Optical constants of rf sputtered hydrogenated amorphous Si

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The transmission spectra of $a\text{-Si}_{1-x}H_x$ alloys prepared under various combinations of substrate temperature T_s and hydrogen partial pressure p_H have been measured over the region of the spectrum encompassing the absorption edge. The dependence of the refractive index on T_s and p_H and the photon energy has been established. The displacement of the absorption edge with T_s and p_H has been studied and related to the hydrogen content of the films and the detailed parameters of deposition. Changes in the absorption edge spectrum resulting from annealing have been correlated with the evolution of hydrogen. The addition of P and B dopants produces absorption at photon energies below the edge of the undoped material. Finally, the temperature dependence of the absorption edge between 4 and 300 K has been measured.

I. INTRODUCTION

The spectral dependence of the imaginary part of the dielectric constant over a photon energy range up to 10 eV is a commonly used source of information about the energy spectrum of electrons in semiconductors. Although this paper will deal almost entirely with a minute part of this spectral dependence, that near the low-energy absorption edge for amorphous silicon, a few general remarks may help set our work in perspective. Figure 1 compares the spectra of crystalline silicon (c-Si)[1] and amorphous silicon (a-Si).[2] There is no significant variation of the gross features of the spectrum with the preparation conditions of the a-Si. The sharp features in the spectrum for c-Si, which can be correlated instructively with theory to infer the band structure, are missing for the amorphous phase. Nevertheless, the overall width and shape of the spectrum, and the deduced average or Penn gap, are about the same.

Closer scrutiny of the absorption spectrum $\alpha(h\nu)$ near the absorption edge shows a strong dependence on the details of the method of preparation. Figure 2 illustrates this with the edges for a-Si evaporated in high vacuum,[3] sputtered in Ar,[4] produced by ion bombardment of the crystal,[5] and grown by the thermal[6] and glow discharge[7] decomposition of SiH_4; also included is the edge for c-Si[8] and three edges for a-Si taken from the present study. The differences among these absorption edges are almost certainly attributable to different densities of states in the gap produced by different densities of natural defects. The density of these defects, of which the single dangling bond is probably the prototype (although it is unlikely to be the exclusive cause) may be reduced by deposition or annealing at elevated temperatures.

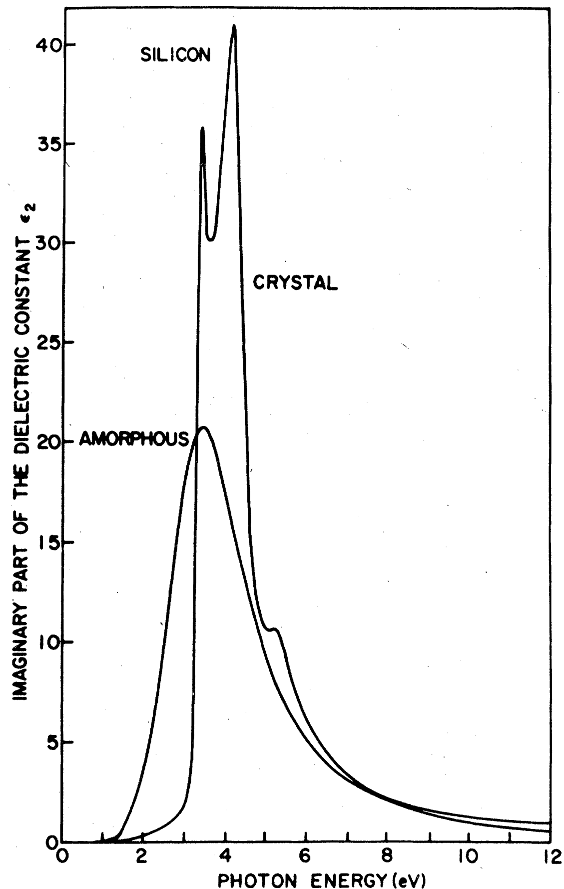

FIG. 1. Comparison of ϵ_2 spectra for crystalline and unhydrogenated amorphous Si (after Pierce and Spicer, Ref. 2).

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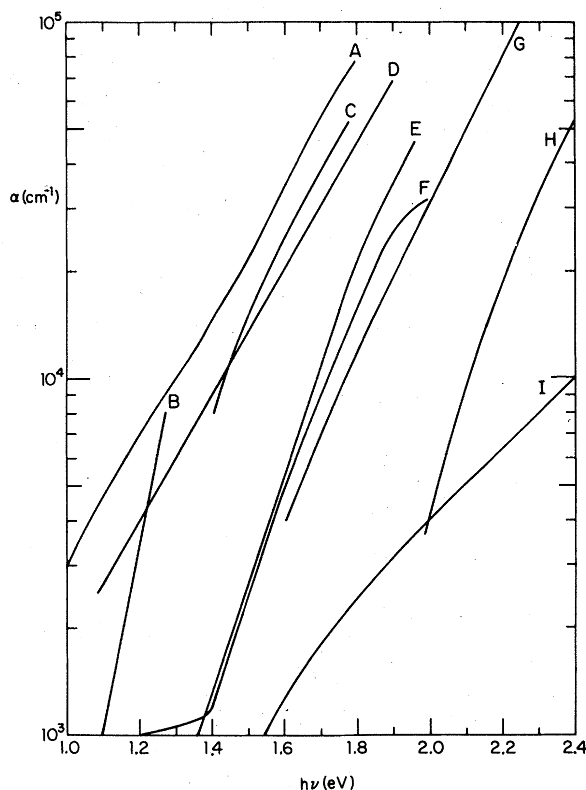

FIG. 2. Absorption edge spectra for amorphous Si films prepared by different methods. (A) Sputtering, $T_s = 25\,°C$, Brodsky *et al.*, Ref. 4. (B) Ion bombarded *c*-Si, Crowder *et al.*, Ref. 5. (C) Sputtering, no H added, $T_s = 200\,°C$, this work. (D) Evaporation, $T_s = 20\,°C$, Beaglehole and Zavetova, Ref. 3. (E) Sputtering with $p_H = 0.16\,\mu$, $T_s = 200\,°C$, this work. (F) Chemical vapor deposition of SiH_4, $T_s = 650\,°C$, Hirose *et al.*, Ref. 6. (G) Glow discharge decomposition of SiH_4, $T_s = 195\,°C$, Zanzucchi *et al.*, Ref. 7. (H) Sputtering with $p_H = 0.44\,\mu$, $T_s = 200\,°C$, this work. (I) *c*-Si, Dash and Newman, Ref. 8.

However, the most dramatic effects result from the deliberate or fortuitous addition of hydrogen in the preparation of the sample: the H, by forming strong Si-H covalent bonds, is supposed to shift states from the gap deep into the valence bands and so remove the cause of most of the low-energy optical absorption. We have already reported detailed studies of this type on *a*-Ge,[9] and preliminary work on *a*-Si.[10] In the course of this work[11] it was also suggested that hydrogenation was the cause of the special properties of *a*-Si and *a*-Ge prepared from SiH_4 and GeH_4, respectively. Since this has now come to be accepted as a correct prediction, we shall in this paper occasionally compare the spectra of $a\text{-}Si_{1-x}H_x$ prepared by rf sputtering and glow discharge decomposition of silane.

In this paper we present the optical constants of $a\text{-}Si_{1-x}H_x$ produced by rf sputtering of a *c*-Si target in a plasma of Ar and H. A considerable advantage of this method is that control of the preparation conditions and variation of the substrate temperature T_s and partial pressure of H, p_H, permits a systematic study of the dependence of the optical constants on defect concentration. Thereby the optical constants of the defect-free, fully-coordinated *a*-Si and $a\text{-}Si_{1-x}H_x$ alloy may be inferred.

In Sec. II we describe our experimental procedure. Section III gives the results, which are further discussed in Sec. IV. Our conclusions are summarized in Sec. V.

II. EXPERIMENTAL METHODS

Films of $a\text{-}Si_{1-x}H_x$ were prepared by rf sputtering an optical grade polycrystalline target with argon (Ar) ions while a variable but controlled partial pressure of hydrogen (H) was added to the plasma. A fuller account of our sample preparation and structural characterization has been given in a recent paper,[12] and will not be repeated here.

For this study Corning 7059 glass which had been degreased in trichloroethylene and subsequently ultrasonically washed in acetone, methanol, and distilled water was used as the substrate. Only two parameters of the sputtering conditions were varied during the sample preparation, the substrate temperature (T_s) and the H partial pressure (p_H). The Ar pressure was kept at 5×10^{-3} Torr and the deposition rate at 1 Å/sec. Films of approximately 1 and 10 microns thickness were prepared in order to obtain a wide range of absorption coefficients at the absorption edge.

By varying p_H and T_s, we were able to control the hydrogen content, C_H, of our films. We measured the infrared vibrational absorption of the Si-H stretching modes near 0.26 eV on films deposited on *c*-Si substrates simultaneously with those on the Corning 7059 glass.[13] The integrated area of this absorption, A_s, may be used as a relative measure of the (bonded) H-content. Since the three principal absorption bands near 0.26, 0.1, and 0.08 eV have been assigned by all workers to the stretching, bending, and wagging vibrations of SiH and SiH_2, respectively, and there are no other absorptions observed, it seems reasonable to use A_s to measure the H-content. The total gas content has also been estimated from evolution experiments[14] and the H-concen-

tration from nuclear reactions[15]; these agree, as a function of p_H at all p_H, and the comparison may be used to establish a relation between A_s and C_H.[12] We have earlier reported $A_s = 0.95 C_H$ eV/(cm at.%) and deduced therefrom an average matrix element for the vibrational absorption.[12]

In Figure 3 we show the dependence of A_s on p_H for three values of T_s.[12] The nonmonotonic variation of A_s with p_H suggests that either the plasma in the sputtering chamber or the chemical reactions at the growing film surface are being altered as the partial pressure of H becomes comparable with that of Ar. Although it might appear that C_H is the more important parameter for analysis of the properties, it will turn out that the film history, which results in the same C_H for different p_H, is also significant.

The effect of H desorption (and also annealing) was studied by remeasuring the optical-absorption spectrum at room temperature after a sample had been heated to successively higher temperatures at a rate of 100 °C/hour 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 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 to room temperature by radiation in the vacuum. In most annealing studies samples are typically held at the desired annealing temperature for an extended period. This desorption experiment, however, was designed to be comparable in procedure to that in our experiments on the kinetics of H evolution on heating,[14] where the temperature is increased at a uniform rate up to the crystallization temperature.

The influence of dopants on the absorption edge was also measured. Phosphorus (P) or boron (B) were added to the films by adding PH_3 or B_2H_6 to the sputtering gas, respectively.[16] Lithium (Li) was also added to the films by evaporating 99.9+% pure Li

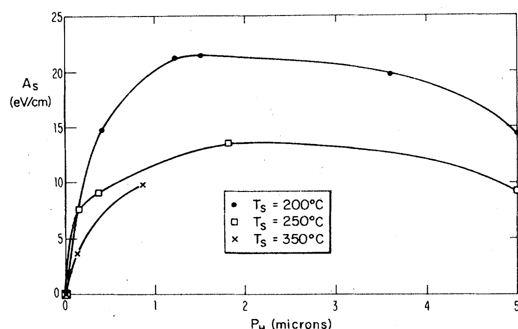

FIG. 3. Dependence of the integral of the stretching vibrational absorption A_s on p_H for different T_s.

metal[17] in a base vacuum of $\sim 10^{-5}$ Torr onto the Si films after their removal from the sputtering system. The films, which were one micron thick, were then held in the vacuum at 250 °C for an hour to permit the Li to diffuse through the film.[18] After removal from the evaporator, the Li remaining on the surface was washed off with deionized water.

The variation with temperature of the optical-absorption edge was measured using liquid He as a coolant for an Air Products Heli-Tran optical Dewar[19] with glass windows. The flow of the liquid helium and the current from a PAR Model 152 temperature controller[20] were adjustable so that the temperature was stable to ±0.2 °C.

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 a resolution of 0.0002 eV which had two specular reflectance accessories. For photon energies greater than 0.5 eV, a Cary Model 14 double beam spectrometer with 0.0003 eV resolution was used.

The low-temperature measurements could not be performed in a double beam spectrometer because of the lack of a second Dewar for a reference. For this study, we used a single beam spectrometer with a stabilized tungsten halogen source and a Jarrel-Ash 82-020 half-meter grating monochrometer with 0.0006 eV resolution. Higher-order wavelengths were filtered with Corning color filter glasses. The light was phase sensitively detected with either an RCA IP21 photomultiplier or a room-temperature PbS cell. For normalization, a reference was separately measured.

The index of refraction, n, was obtained from examination of the interference fringe minima in reflection to determine their order numbers, m. Then, $n = m\lambda_m/2t$, where λ_m is the wavelength at the mth minimum and t is the measured thickness. Since m is a small integer, it could be determined without error. The uncertainty in the value of λ_m is so much smaller than the error in t, which we estimate at ±4%, that the error in n may be taken equal to the error in t.

When there is a substrate in the reference beam, the absorption coefficient α is given by

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

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.[21]

For $\alpha \lesssim 10^5$ cm^{-1}, the imaginary part of the index of refraction is much less than n, so that it is valid to calculate the reflectance of a surface between media a

and b, refractive indices n_a and n_b, using

$$R_{ab}=\left(\frac{n_b-n_a}{n_b+n_a}\right)^2 .$$

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

III. EXPERIMENTAL RESULTS

A. Refractive index

Figure 4 presents the refractive index n as a function of photon energy $h\nu$ for an unhydrogenated and a hydrogenated sample. The unhydrogenated sample has a notable resonance near 0.06 eV, which is the energy of the a-Si optical phonon. The refractive index of the hydrogenated sample is much lower between 0.04 and 0.50 eV. The resonance at 0.06 eV is not observed, but other resonances are seen, which correspond in energy to the Si-H localized mode vibrations.[12]

Since n changes quite slowly with $h\nu$, it is legitimate to study the variation of n with conditions of preparation for a single energy $h\nu$ of 0.3 eV. For a single p_H of 0.1 microns, we found n varied from 3.28 to 3.37 to 3.48 with substrate temperatures of 200, 250, and 350 °C, respectively. (Recall that, from our earlier paper,[12] this does *not* correspond to constant H content, C_H.)

Figure 5 shows the dependence of n on p_H for a fixed T_s of 200 °C. There is a large drop for a small increase in p_H from zero, followed by a very slow decrease.

The study of the effect on the optical constants of heating amorphous hydrogenated silicon showed no measurable change in the refractive index.

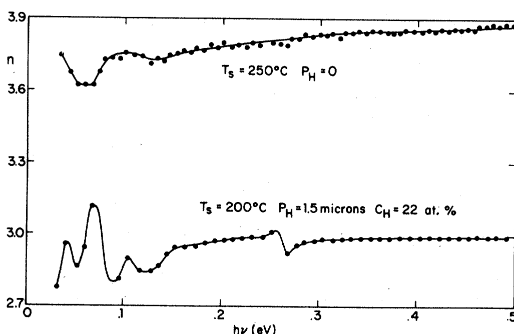

FIG. 4. Refractive index n as a function of photon energy for a hydrogenated and an unhydrogenated sample.

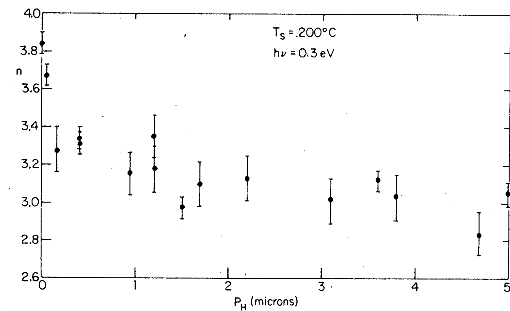

FIG. 5. Refractive index at 0.3 eV as a function of p_H.

B. Absorption edge

Figure 6 shows the shift of the absorption edge as T_s is varied at fixed p_H. Between $T_s = 25$ and 200 °C the edge shifts to larger photon energies, but as T_s is further increased, the edge shifts continuously back to lower energies. As we shall explain below, this seemingly odd behavior correlates exactly with the

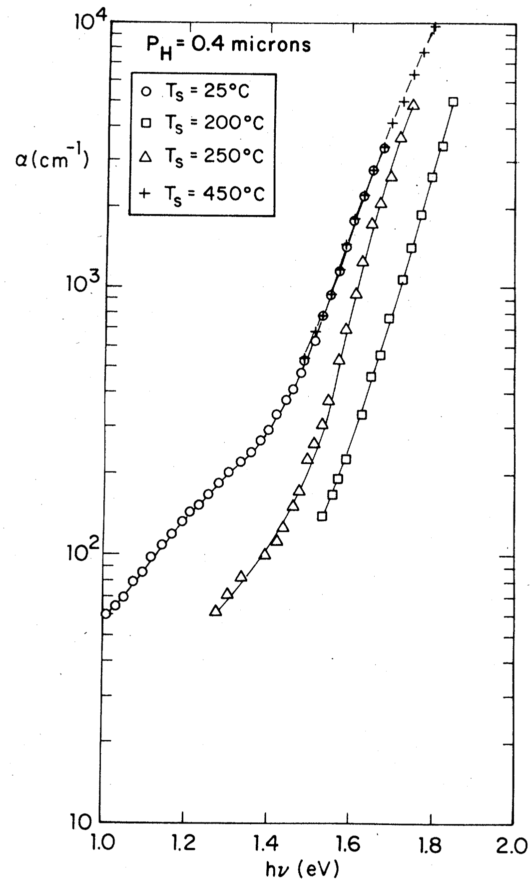

FIG. 6. Shift of absorption edge with T_s.

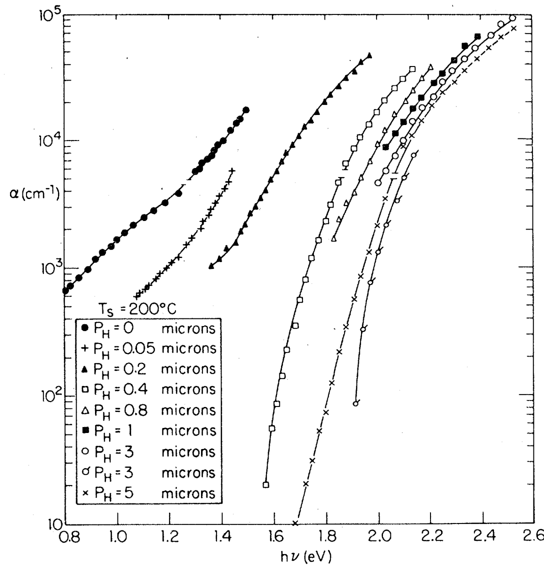

FIG. 7. Shift of absorption edge with p_H. The data were taken on two series of films, one thick, the other thin. Note the sharpness of the edge at low α for high p_H films.

variation in C_H with T_s when p_H is kept constant.

The partial pressure of hydrogen added to the plasma affected the absorption edge in the way shown in Fig. 7, which was established with two series of films, one ~10 microns thick and the other ~1 micron thick.

As p_H was increased, the edge shifted to higher energies and also became steeper.

When we heated thick films of a-Si, they invariably lost surface quality and/or disintegrated before crystallization, and this prevented a good study of the changes in the low α part of the absorption edge. Thin films do, however, survive temperature cycling, and the results for a film on which we took the most extensive data are given in Fig. 8. No change was seen for a heating temperature T_H below 300 °C. At higher T_H, the edge shifted continuously to lower energies.

The effect on the absorption edge of adding hydrogenic dopants to the film is shown in Fig. 9. For small p_{PH_3} and $p_{B_2H_6}$, the edge is shifted to lower energies and changes its shape. This is quite different from the rather small shape changes observed between $p_H = 0$ and $p_H =$ finite in Fig. 7.

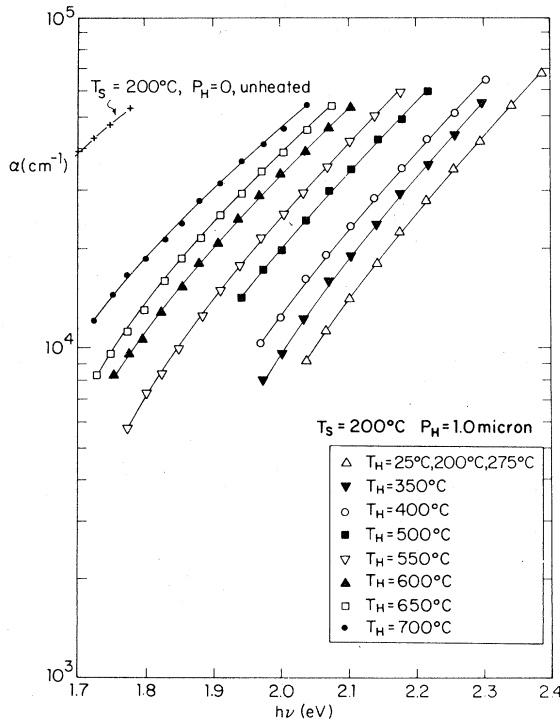

FIG. 8. Shift of absorption edge measured at room temperature due to heating of a film.

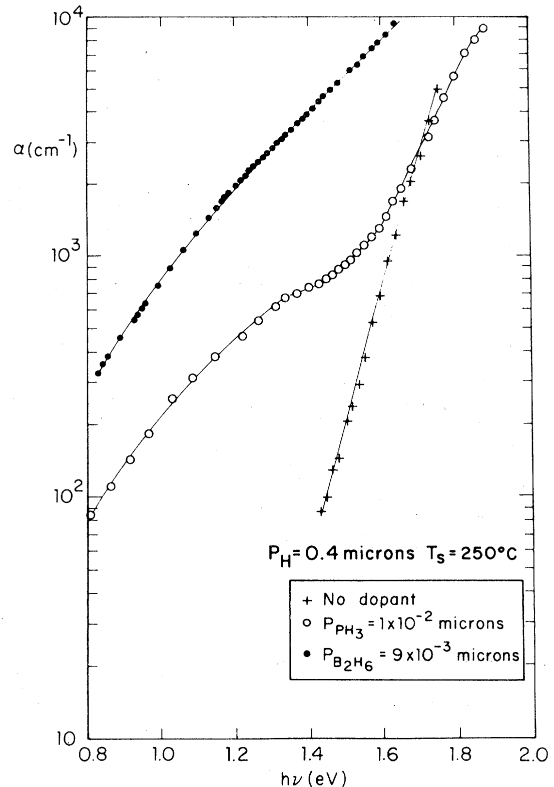

FIG. 9. Influence of P and B dopants on shape of absorption edge.

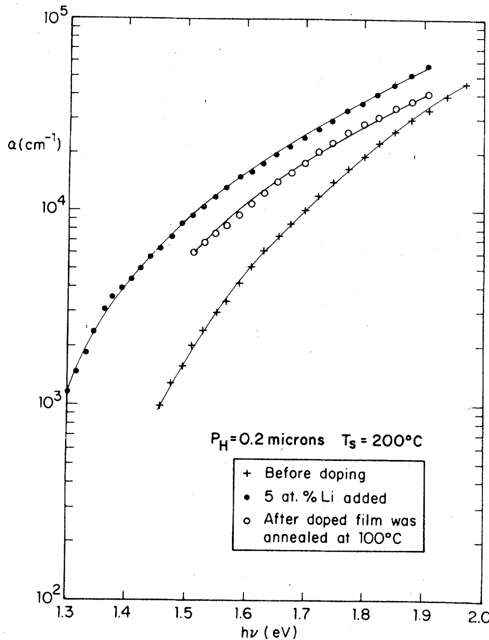

FIG. 10. Influence of Li dopant on shape of absorption edge.

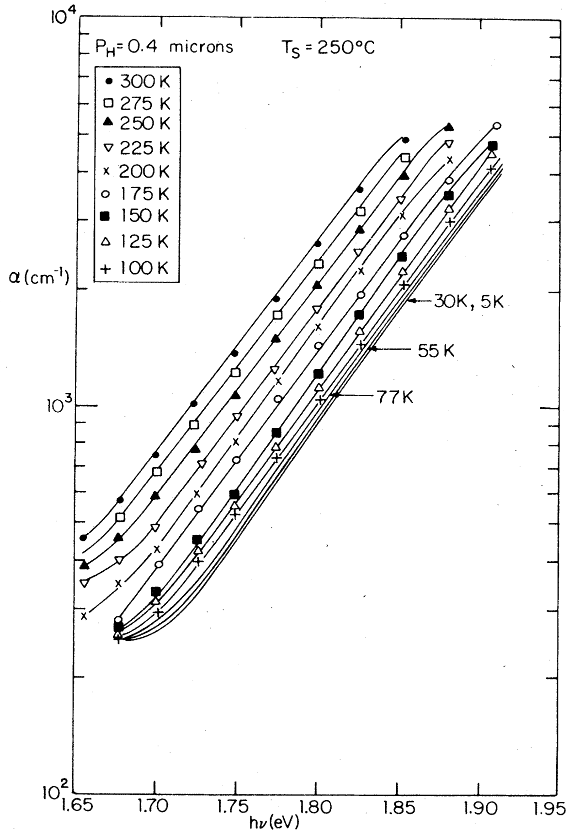

FIG. 11. Shift of absorption edge with measurement temperature. Data points were omitted for the lowest temperatures because of lack of space.

Figure 10 shows the effect of adding Li to the film. The absorption edge shifted by about 0.18 eV to lower energies after the addition of the estimated 5 at.% of Li. This was stable (at least for a period of three days) when the film was maintained at room temperature, but heating to only 100 °C for a few minutes shifted the edge back towards the undoped position. It is presumed that this is caused by out diffusion of the Li[18] from interstitial sites.[22]

Adding Li to a-Si films caused notable deterioration of the samples. Highly hydrogenated films crumbled to dust and lightly hydrogenated and unhydrogenated ones had damaged surfaces.

Finally, in Fig. 11 we show the temperature dependence of the absorption edge for a sample prepared at $T_s = 250\,°C$ and $p_H = 0.4$ microns. The edge displaces to higher energies without significant change of shape as the measurement temperature is lowered. The shifts of an unhydrogenated sample and of samples of different C_H are very similar qualitatively to those of Fig. 11.

IV. DISCUSSION

A. Refractive index

The data in Fig. 5 on the variation of refractive index with p_H, the quoted results for the variation of n with T_s and the constancy of n with heating temperature T_H can be rationalized, as will be argued below, but not fitted to a quantitative model in a unique way. Generally speaking, the refractive index might be expected to depend on the density of the sample and its electronic band structure. A general approximate expression is

$$n^2 - 1 = \frac{4\pi N e^2 \hbar^2}{m E_g^2} ,$$

where N is the density of valence-band electrons per unit volume, m their mass, $\hbar$ is Planck's constant, and E_g an average energy gap between valence and conduction bands.[23] The density of the sample enters through N and the band structure through E_g. Detailed analysis of the small variation of n with T_s, T_H, and p_H encounters three problems: (i) The refractive index is determined in our experiments from the pattern of interference fringes and its accuracy is determined by the accuracy of measurement of the thickness t. This thickness is determined by a Sloan Dektak Surface Profile Measuring System, which tracks a diamond stylus across the edge between the surface of the sample and the glass substrate. The error in

this method, estimated from measurements at several edges of the same film, is $\pm 4\%$. This is higher than the $\pm 2\%$ quoted error of the instrument[24] and is probably caused by nonuniformity in the glass substrate near the edge of the sample, which is produced by the 20-second presputtering Ar bombardment used to clean that surface. This accuracy is adequate for the determination of absorption spectra which shift over large ranges of $h\nu$ with H content, but is marginal for the analysis of small changes in n. (ii) The density, and therefore N, is determined by floating a small sliver of sample, removed from a substrate, in a mixture of zinc bromide and water whose density can be adjusted by adding water. The density of the liquid is determined using an Eppendorf Pipet 4700. Errors can enter this method of determining the density because of inadequacies of the pipette construction. Figure 12 illustrates the densities we have determined for a series of samples made at different T_s and p_H. There is a clear trend to lower densities as p_H is increased and no evident dependence on T_s. However, there is a superimposed scatter in the data which we attribute to the experimental determination of ρ. (iii) Determination of the change with T_s, T_H, and p_H of the average energy gap E_g would require a measurement of the absorption spectrum over a range of energies up to, say, 6 eV. We have not carried out such measurements. The variation of the absorption edge probably gives the correct sign of the effect of band-structure changes, but cannot be used in a quantitative correlation.

These caveats made, we illustrate in Fig. 13 the variation of n^2-1 with density for a series of samples produced at different p_H and T_s. Although the aforementioned errors prevent a quantitative fit, the index clearly increases with increasing density, which, from Fig. 12, occurs for low p_H and C_H. The percentage increases in n^2-1 and ρ over the range investigated are roughly 60% and 20%, respectively. Equation (1) then suggests that a decrease in average band gap E_g at high ρ (low p_H) contributes the larger fraction of the overall effect. Although we do not know

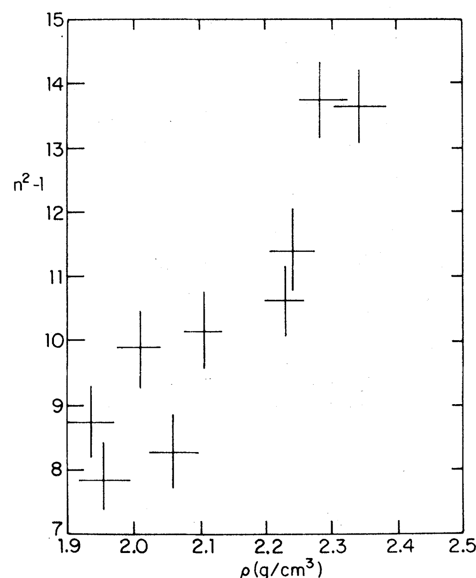

FIG. 13. Relation between dielectric constant n^2 and density.

the change in E_g, the square of the smallest energy gap (measured by the energy at which $\alpha = 10^4$ cm^{-1}) decreases by about 60% over the range of p_H (C_H) considered.

A similar result of a decrease in refractive index with hydrogenation was found earlier for a-Ge:H by Connell and Pawlik.[9] A different dependence on ρ was found in a study of the effect of varying the substrate temperature T_s for a series of unhydrogenated films of amorphous Ge.[25] There, the effect of raising T_s was to increase the density but to decrease the refractive index. This effect is explained by a shift of the absorption spectrum to *higher* energies with increasing T_s or ρ.

In Sec. III we reported a mild increase, some 6%, of n for an increase of T_s from 200 to 350 °C. Figure 12 shows no evidence of an increase in ρ with T_s (ef-

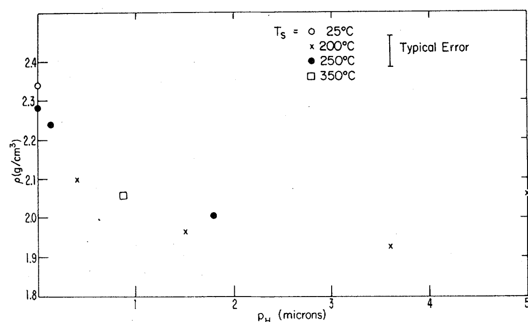

FIG. 12. Dependence of density ρ on p_H.

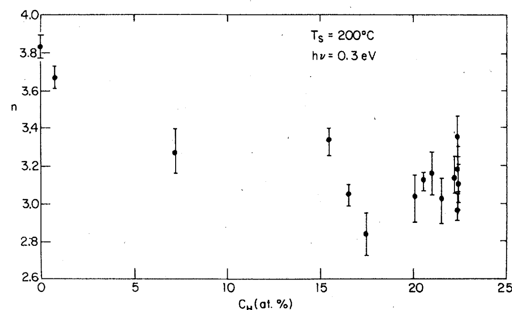

FIG. 14. Dependence of refractive index on hydrogen content, C_H.

fects of varying C_H excluded). Although a small increase might be expected, the data are too sparse and scattered for any conclusion to be made. On the other hand, Fig. 3 shows that C_H decreases some 40% as T_s is increased at fixed p_H; this *should* lead both to an increase in ρ and the decrease in optical gap reported in Fig. 6. Thus the observed effect of T_s on n at least has the correct sign.

It is evident from Figs. 3, 5, and 12 that the major changes in property occur for low p_H and are caused by the change in C_H. Figure 14 shows n plotted against C_H rather than p_H.

The constancy of n with annealing temperature is inconsistent with the very considerable red shift of the absorption edge shown in Fig. 8. At present we can offer no explanation for this.

B. Shift of absorption edge with p_H

From Fig. 7 we can determine the dependence on p_H of an optical energy gap. This may be taken as E_{03} or E_{04}, the photon energies where the absorption coefficient equals 10^3 or 10^4 cm^{-1}, respectively. Alternatively, one can plot, as shown in Fig. 15, $(\alpha h\nu)^{1/2}$ vs $h\nu$ to obtain E_0 from a formula appropriate for densities of valence and conduction-band states that increase according to the square root of the departure from the band-edge energy, and a constant transition matrix element

$$(\alpha h\nu)^{1/2} = B(h\nu - E_0) \ .$$

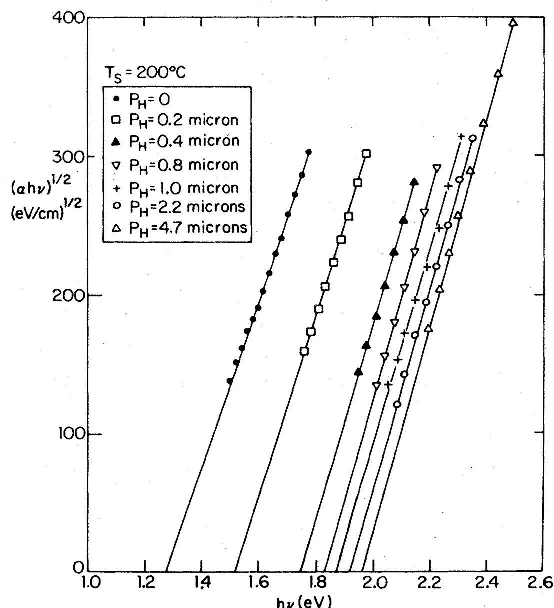

FIG. 15. Shift with p_H of linear portion of plot of $(\alpha h\nu)^{1/2}$ as a function of $h\nu$.

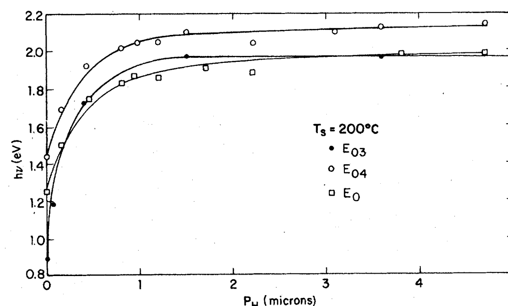

FIG. 16. Plot of three definitions of the band gap, E_0, E_{03}, and E_{04}, as a function of p_H.

Figure 16 shows the dependences of E_{03}, E_{04}, and E_0 on p_H, and Fig. 17 the dependence of E_{03} on C_H, using the data of Fig. 3. All gaps increase rapidly as hydrogen is first added; we attribute this to removal of dangling bond states and reconstructed dangling bond states from the pseudogap by the hydrogen. The gaps approach an asymptote for $p_H \geq 1$ micron, whereas the hydrogen concentration decreases. Thus Fig. 17 shows two different gaps for the same C_H for $C_H \geq 10$ at.%. We interpret this as the result of the hydrogen entering the network in different configurations at different p_H that produce the same absolute H concentration. These different H configurations [we might speculate on H attached to single dangling bonds in the bulk, or on a void surface, or the occurrence of $(SiH_2)_n$ complexes] might give different electronic states in the pseudogap. An interpretation involving different sites for single H attachment to a Si atom conforms to our speculations on the proper interpretation of our infrared absorption spectra[12] and it is also consistent with a previously published interpretation from our laboratory[9] on a-Ge:H.

It is tempting to interpret the initial steep rise of E_{03} with C_H as the compensation of defect pseudogap states and the slower subsequent increase beyond

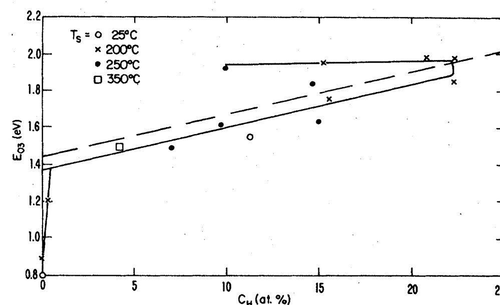

FIG. 17. E_{03} as a function of hydrogen content C_H. Points above and below dashed line have p_H greater than or less than one micron, respectively.

$C_H = 1$ at. % as the modification of the valence- and conduction-band densities of states in the a-$Si_{1-x}H_x$ alloy. Extrapolating the slow increase back to $C_H = 0$ then gives an E_{03} gap for the completely coordinated pure a-Si of 1.4 eV. Regarded as "the energy gap" of a-Si, this value is the same as that previously reported in the literature for the E_{03} of annealed samples of unhydrogenated a-Si.[26]

C. Shift of absorption edge with T_s

From Fig. 6, the values for E_{03} as T_s is changed are

$$T_s = 25\ ^\circ\text{C},\quad E_{03} = 1.56\ \text{eV}\ ;$$

$$T_s = 200\ ^\circ\text{C},\quad E_{03} = 1.72\ \text{eV}\ ;$$

$$T_s = 250\ ^\circ\text{C},\quad E_{03} = 1.63\ \text{eV}\ ;$$

$$T_s = 450\ ^\circ\text{C},\quad E_{03} = 1.56\ \text{eV}\ .$$

The increase in E_{03} between $T_s = 25\ ^\circ\text{C}$ and $T_s = 200\ ^\circ\text{C}$ can probably be attributed to a reduction in defect density at the higher temperature.[25] While we have no evidence on the change in H incorporation for this change in T_s, studies in silane-produced a-Si suggest that more H is incorporated at the lower temperature[7] — an effect which would lead to a *reduction* of E_{03} with increase in T_s. This annealing effect also results in an increase in photoconductivity.[25]

When T_s is raised above 200 °C, the decrease in the amount of hydrogen incorporated in the film (Fig. 3) is paralleled by a decrease in E_{03} which overwhelms the annealing effect. The data taken from Fig. 6 are sparse, but the noted trend is supported by similar results on films prepared at different p_H. However, the magnitudes of the photoconductivity[27] and the conductivity activation energy[28] change rather little as T_s is raised from 200 to 250 °C. A self-consistent explanation of these observations requires that the principal effect of the hydrogen lost above 200 °C be to introduce states in the gap which are detected in optical absorption but not in dark or phototransport. This may come about in the following way. At higher T_s there are probably fewer void surfaces and dangling bonds to accept the hydrogen. There may also be a reduction in the probability of a hydrogen atom "substituting" for a silicon in a network site. Both eventualities lead to a reduction in C_H. A reduction in the probability of substitution of a H atom for a Si atom at a network site leads to an increase in the state density near and just above the valence-band edge. This result agrees with the observation from photoemission studies of von Roedern *et al.*,[29] that the density of states at the top of the valence band is reduced when a large amount of hydrogen is incorporated. Thus E_{03} is decreased. However, the activation energy for dark transport is unaffected, because the state density in the upper half of the band gap is unchanged. The photoconductivity is similarly affected rather little, because it depends on the mobility and lifetime of the electrons, and these are not altered by changes in state density near the valence-band maximum.

D. Effect of heating to high temperatures

The shift of the absorption edge to lower energy as a sample is heated is consistent with the fact that hydrogen is evolved from our samples in the same temperature range.[14] The detailed features of the hydrogen evolution versus temperature relation are not accessible because of the time scale on which repeated optical measurements must be carried out. The absorption edge shift is also roughly similar to that found by the Chicago group[30]; in both investigations, the shift with heating becomes discernible near 300 °C.

Figure 8 also shows the absorption edge for a sample prepared at $T_s = 200\ ^\circ\text{C}$, $p_H = 0$. Comparison of that curve with the edge for the hydrogenated sample measured after $T_H = 700\ ^\circ\text{C}$,[31] when all (or nearly all) of the H has been driven off, gives a measure of the annealing effect of the high temperature. As expected, there has been an increase in energy gap with anneal, corresponding to the removal of some of the states in the gap.

E. Effect of doping on the absorption edge

Figure 9 shows that addition of P introduces a pronounced bump into the absorption edge near 1.4 eV. The B doped sample does not exhibit any obvious bump, but has a higher absorption for the measured energies. These results fit generally with results of an earlier measurement of the optical spectra of doped films[32] and with results on the photoconductivity of B- and P-doped films.[33]

The first difficulty in interpreting the magnitude of the absorption caused by the inclusion of P or B results from our ignorance of the atomic percent of the elements actually incorporated from the PH_3 and B_2H_6. The second is the result of our imprecise knowledge of the coordination adopted by the P or B on incorporation, since we might expect either ele-

ment to choose threefold or fourfold coordination as local free-energy minimization demands. It must be recognized that the symmetry in creating donor or acceptor centers shown by fourfold coordinated P and B in crystalline Si does not extrapolate to the amorphous phase. Fourfold coordinated P will indeed have a fifth electron in a "hydrogenic" donor state. This electron will move in a large orbit in a medium whose dielectric constant is very close to that of crystalline Si. Since the effective mass is not known, we cannot estimate the orbit radius precisely, but if the mass is the free-electron mass, the orbit radius will be approximately 6 Å. If the orbit radius were larger (mass smaller than the free-electron mass), then we could argue that the electron is sampling a sufficiently large volume of the disordered solid that the ground-state energy of different P donors would be essentially the same. For the quoted radius and smaller radii, it might be more accurate to suppose a spread in energies that reflects the disorder in the potential. Kivelson has calculated this spread using effective mass theory[34] for fourfold coordinated B in a-Si and finds it to be of the order of 0.02 eV. Thus it seems reasonable, as a first approximation, to suppose that P donors have an ionization energy of between 0.1 and 0.2 eV and a spread of the order of 0.02 eV. When P is threefold coordinated, it is probable that it will have two electrons in an s state and three in bonding p states. The P atom having achieved closed shell configuration, it is not obvious that there will be any states in the pseudogap.

If B is incorporated in fourfold coordination, it is expected to give a "hydrogenic" acceptor level with about 0.1 to 0.2 eV binding energy. If, on the other hand, B is incorporated in threefold coordination, it will probably form three sp^2 bonds and also have an unfilled double-acceptor p level with an energy near the middle of the energy gap.

We now inspect Fig. 9, keeping these ideas about the P and B energy levels in mind. The P donor level would be expected to provide a lower edge to the main absorption edge structure, displaced by 0.1 to 0.2 eV. It is clear that the extra absorption extends to much lower energies. This suggests either that our qualitative ideas about the P donor are wrong or that P is the source of other defects or impurity-defect configurations that yield energy levels deep in the energy gap.

The absorption spectrum for the B impurity is entirely consistent with the model of shallow hydrogenic states and deeper double acceptor states. The higher absorption for the B doping over the P doping is also consistent with the proposal that B always gives acceptor states, no matter what its configuration is; but, on the other hand, we cannot ignore the presence of twice as much B for the same partial pressures of B_2H_6 and PH_3, nor the possibility of more efficient incorporation of B from the gas plasma.

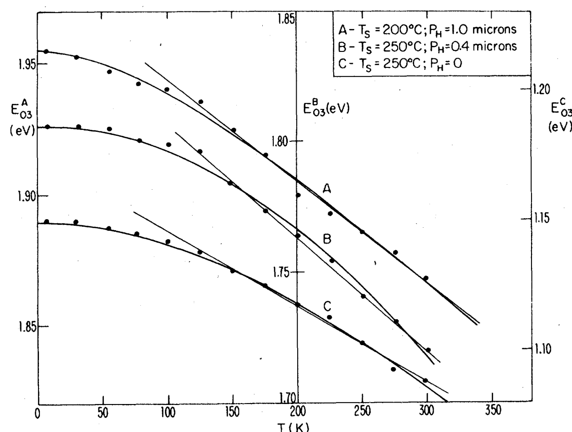

FIG. 18. E_{03} as a function of temperature for three samples. With the energy in eV and the temperature in Kelvin, the straight line sections are fitted by: $E_A = 1.98 - 3.87 \times 10^{-4} T$; $E_B = 1.85 - 4.37 \times 10^{-4} T$; and $E_C = 1.17 - 2.90 \times 10^{-4} T$. The entire curves (Ref. 35) are fitted by: $E_A = 1.96 - 4.89 \times 10^{-4} T^2/(T + 190)$; $E_B = 1.81 - 1.68 \times 10^{-2} T^2/(T + 16\,500)$; $E_C = 1.15 - 7.28 \times 10^{-4} T^2 (T + 720)$.

F. Shift of the absorption edge with temperature of measurement

Figure 18 shows the variation with T of E_{03} for three samples prepared under different conditions. It is evident that all three possess energy gaps which approach an asymptote as $T \to 0$ and decrease roughly quadratically at higher temperatures. The rate of change with T of the E_{03} for the hydrogenated films appears to be greater than that of the unhydrogenated one reported here and also of a previously reported unhydrogenated film.[36] The quantitative differences between the three curves may be significant, and a more extensive examination involving more samples prepared at different p_H is planned.

G. Comparison with the literature

We have found it instructive to compare the results from various laboratories for the optical properties of a-Si prepared by glow discharge decomposition, or by evaporation or sputtering, with or without the presence of hydrogen. The data for representative films are given in Table I. The silicon films prepared by sputtering in a plasma with hydrogen added, glow discharge decomposition of SiH_4 or chemical vapor deposition with SiH_4 have either been reported to have hydrogen in them or presumed to have it.

TABLE I. *Optical properties and density of representative films of a-*Si. In the table, ρ is the density, n the refractive index, E_{04} and E_{03} the photon energies $h\nu$, at which the absorption coefficient α is equal to 10^4 and 10^3 cm^{-1} respectively, and E_0 and B are defined by the relation $(\alpha h\nu)^{1/2} = B(h\nu - E_0)$.

Method of preparation	ρ (g/cm^3)	n	E_{04} (eV)	E_{03} (eV)	E_0 (eV)	B $(eV\ cm)^{-1/2}$	Ref.
Sputtering with H present	1.96	2.97	2.12	1.98	1.98	760	This work
	2.10	3.34	1.93	1.74	1.74	690	This work
Glow discharge decomposition of SiH_4	...	...	2.1	1.8	...	...	37
	1.9	3.4	1.8	1.4	...	...	38
	2.13	...	1.9	1.75	...	...	32
	...	3.76	1.9	1.0	1.72	640	7
	2.17	3.45	1.92	1.74	1.78	780	30
Chemical vapor deposition from SiH_4	2.26	3.5	1.7	1.1	1.45	...	6
Sputtering without H present	2.29	3.84	1.44	0.90	1.26	580	This work
	...	3.7	1.3	0.8	1.26	650	4
Evaporation without H present	2.2	3.7	...	...	1.36	570	39
	...	3.45	...	...	1.44	540	40
	1.9	3.39	1.8	1.4	...	...	41
	2.16	3.44	1.4	...	...	...	3
	...	4.1	1.57	...	1.36	560	42

Films prepared by sputtering or evaporation with no dopant gases are presumed to be pure *a*-Si.

In our laboratory we have measured a range of densities from 1.90 to 2.33 g/cm^3. Most of the films in the literature fall in this range, although some films have been reported[15,32] which have ρ as low as 1.40 g/cm^3.

Increasing the amount of hydrogen in a film decreases its density, but some of the evaporated films have low densities as well. The latter are believed to have large voids.

We have observed indices of refraction ranging from 2.8 to 4.2, which also covers the reported values from the literature.

When one examines the absorption edge parameters, E_0, E_{03}, E_{04}, and B, a distinction between hydrogenated and unhydrogenated films is apparent. All of these quantities are larger in hydrogenated films than in hydrogen-free films. E_{03} is occasionally an exception, because some hydrogenated films[6,7] have low-energy tails to their absorption edges[43] which extend to absorption coefficients as high as 10^3 cm^{-1}. This indicates that at least some configurations of incorporated hydrogen are not effective in removing states from deep-lying parts of the pseudogap. As we have never observed absorption edge tails in our films, we cannot speculate on the cause.

V. CONCLUSIONS

The transmission spectra of a-$Si_{1-x}H_x$ alloys, prepared under different combinations of substrate temperature T_s and hydrogen partial pressure p_H, have yielded information about the dependences of the refractive index and the absorption edge on these parameters. The refractive indices of both unhydrogenated and hydrogenated films show very little dependence on photon energy for energies below 0.5 eV, except that the hydrogenated samples show resonances that can be related to the optical absorption caused by several localized Si-H vibrational modes. The refractive index of unhydrogenated material is rapidly reduced, by about 25%, on hydrogenation, consistent with the displacement of the optical-absorption edge to higher energies. An appropriate average index for films of hydrogen content of about 20 at.% is 3.0. The refractive index increases with increasing substrate temperature at constant partial pressure of hydrogen in the sputtering gas, an effect which is very plausibly related to the decrease in hydrogen content at higher deposition temperatures. The refractive index variation with hydrogen content of the alloy is caused both by a decrease in density (about 20% in the range of H-content measured) and an increase in average energy gap. While the data are

consistent with the expectations of a simple theory for these effects, a truly quantitative fit is prevented by the smallness of the effects and the experimental errors in measurement or estimation of thickness, mass density, and average gap.

The absorption edge, and therefore any arbitrarily defined energy gap, shifts to higher energies as the hydrogen content is increased. When hydrogen is first added, the shift is very rapid, and this is presumed to be caused by the elimination of states in the gap through compensation of dangling bonds. Thereafter the shift is slower, as hydrogen addition alters the state densities near the band edges. Estimates can be made of the extrapolated energy gap for zero gap state density; if the criterion chosen to estimate the gap is E_{03}, the photon energy at which the absorption constant is 10^3 cm^{-1}, then this gap is 1.4 eV. However, it is necessary to specify the criterion for gap that is used, since the value found depends on this. The energy gaps corresponding to E_{03} and E_{04}, and that found from extrapolation of a plot of $(\alpha h\nu)^{1/2}$ vs $h\nu$, range between 2.0 and 2.2 eV for hydrogen contents in the alloy between 10 and 20 at. %. It is found that films produced at very high partial pressures of hydrogen have energy gaps that do not vary as the hydrogen content does. This is attributed to a change in the configurations in which hydrogen is incorporated and a resultant change in the modification of the electronic density of states produced by the hydrogen. The configurational changes are not identified, but it is noted that the model suggested is consistent with the conclusions drawn from studies of changes in the spectrum of vibrational absorption of localized Si-H modes.

The absorption edge shifts to lower photon energy as the substrate temperature is increased above 200 °C at fixed p_H. It is suggested that this is a balance between an increase of gap with T_s caused by annealing out of defects and a decrease of gap with T_s caused by decreased incorporation of hydrogen. The changes in energy gap deduced from the absorption edge shifts do not correlate precisely in the T_s range between 200 and 250 °C with much smaller changes in the photoconductivity and the conductivity activation energy. An explanation is offered for this difference in terms of a model for the changes in H-incorporation with T_s and predicted results for their effect on the profile of state density in the pseudogap and at the top of the valence band.

The absorption edge shifts to lower energy on heating, consistent with the observed evolution of hydrogen, although the magnitude of the shift is governed by the *net* effect of hydrogen evolution and annealing of defects.

Doping with either P or B shifts the absorption edge to lower energy and changes its shape. The effects are very large: approximately 0.5 eV shift at an α of 10^3 cm^{-1} in the P-doped film and 0.5 eV at an α of 10^2 cm^{-1} in the B-doped one. The shifts are *not* explained by the postulate of hydrogenic levels approximately 0.1 to 0.2 eV from the appropriate band edge. The large shift for the B-doped film is expected on the basis of a model that threefold coordinated B atoms yield a double acceptor level of *p*-symmetry in the middle of the pseudogap. The large shift in the case of P more likely is the result of some phosphorus-defect or phosphorus-impurity configuration that so far has not been identified.

The variation of the absorption edge with temperature resembles quite closely that for the silicon crystal. There are differences depending on H-content of the alloy measured, but our present results are too preliminary for any quantitative description to be developed. Nevertheless, the present results are meaningful for the appropriate interpretation of photoconductivity and photoluminescence[44] measurements made on the same films.

Finally, we have compared representative optical parameters on differently prepared films, taken from the literature on the subject. Two quite general conclusions emerge: (i) hydrogenated *a*-Si prepared by sputtering in H and that prepared by decomposition of SiH_4 have similar properties, and (ii) hydrogenated material tends to have lower density, lower refractive index, and higher energy gap than its unhydrogenated counterpart.

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