 10. Comparison of the stretching vibrational absorption spectra of two films, one prepared with H and O in the sputtering gas, the other with H only.

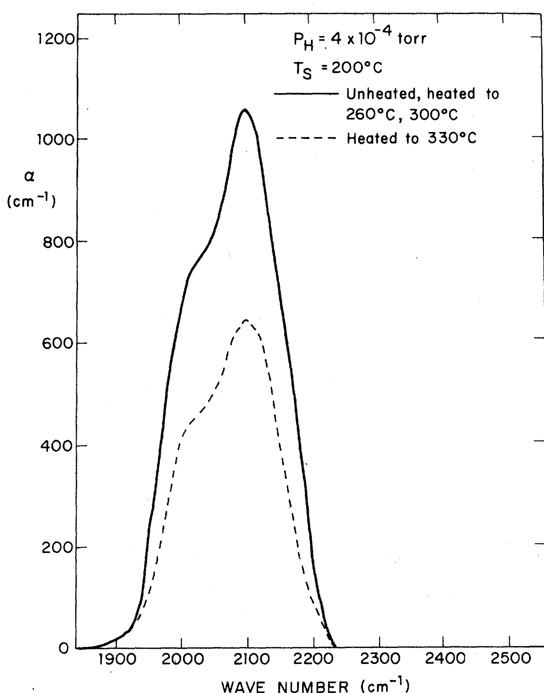

FIG. 11. Stretching vibrational absorption spectra of films heated successively to higher temperatures after preparation.

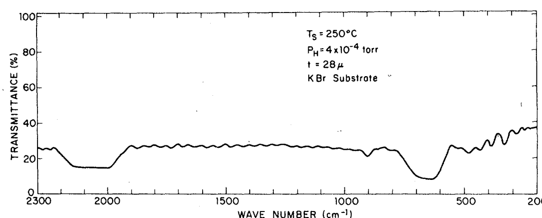

FIG. 12. Vibrational spectrum of a film prepared on a KBr substrate.

source of the 850-cm^{-1} mode; IBM prefers SiH_3, while Xerox favors $(SiH_2)_n$ complexes. If SiH_3 were the cause, we should see modes due to SiH_3, SiH_2D, $SiHD_2$, and SiD_3; in fact we do see one extra mode at 790 cm^{-1} attributed to SiHD, but unfortunately the mode at 850 cm^{-1} attributed to SiH_3 is absent. Our test is thus inconclusive, but measurements on films containing higher percentages of H and D might still resolve the issue.

Brodsky *et al.*[10] attribute the 2140-cm^{-1} mode to a stretching vibration of SiH_3, and it should therefore be considered along with the 850-cm^{-1} mode which they attribute to a SiH_3 bending mode. Our Fig. 3 shows a strong vibration at 2140 cm^{-1} but no trace of an 850-cm^{-1} line. We conclude that the postulated attribution of the 2140-cm^{-1} absorption to SiH_3 is inadmissible.

We have considered the possible effects of the presence of O on the Si-H vibrational spectra. First, it should be noted that the most natural explanation of the background absorption around 900 cm^{-1} is indeed the presence of O, since the deliberate introduction of that element replicated the background. It should also be noted that the oscillator strength of the absorption is strong,[29] and it is quite likely that both a-Si prepared by sputtering and a-Si prepared by glow decomposition of SiH_4 usually contain enough O to give Si–O vibrational absorption. The question arises whether the attachment of an O to a tetrahedron containing a Si–H bond would affect the frequency and oscillator strength of the Si–H vibration, say through the strong electronegativity of the O affecting the charge distribution of the complex. Whether or not this is the case, it is easy to argue that this is not the cause of our high-frequency stretching vibrations. Sari *et al.*[29] have related the atomic percentage of oxygen to the integrated optical absorption by using oxygen concentrations derived from electron microprobe analysis. Their results may be expressed as

$$C_O(\text{at.}\%) = 6.04\times10^{-2} \int_{\omega_s} \alpha \, d(\hbar\omega) \text{ at.}\% \text{ cm/eV},$$

where C_O is the atomic percent of oxygen, $\hbar\omega$ the photon energy, and the integral is over the width

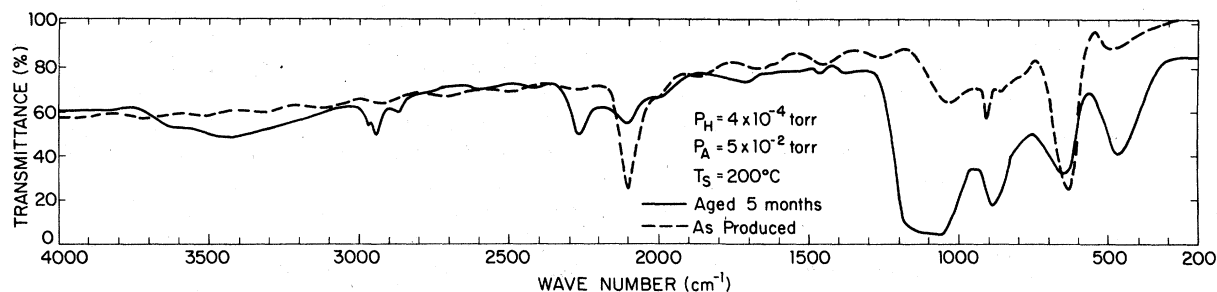

FIG. 13. Vibrational spectra of a film prepared at high argon pressure, immediately after production and after a lapse of 5 months.

of the Si–O stretching vibrational absorption. Applying this same analysis to the two films (T_s = 200°C and T_s = 250°C) of Fig. 2, and to the films of Figs. 3, 5, and 9 gives oxygen concentrations of 0.26 and 0.29, and 0.12, 0.27, and 0.26 at.%, respectively. The films in Figs. 1, 6, 7, and 8 have very little (<0.1 at.%) incorporated oxygen. The oxygen content of the film in Fig. 10, to which O had been deliberately added, was 1.1 at.%. For comparison, the H concentrations of the two films (T_s = 200°C and T_s = 250°C) of Fig. 2 and of the film of Fig. 3 were 16, 10, and 2 at.%, respectively.

The film with the least H content (Fig. 3) still has, therefore, 30 times as much H as O. It is very unlikely that any new line attributable to Si–H–O complexes will be observed; first, all of the O would have to find its way to H sites, and second, the matrix element for the Si–H vibrational absorption would have to be increased by at least an order of magnitude by the presence of neighboring O. A more conclusive test of the effect of O on the Si–H frequency might be to ensure that most H have O on the same tetrahedron by, roughly speaking, inverting the ratio of p_H to p_O in the sputtering gas. We have not yet carried out this experiment.

It remains to discuss a possible source for the doublet vibration near 2000 cm^{-1}. In the earlier work[31] of this group on a-Ge:H, it was suggested that the doublet stretching absorption was produced by H atoms on two identifiably different sites. Connell and Pawlik felt that these two sites corresponded to H incorporated either on a void surface or in the bulk of the film.[1] We propose, although we cannot prove, that the 2000- and 2140-cm^{-1} lines similarly correspond to H atoms in two different environments. One of these environments almost certainly corresponds to the H attached covalently to one Si atom. The other we can only speculate about, along the following lines. (i) The crystalline Si surface is a good starting point for modeling the structural and electronic properties in the bulk and near the void surfaces of a-Si. Work on the chemisorptive bonding of H to crystalline surfaces has suggested

TABLE I. Observed frequencies of vibrational absorption in $Si_{1-x}H_x$.

Frequency (cm^{-1})	Mode description	Conditions of preparation
650	Si–H wag	All p_H
850	$(Si-H_2)_n$ bend or $Si-H_3$	Highest p_H. $p_H \geq 1\times10^{-3}$ Torr Always weaker than 890 mode.
890	$Si-H_2$ bend	All p_H. Magnitude relative to stretch mode low at low p_H.
2000	Si–H stretch	All p_H. Magnitude relative to total stretch mode highest at low p_H. Never the dominant mode.
2090	$Si-H_2$ stretch	$p_H > \sim 2\times10^{-4}$ Torr Dominant stretch mode above about 5×10^{-4} Torr.
2140	Si–H stretch	Dominant stretch mode for $p_H < \sim 3\times10^{-4}$ Torr.

more than one location for the H. The first and obvious site is the conventional bond of the H with a surface atom that has a broken bond. Pandey, Sakurai, and Hagstrum[32] have suggested the possible formation of a trihydride (SiH_3) surface phase on a *c*-Si (111) surface. Appelbaum, Hamann, and Tasso[33] have argued that it is possible to have a H atom bonded to subsurface (second-layer) atoms at the (100) surface with a binding energy about 1 eV less than the conventional H–Si covalent bond on the surface. It is also argued that such a state could be found for any relaxed or reconstructed Si surface with approximately tetrahedrally coordinated Si atoms.

(ii) Singh *et al.*[34] have studied the lowest-energy positions for H incorporated near a vacancy in *c*-Si. Besides the conventional H attachment to an otherwise dangling bond at the vacancy site, they advance two other configurations. The first is the tetrahedral interstitial site. The second is an unexpected stable position along the axis joining the vacancy site and any one of the four nearest neighbors, but at a distance of 0.4 times or more the bond length beyond that nearest neighbor, i.e., the side opposite the one required to saturate the dangling bond. This site is energetically less favorable than the normal bonding (compensation of a dangling bond) site by about 2 eV. It is pointed out, however, that the probability of some occupancy when there is a high concentration of H atoms is very considerable.

It is much too early to decide which of these H configurations is likely in our *a*-Si. At this stage we simply argue the plausibility of there being a second site, while pointing out the great significance of this for the overall electronic density of states function. As Singh *et al.* emphasize, the "unconventional" H sites can lead to electronic states in the pseudogap which might then dominate many of the optical and transport properties.

Since the 2090- and 890-cm^{-1} absorption peaks have been attributed to stretching and bending of SiH_2, it follows that the ratio of the integrated areas under them should be constant. We did not find this to be true, but it is possible that the presence of the Si–O stretching vibration overlapping with the SiH_2 bending mode has interfered with an accurate analysis.

Although the results of our experiments to determine if H could be incorporated only as SiH at low p_H, with no SiH_2 complexes, were rendered unsuccessful by the background O absorption, we can infer some conclusions from the data on D incorporation. For the lowest p_D (Fig. 5), we get a bending vibration. We conclude that, for our conditions of preparation, either SiD_2 (and SiH_2) are formed in the plasma at low pressures of H or D, or they are energetically favored at the surface of the growing film.

B. Concentration of hydrogen

The concentration of H in our films has been estimated by evolution under heating, as described in Sec. III. The atomic fraction C_{gas} of evolved species is determined by experiment and corrections made for Ar content to give the H content C_H. The relative H content may also be estimated from the integrated area under the complex of stretching vibrations near 2000 cm^{-1}, provided one assumes that the matrix element is relatively independent of the structural and chemical environment of the Si–H bond. Since the frequencies involved are so close, this is considered a good approximation. The absolute H content may then be derived either from an estimate of the oscillator strength or as a result of calibration against

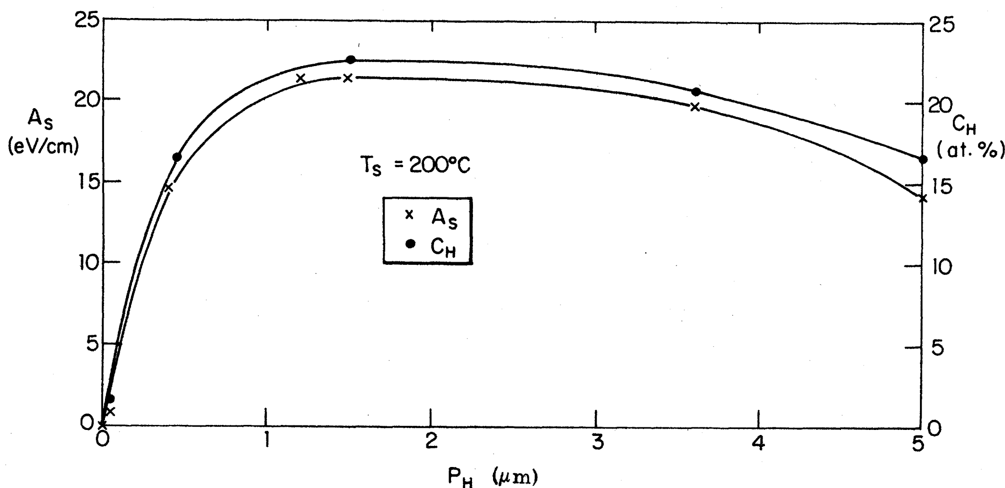

FIG. 14. Dependence of the integral of the stretching vibrational absorption, A_s on p_H, compared with the similar dependence of the gas concentration C_H measured in evolution experiments.

a sample whose H content has been otherwise determined.

In Fig. 14 we show the integrated area A_s as a function of p_H, as well as the C_H determined by evolution. Then in Fig. 15 we plot A_s vs C_H. A least-squares fit gives a slope of 0.947 eV/cm at. %.

Using the experimentally determined relation between A_s and C_H of 0.947 eV/cm at. %, we write

$$C_H(\text{at.}\%) = 1.06 \int_{\omega_s} \alpha \, d(\hbar\omega) \, \text{at.}\% \, \text{cm/eV},$$

where $\hbar\omega$ is the photon energy in electron volts, α is the absorption coefficient in cm^{-1}, and the integration is over the stretching vibrational absorption. Then

$$N_H(\text{mmole/cm}^3) = 1000\rho C_H/(C_H m_H + C_{Si} m_{Si}),$$

where N_H is the number of millimoles of hydrogen per cubic centimeter of a-Si, ρ is the density in g/cm^3, C_{Si} is the atomic percentage of silicon in the alloy, and m_H and m_{Si} are the atomic masses of hydrogen and silicon in amu, respectively. We have found experimentally that

$$0.83 < 1000\rho/(C_H m_H + C_{Si} m_{Si}) < 0.87.$$

We may therefore write that

$$N_H = 0.90 \int_{\omega_s} \alpha \, d(\hbar\omega) \, \text{mmole/cm}^2\,\text{eV}.$$

The oscillator strength Γ_H^s, is defined as

$$\Gamma_H^s = \frac{1}{N_H} \int_{\omega_s} \frac{\alpha}{\hbar\omega} \, d(\hbar\omega).$$

Since the stretching absorption band is not very wide, we can approximate Γ_H^s by

$$\Gamma_H^s = \frac{1}{N_H \hbar\omega} \int_{\omega_s} \alpha \, d(\hbar\omega).$$

Using $\hbar\omega = 0.26$ eV, we obtain

$$\Gamma_H^s = 4.3 \text{ cm}^2/\text{mmole}.$$

This oscillator strength should be compared with 3.7 cm^2/(mmole bond) for SiH_4.[35] Except for extremely small concentrations of hydrogen, the dielectric constant did not vary, so we have not considered any local-field corrections.

Using a dielectric constant of 10, the theoretical calculation presented by Brodsky *et al.*[10] predicts

$$N_H = 1.76 \int_{\omega_s} \alpha \, d(\hbar\omega) \, \text{mmole/cm}^2\,\text{eV}.$$

This overestimates the experimental result by about a factor of 2, which Brodsky *et al.* said was likely to happen. Their difference is due to using an oscillator strength of 3.5 cm^2/mmole and having an effective-field correction which is too small.

The experimentally determined oscillator strength may now be combined with the integrated vibrational absorption to give a direct measurement of the H content of our films by infrared absorption.

Figure 16 shows the dependence of A_s on p_H for three values of T_s. Progressively less hydrogen is incorporated at temperatures above 200°C. The resultant reduction in dangling bond compensation is consistent with the fact that the properties of our high T_s samples suggest a higher density of states in the pseudogap.[2,36] It is also presumed to be the cause of the reported red shift of the absorption edge of a-Si prepared from silane at high temperatures.[37]

The upper limit of 25-at. % H in our films is not supposed to be an inherent limitation on amorphous

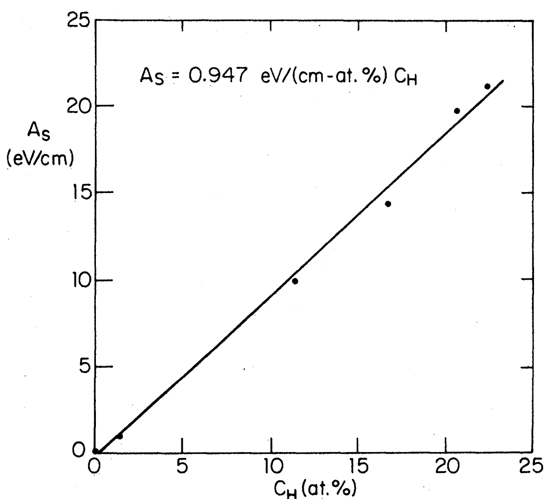

FIG. 15. Plot of the relationship between A_s and C_H. The line drawn is a least-squares fit through the experimental points.

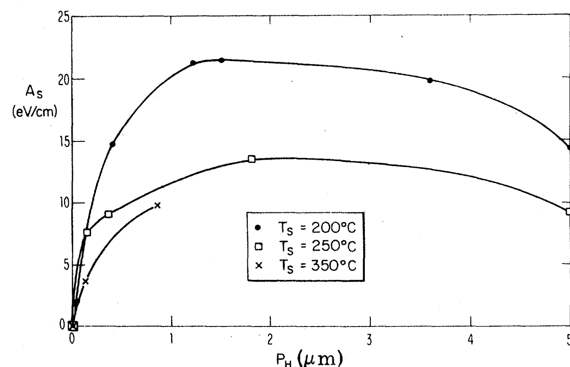

FIG. 16. Dependence of the integral of the stretching vibrational absorption on p_H, for different T_s.

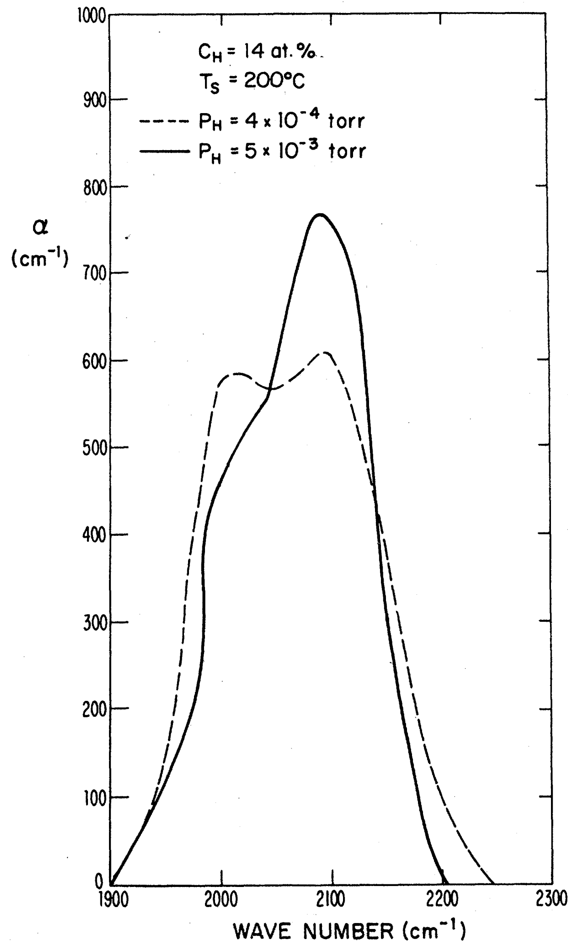

FIG. 17. Comparison of the absorption spectra versus energy for two films of the same C_H, prepared at different p_H.

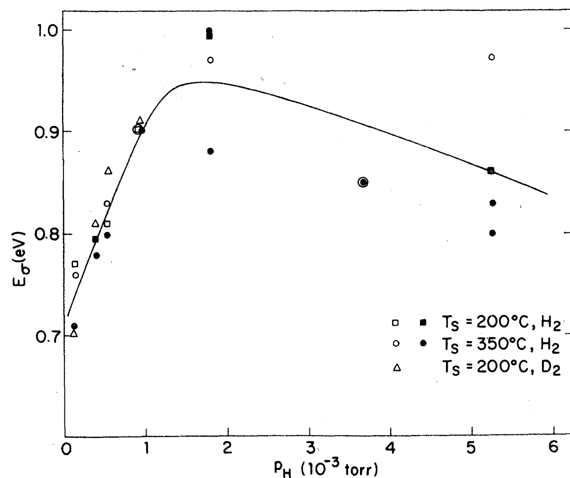

FIG. 18. Dependence of the activation energy for conduction on p_H for films prepared at several T_s. See Ref. 38.

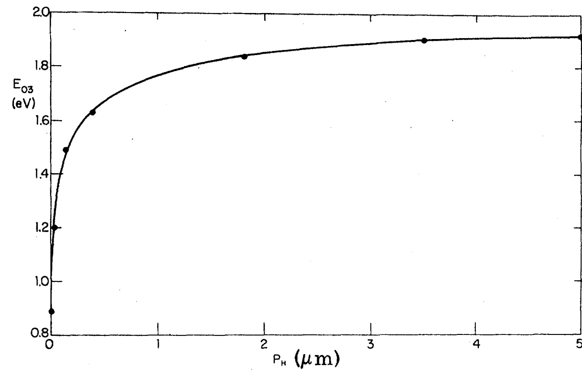

FIG. 19. Dependence on p_H of the photon energy E_{03} at which the absorption coefficient of the absorption edge reaches 10^3 cm^{-1}. See Ref. 36.

Si–H alloys, but rather a property of our sputtering conditions and apparatus. The nonmonotonic variation of A_s and p_H suggests that the plasma is being altered when the pressure of H becomes comparable to that of Ar. One might suppose that when the rf power is kept constant (our imposed condition), the fraction of the current carried by the Ar decreases, the sputtering rate of Si decreases, and the incorporation of H increases. The deposition rate of Si on the substrates does indeed go down, but the H content does also. It does not seem likely that we can satisfactorily explain this experimental result without exploring the mixture of species (SiH, SiH_2, SiH_3, H_2, etc.) in the plasma as a function of the sputtering pressures and voltages.

Whatever the reason for the A_s (p_H) relation, we can produce films of the same C_H at two different p_H. Figure 17 shows the stretching vibrational absorption for two such films. The absorp-

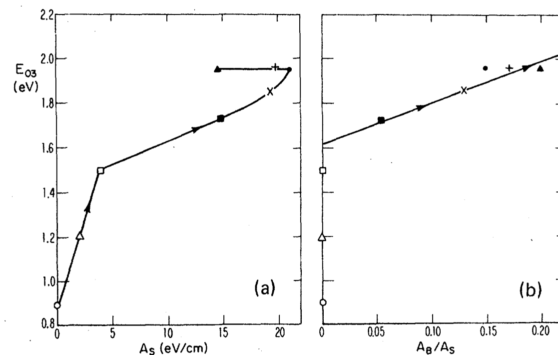

FIG. 20. Dependence of the photon energy E_{03} at which the absorption coefficient of the absorption edge reaches 10^3 cm^{-1} on (a) A_s, and (b) the ratio A_B/A_s, where A_B is the integral under the bending vibrational absorption at 890 cm^{-1}. Arrows follow the direction of increasing p_H.

tion at 2090 cm^{-1} is higher relative to that at 2000 cm^{-1} for the higher p_H film. This is reasonable, given that the 2090-cm^{-1} line is associated with a stretching vibration of SiH_2,[10] if one supposes that a higher p_H should lead to more SiH_2 molecules forming in the plasma.

The discovery that the H content of our films varies nonmonotonically with p_H clarifies some of our previously published results. As one example, it was found[38] that the activation energy for conduction, E_σ, of films produced at different p_H passed through a maximum at a p_H of $\sim 9\times 10^{-4}$ Torr, as shown in Fig. 18. The activation energy is apparently closely related to the H content. It should be added immediately that H content *alone* does *not* determine many of the physical properties measured. An example is given in Figs. 19 and 20, where we have plotted E_{03}, the photon energy at which the optical absorption coefficient reaches 10^3 cm^{-1}, against p_H,[36] A_s, and the ratio A_B/A_s. The interpretation of Figs. 19 and 20 is that the same total amount of H is differently incorporated at different p_H. Different SiH_n complexes may be incorporated, which may possibly entail the presence of associated defects. We have no information, only guesses, as to what the complexes and defects might be.

ACKNOWLEDGMENTS

This work is part of an integrated program of study of amorphous $Si_{1-x}H_x$ alloys participated in by D. A. Anderson, G. Moddel, T. D. Moustakas, S. Oguz, M. A. Paesler, and J. R. Pawlik. Special thanks are due to S. Oguz and M. A. Paesler for use of their results on the determination of H content from evolution experiments, to G. A. N. Connell for early instruction to E.C.F. on the measurement and interpretation of vibrational spectra, and to M. H. Brodsky, J. C. Knights, and G. Lucovsky for very helpful conversations on their measured Si–H spectra. We should also like to thank R. Centamore and D. MacLeod, and, more recently, P. Ketchian for the preparation of the samples. Work supported by the NSF Grants No. DMR76-01111 and DMR76-15325.

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[16]Thanks are due to A. J. Lewis and Texas Instruments for supplying the c-Si substrates.

[17]We are indebted to M. H. Brodsky for drawing our attention to the fact that c-Si could be used as a substrate at our deposition temperatures without incurring

the risk of its inducing crystallization.

[18]In most annealing studies, the sample would probably be held at the desired temperature for a certain time. This experiment, however, was designed to be comparable in procedure to that in our experiments on the kinetics of H evolution on heating (Ref. 30), where the temperature is increased at a uniform rate up to the crystallization temperature.

[19]Samples which were partly crystallized had much shallower absorption edges and weaker vibrational absorptions than completely amorphous ones.

[20]The Dektak determines thickness by running a stylus over the edge between film and substrate and measuring the displacement of the stylus.

[21]Eppendorf pipet 4700, available through VWR Scientific, Inc., Boston, MA.

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[25]The mass density is about 18% lower than that of the crystal for films with about 20 at.% H. The attitude adopted here would seem to disregard comments occasionally found in the literature a-Si produced from SiH_2 has the same diffraction spectrum and radial distribution function as a-Si produced by evaporation or sputtering. We take the view that more structural measurements on the SiH_4-derived material of high H content are advisable.

[26]See M. H. Brodsky, M. Cardona, and J. J. Cuomo, in Ref. 10.

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