

Influence of hydrogen on vibrational and optical properties of $a\text{-Si}_{1-x}\text{H}_x$ alloys

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The effect of hydrogen on the optical gap and network short-range order has been obtained in $a\text{-Si}_{1-x}\text{H}_x$ alloys by optical-absorption and Raman-scattering measurements. Distinct differences are observed in the role of hydrogen for homogeneous chemical-vapor-deposited (HMCVD) and rf-diode-sputtered (RFS) films. A comparison of the correlation between the Raman TO peak width and the optical gap for films with and without H allows a separation of the roles of H-induced bond-angle ordering and alloy energy-band changes. While the primary effect of H in the HMCVD films is alloy band changes for $x > 0.05$, RFS films indicate comparable structural ordering effects. The effect of hydrogen on the optical gap is found to be $\sim 3\text{--}4$ times greater than that in $a\text{-Ge}_{1-x}\text{H}_x$ alloys. In addition to the ordering of bond angles about Si atoms, the Raman spectra indicate changes in the TA-TO and LA-TO ratios due to hydrogen incorporation. These are interpreted in terms of the relative reductions in the number of bond-bending modes as the concentration of triads of Si atoms decreases with hydrogen.

INTRODUCTION

Although H plays a central role in modifying the electrical and optical properties of amorphous (a -) Si and Ge, its detailed structural and bonding roles are not yet well understood.¹ The addition of H modifies the structure by changes in short- and intermediate-range order. Short-range order changes involve both a decrease in the number of first and second neighbors within the Si or Ge first-coordination sphere as well as possible changes in network bond-length and bond-angle distributions. The latter, indirect, effect may be termed changes in ordering in that it may result in alterations of the bond-angle distribution of neighboring Si atoms, for example. The introduction of H also results in changes in structural topology given the univalent nature of H. This will result in modifications of intermediate-range order and topology of the existing network. At present the evidence is not strong, however, for any appreciable intermediate-range order in $a\text{-Ge}$ or $a\text{-Si}$.^{2,3} The presence of a narrow bond-length distribution and an $\sim 10\%$ width to the bond-angle distribution does not preclude, however, structural, dynamical, and electronic-state correlations beyond second neighbors.

The presence of Si—H bonds also results in the creation of new states in the electron and phonon densities of states as well as modifications of network states either by these bonds or by short- or intermediate-range structural ordering. Photoemission studies of the valence bands have thus shown the creation of new inband electronic states associated with Si atoms bound to one of two H neighbors.⁴ Similarly, new vibrational local-mode states of H have also been observed in infrared and Raman studies of $a\text{-Si}$ and $a\text{-Ge}$ alloys with H.⁵ Evidence for the modification of the near-band-edge $a\text{-Si}(p)$ electronic states have also been observed in photoemission⁶ and optical-gap studies of $a\text{-Si}$ and $a\text{-Ge}$.^{7,8} Structural ordering by the addition of H may modify the host electron-

ic and vibrational densities of states directly, by changes in band shape and peak energies. In addition, a reduction of fluctuations in the local interaction parameters describing the electron and phonon Hamiltonians may also modify the densities of states. The observation of relatively similar Raman peak frequencies of $a\text{-Si}$ -derived vibrational bands suggests that short-range Si-Si first- and second-neighbor average force constants are not significantly modified with the addition of H. Raman-scattering studies of $a\text{-Si}_{1-x}\text{H}_x$ prepared by homogeneous chemical-vapor deposition have indicated modifications of the high-frequency TO band in $a\text{-Si}$ and $a\text{-Ge}$ due to H-induced short-range ordering.⁹ This ordering is similar to that observed in pure $a\text{-Si}$ and $a\text{-Ge}$ with increasing substrate or annealing temperature.¹⁰⁻¹²

The separation of the roles of H in modifying Si or Ge densities of electronic and vibrational states into contributions due to changing local structural order and alloy band shifts has not been extensively pursued. In addition, existing studies indicate that this separation may depend on the conditions of H incorporation, i.e., the method and details of film preparation.^{13,14} In this study we address the roles of H in structural ordering and on the electronic states by combining Raman scattering and optical-absorption measurements.

Extensive Raman scattering measurements in $a\text{-Si}$ and $a\text{-Ge}$ have shown that this method yields information on the short-range bond-angle-distribution width.¹⁵ Recent inelastic neutron studies in $a\text{-Ge}$ have confirmed that the dominant effect of changes in structural order on the phonon density of states is on modes with predominant stretching character.¹⁶ Matrix-element or coupling-parameter effects appear to less significantly change with structural order.¹⁷ In addition to separating the roles of ordering and alloy electronic states, it is useful to address the role of H concentration on specific changes in network vibrational states. It is suggested here that at large H concentrations the Raman spectra exhibit substantial

changes in their low-frequency bands that indicate a reduction in the number of low-frequency bond-bending modes associated with Si triads.

The present study considers the separate roles of H in two very different methods of $a\text{-Si}_{1-x}\text{H}_x$ alloy formation: homogeneous chemical-vapor deposition (HMCVD) and rf diode sputtering (RFS). A previous study of the former has shown the predominance of H-alloy electronic-state changes on the properties of the material.⁹ For RFS $a\text{-Si}$ the results presented here indicate a comparable role for structural ordering. Although the observed structural ordering is primarily attributed to short-range, bond-angle modifications, dynamical correlations beyond second neighbors may also influence the Raman spectra at intermediate and lower frequencies. Comparisons with $a\text{-Ge}_{1-x}\text{H}_x$ also indicate a much larger influence of H on changes in the optical gap in Si alloys.

EXPERIMENT

Films with H concentrations ranging from 0 to as large as 0.4 (HMCVD) and 0.25 (RFS) were provided by Dr. B. A. Scott of IBM Watson Laboratory and Dr. R. F. Messier of the Materials Research Laboratory at The Pennsylvania State University, respectively. Selected RFS samples with positive substrate bias, obtained from Dr. T. Moustakas of Exxon Laboratories, were found to yield similar trends to those studied here. The reactively sputtered $a\text{-Si}_{1-x}\text{H}_x$ films, prepared at Penn State, were deposited at a substrate temperature of $\sim 200^\circ\text{C}$. Argon pressure was kept constant at 15 mTorr while hydrogen partial pressure was varied between 0 and 1.3 mTorr. Hydrogen content was determined by ir absorption and ^{15}N reactions. Preparation details have been given by Ross.¹⁸ HMCVD involves decomposition of SiH_4 at a high temperature and film deposition onto substrates which were held at a lower and variable temperature. The film growth mechanism has been described by Scott *et al.*¹⁹ Infrared absorption and secondary-ion-mass spectroscopy were used to determine hydrogen content at low and high ($x \leq 0.1$) concentrations, respectively.

Figure 1 shows variation of x with hydrogen partial pressure and substrate temperature for the RF and HMCVD films, respectively. For the sputtered films the substrate temperature, which is one of the parameters influencing structural order, is kept constant. It is to be noted, however, that x is very sensitive to the partial pressure of hydrogen. Figure 1, for example, shows that x increases from 0 to 0.10 for a relatively small variation in P_{H_2} from 0 to 0.50 mT. For HMCVD films, on the other hand, it is easier to control hydrogen content at low values. Figure 1 shows that a temperature variation of 200°C is needed to increase x by 0.06 at high temperatures.

Reflectance and transmission measurements were used to determine the gap for both sets of films. Raman spectra in VH and HH configurations were recorded at room temperature using 5145-Å excitation and a Spex third-monochromator system.

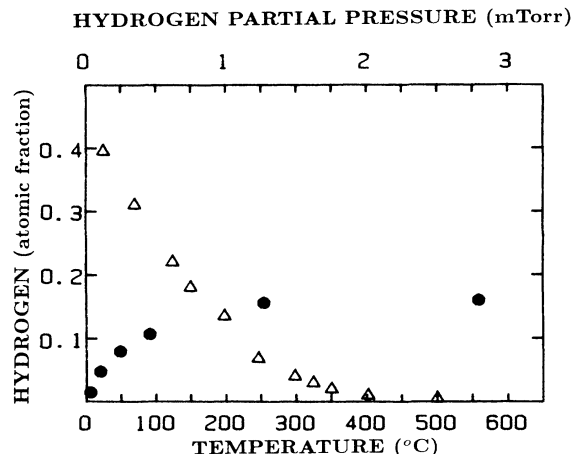


FIG. 1. Hydrogen content vs T for HMCVD (triangles) and P_{H_2} for RFS (circles) in $a\text{-Si}_{1-x}\text{H}_x$ films.

RESULTS AND DISCUSSION

Effect of hydrogen: short-range order versus alloying

Figure 2 shows area-normalized VH Raman spectra for three of the RFS $a\text{-Si}_{1-x}\text{H}_x$ films with $x = 0.02$, 0.08, and 0.16. Significant changes are seen to occur throughout the spectra, and particularly in the high-frequency "TO" region, with increase of x . Theoretical,^{20,21} as well as experimental^{5,22} Raman studies have shown that Δ , the TO-peak width, is a sensitive measure of short-range structural order, being approximately proportional to the $\Delta\theta$, the bond-angle distribution width.

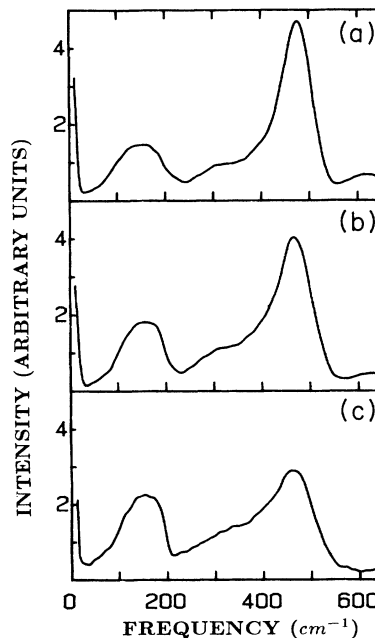


FIG. 2. VH Raman spectra for three RFS $a\text{-Si}_{1-x}\text{H}_x$ films (a) $x = 0.16$, (b) 0.08, and (c) 0.02. Spectra are area normalized.

Since x is the only variable for the films of Fig. 2, the decrease in Δ suggests that hydrogen improves the structural order in these films. The maximum amount of hydrogen that can be incorporated into the RFS films depends on T_S and P_{Ar} . For the present set of films made at $T_S \approx 200^\circ\text{C}$ and $P_{Ar} = 15$ mTorr, x had a maximum value of ~ 0.16 . Raman measurements were made on additional films sputtered at lower temperatures with hydrogen content in the range 0.20–0.25. There was no observable decrease in Δ for films with $x > 0.16$.

Figure 3 compares the Raman spectra for two of the HMCVD samples with $x = 0.01$ and 0.32 and the RFS sample of Fig. 2 with $x = 0.02$. There are clearly large differences between the two films with low hydrogen content. This is to be expected since the HMCVD film is made at $\sim 500^\circ\text{C}$ while the sputtered film is made under conditions that produce more disorder, including lower temperature and more film bombardment. At low hydrogen concentrations, with increasing x (< 0.06), a small but reproducible and systematic decrease is observed in the "TO"-peak width of the HMCVD films. As mentioned earlier, in HMCVD films the increase in hydrogen content is obtained through a decrease in the substrate temperature. A temperature decrease by itself would lead to more-disordered films. Since this is contrary to what is observed, it is clear that hydrogen incorporation is improving the structural order in HMCVD as well as RFS films. For $x > 0.13$ there are no observable changes in the "TO"-peak width for the HMCVD films. This may, in part, be due to the opposing effects of lower temperature and higher hydrogen content. However, a similar result is observed for the RFS films for which temperature is not a

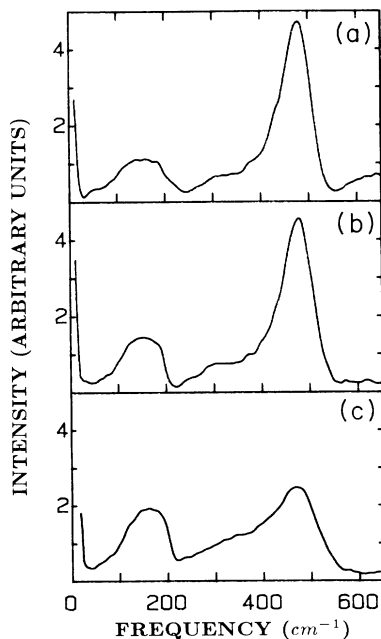


FIG. 3. VH Raman spectra for three $a\text{-Si}_{1-x}\text{H}_x$ films with (a) $x = 0.32$ and (b) 0.01 , prepared by HMCVD; (c) $x = 0.02$, prepared by rf sputtering. Spectra are area normalized.

factor. The result that hydrogen does not continually improve structural order thus implies that there is a minimum amount of bond-angle disorder required for the sample to remain amorphous. This observation is consistent with theoretical studies of structural relaxation²³ and Raman studies on liquid quenched $a\text{-Si}$,²⁴ and provides a basis for separating the effects of hydrogen on network ordering and alloying.

Figure 4 shows the variation of E_O , the optical gap, with x for both HMCVD and RFS films. It can be seen here that E_O is lower for the RFS films at low x but increases more rapidly with x . The reasons for this becomes clear on comparing variations in structural order and E_O for the two sets of films.

Previous studies in unhydrogenated $a\text{-Si}$ samples prepared by rf sputtering at 7 mTorr Ar pressure and variable substrate temperature showed a strong correlation between Δ^{-1} and the optical gap.¹⁰ Figure 5 presents a comparison of the variation of Δ^{-1} with optical gap for these and the hydrogenated samples. For HMCVD films with low hydrogen content, the approximately linear correlation between Δ^{-1} and E_O is seen to be similar to that observed for the unhydrogenated films. At higher concentrations, however, the gap for HMCVD films is seen to increase while the structural order parameter is relatively constant. This suggests that for small values of x the gap increases due to predominant changes in structural order while at higher concentrations alloying effects become the major factor.

There is a correlation between Δ^{-1} and E_O for the RFS $a\text{-Si}_{1-x}\text{H}_x$ films as well. However, Fig. 5 shows that for a comparable value of Δ^{-1} the hydrogenated films have a larger optical gap than the unhydrogenated films. In addition, the difference is seen to increase with hydrogen content. It is also seen that at lower hydrogen concentrations changes in Δ^{-1} with x are comparable for both HMCVD and RFS films. The increase in optical gap, however, is much higher for the sputtered films. These differences suggest that E_O increases in the reactively sputtered material from alloying effects, as well as improved order. While structural order influences the gap through sharpening the valence-band and possibly

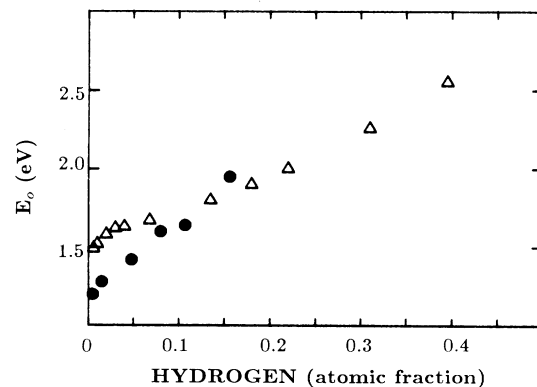


FIG. 4. E_O vs hydrogen content for HMCVD (triangles) and RFS (circles) films.

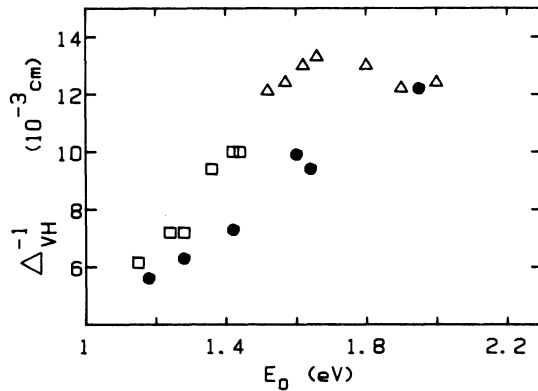


FIG. 5. Δ^{-1} vs E_0 for pure and hydrogenated *a*-Si films. Data for unhydrogenated RFS films (squares) and HMCVD (triangles) and RFS (circles) a -Si $_{1-x}$ H $_x$ films are shown.

conduction-band edges, alloying leads to large overall changes in the bands.

Photoemission and inverse photoemission studies show significant changes in the valence-band and near the conduction-band edge as a function of hydrogen content.^{6,25} Modification of optical properties due to alloying effects can also be independently confirmed by spectroscopic ellipsometric measurements of the peak in $\epsilon_2(\omega)$, the imaginary part of the dielectric function. For the hydrogenated RFS films in the present study such measurements show significant changes in the position and intensity of the ϵ_2 peak with x .²⁶ No $\epsilon_2(\omega)$ measurements are available for the HMCVD films to determine whether the increase in gap at low x is solely due to improved structural order. Ellipsometry results for the sputtered unhydrogenated films of Fig. 5 suggest that the observed increase in gap is due to improved structural order. Since the correlation between Δ^{-1} and E_0 is very similar for the low-hydrogen HMCVD and the unhydrogenated RFS films it is reasonable to assume that the changes in E_0 for the CVD films with $x < 0.06$ are primarily due to improved order.

Decomposition of the optical-gap variation

The changes in the optical gap in Fig. 4 for rf-sputtered films may be decomposed into two terms whose total is

$$(dE_0/dc_H)_t = (dE_0/dc_H)_{\text{alloy}} + (dE_0/dc_H)_{\text{order}}. \quad (1)$$

The first term $(dE_0/dc_H)_{\text{alloy}}$ considers changes in the electronic energy states for fixed local order of the first-neighbor Si atoms bonded to a hydrogenated Si. The term $(dE_0/dc_H)_{\text{order}}$ considers the change in this local order due to the presence of H-Si bonding. These terms include multiple H bonding due to Si-H $_n$ ($n = 1, 2, 3$) formation. The alloy term is associated with changes in the gap due to modifications of the valence and conduction bands of *a*-Si as H is added. Photoemission studies have shown that this is primarily due to the formation of deep-lying Si(*p*)-H(*s*) states within the valence band and simultaneous erosion of the Si(*p*) near-edge states.⁶ The order

term is a consequence of interactions between the Si-H orbitals and neighboring Si-Si orbitals that result in a lower bond-angle deviation than would be present when $c_H = 0$.

A quantitative estimate of these separate contributions may be obtained from the TO Raman width variation with and without H present. For fixed Δ , corresponding to constant order, the changes in E_0 due to H alone may be obtained from Fig. 5. The results, shown in Fig. 6, indicate an approximately linear dependence of $(dE_0/dc_H)_{\text{alloy}} = 2.3 \times 10^{-2}$ eV/at. % H. As $(dE_0/dc_H)_t = 4.7 \times 10^{-2}$ eV/at. % H, the disorder term has a comparable contribution to that of alloying.

A similar decomposition of dE_0/dc_H for HMCVD films is also shown in Fig. 6. For these films, for $c_H \leq 5\%$, the Raman width is approximately constant so that $(dE_0/dc_H)_t \approx (dE_0/dc_H)_{\text{alloy}}$. For this composition range Fig. 6 indicates that $(dE_0/dc_H)_{\text{alloy}} = 2.3 \times 10^{-2}$ eV/at. % H is essentially the same as that for the RFS films. A similar variation of the $(dE_0/dc_H)_t$ has been noted for RFS films prepared at high-Ar pressures of 30 mTorr and at high sputtering powers.²⁷ It has been noted that under similar high-Ar-pressure conditions the resulting films exhibit predominantly the 2000-cm⁻¹ infrared absorption band associated with monohydride Si-H bond stretching. The present RFS films as well as the HMCVD films exhibit substantial dihydride and polyhydride absorption, as seen in their 2100-cm⁻¹ absorption band.²⁸ This tentatively suggests that $(dE_0/dc_H)_t$ may not be highly sensitive to multiple H bonding. Other studies of *a*-Si $_{1-x}$ H $_x$ alloys by Matsuda in plasma-deposited films indicate a value for $(dE_0/dc_H)_t$ consistent with this.²⁹ In these films the alloys contribution is estimated to be constant. Other measurements of higher-temperature films yield a somewhat lower value for $(dE_0/dc_H)_t$.

The effect of H on local order may be further separately analyzed into the effect of H on bond-angle distribution width. As

$$(dE_0/dc_H)_{\text{order}} = (dE_0/d\Delta\theta)(d\Delta\theta/dc_H), \quad (2)$$

the effect of H on bond-angle width, $(d\Delta\theta/dc_H)$, may be estimated if $(dE_0/d\Delta\theta)$ is known. In *a*-Ge films radial-

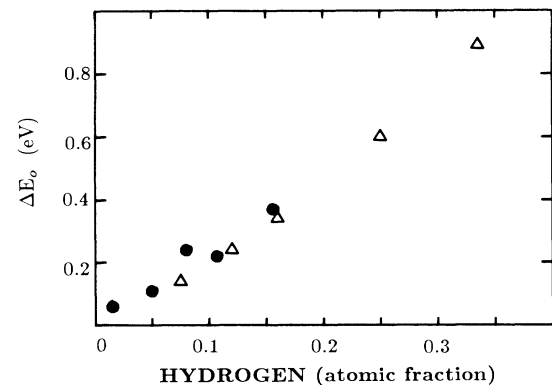


FIG. 6. Changes in E_0 vs hydrogen content for HMCVD (triangles) and RFS (circles) films.

distribution-function and optical-gap studies¹¹ indicate that $(dE_O/d\Delta\theta) \approx 0.35$ eV/deg. Although quantitative information on bond-angle variations in *a*-Si does not exist, the similar variation of the optical gap with Raman width to that of *a*-Ge suggests a comparable value for $dE_O/d\Delta\theta$.²⁷ This yields a value of $(d\Delta\theta/dc_H) = 6.6 \times 10^{-2}$ deg/at. % H in the RFS *a*-Si_{1-x}H_x films studied here.

In the above analysis the Raman spectral changes with c_H clearly imply modifications of local structural order. It is natural to relate changes in the optical gap to structural order. This is supported by experimental studies^{5,7,8} in *a*-Si and *a*-Ge and by recent theoretical³⁰ studies relating E_O to bond-angle disorder. It has alternatively been suggested⁴ that the larger dependence of $E_O(c_H)$ in more-disordered, sputtered films is due to the contribution of defect states to the absorption coefficient. The presence of defect states associated, for example, with dangling bonds, may result in modifications of the exponential Urbach tails. The high values of absorption coefficient, exceeding 10^4 cm⁻¹, employed to determine the present optical gaps are expected to be less significantly modified by defects for dense, low-pressure sputtered films. In contrast, the greater bond-angle disorder in these films is anticipated to result in a larger tailing of the conduction and valence bands. As such, the significant change of the optical gap in these films may be more reasonably attributed to the reduction of these tail states with bond-angle ordering.

Comparison with *a*-Ge_{1-x}H_x

It is interesting to compare the role of H on the optical gap in *a*-Si_{1-x}H_x and *a*-Ge_{1-x}H_x. Optical-gap and Urbach tail measurements in low-pressure rf-sputtered *a*-Ge_{1-x}H_x alloys have been employed to separate the role of alloying and structural disorder.³¹ Estimates of the structural order contribution were obtained for one set of films of constant Urbach slope. Although it has been shown in *a*-P films that structural order may not simply be related to this parameter,³² correlations between the Urbach slope and the TO Raman width have been observed in *a*-Ge films for relatively fixed plasma conditions.³³ Table I indicates the relative contributions of al-

TABLE I. Contributions of H to the gap variations in RFS *a*-Si_{1-x}H_x and *a*-Ge_{1-x}H_x

	<i>a</i> -Si _{1-x} H _x (10 ⁻² eV/at. % H)	<i>a</i> -Ge _{1-x} H _x (10 ⁻² eV/at. % H)	Ratio
$(dE_O/dc_H)^a$	4.7	1.44	3.26
$(dE_O/dc_H)^b$	2.4	0.62	3.87
$(dE_O/dc_H)^c$	2.3	0.82	2.8
$\frac{(dE_O/dc_H)^b}{(dE_O/dc_H)^c}$	1.04	0.76	1.38

^aTotal.

^bAlloy.

^cStructural order.

loying and disorder and their total for Si and Ge alloys with H. The results indicate an ~3–4-factor larger influence of H in the Si-based alloy than that of Ge. For *a*-Ge_{1-x}H_x the ordering contribution is found to be ~30% greater than that of alloying, whereas these are similar in *a*-Si_{1-x}H_x rf-sputtered alloys.

The reduced effect of H in the Ge-based alloys indicates within the tight-binding model a substantial reduction of the V_1 and V_2 interaction matrix elements between Ge (p or sp^3) and H(s) orbitals. The larger binding energy of H(s) and Si(p) bands observed in x-ray photoemission spectroscopy (XPS) studies is consistent with the larger effect observed in Si. Further theoretical and experimental studies of changes in the near gap Ge(p) states with H concentration would be useful to confirm this effect.

Effect of hydrogen on the *a*-Si network

In *a*-Si (and *a*-Ge) the high-frequency "TO" peak at ~475 cm⁻¹ in the phonon and Raman spectra has been attributed to short-range, bond-stretching vibrations and the "TA" peak at ~160 cm⁻¹ to bond-bending modes involving triads of Si atoms. The relative area of the TA and TO bands thus provides information on the role of H on bending and stretching modes of Si. For simplicity, given that the LA band overlaps the TO band at intermediate frequencies, the TO band is estimated from the product $\Delta \times I_{TO}$. As the TA-band shape is essentially constant with [H], the ratio $I_{TA}/I_{TO}\Delta$ provides a measure of changes in the bending versus stretching modes. This is shown in Fig. 7 for both HMCVD and RFS alloy films. The general trend of a decrease in the bond-bending Si modes with increasing [H] is seen to be similar for both film types. The magnitude of the decline is substantial, indicating a reduction of ~30% in this ratio at high values of [H]. Qualitatively this decrease can be understood as a consequence of H atoms more rapidly decreasing the number of bending modes relative to stretching modes. The former require at least a triad of Si atoms, while the latter involve a pair of atoms. For example, the replacement of one of the four neighbors of a Si atom by a

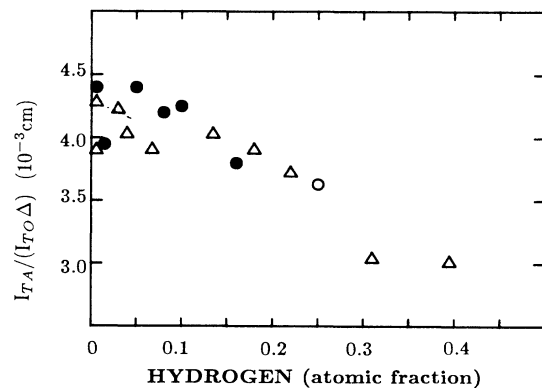


FIG. 7. $I_{TA}/I_{TO}\Delta$ vs hydrogen content for HMCVD (triangles) and RFS (circles) films. ●, $P_{Ar} = 15$ mTorr; ○, $P_{Ar} = 30$ mTorr.

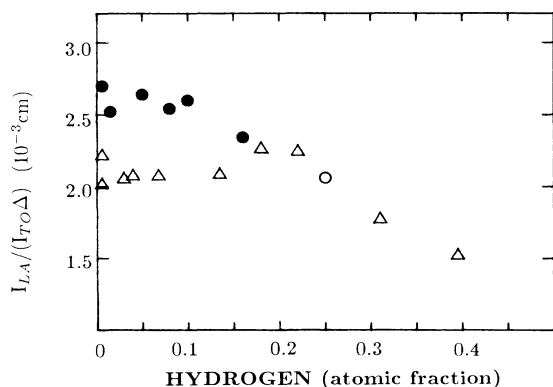


FIG. 8. $I_{LA}/I_{TO}\Delta$ vs hydrogen content for HMCVD (triangles) and RFS (circles) films. ●, $P_{Ar}=15$ mTorr; ○, $P_{Ar}=30$ mTorr.

H atom will decrease the number of stretching modes of a tetrahedral unit from four to three, while the bending modes decline from six to three. For a "dihydride"-type environment with two H atoms, the number of Si triads of a tetrahedral group becomes one, while the number of stretching modes is two. A more semiquantitative estimate of the role of H may be obtained for a simple statistical model that considers the number of such pairs and triplets of Si atoms. Such a model yields a decline of the relative contribution to the TA band qualitatively consistent with the trends of Fig. 7. A more detailed model that includes preferential monohydride and dihydride environments and excludes SiH_3 and SiH_4 configurations is needed, however, for comparison with experiment.

A similar comparison of the LA-band intensity to that of the TO band is shown in Fig. 8. Here the ratio $I_{LA}/I_{TO}\Delta$ exhibits noticeably different behavior for the RFS and HMCVD samples for $x \lesssim 0.15$. Both film types indicate a nearly constant relative LA intensity in this range, although the RFS films exhibit an ~ 20 – 25% larger ratio. This difference may, in part, be due to the TO band significantly overlapping the LA band in more-disordered RFS films producing uncertainties in Δ and I_{LA} . For $x \gtrsim 0.2$ the decrease in the LA-band intensity of Fig. 8 parallels that of Fig. 7 for the TA intensity. This suggests that for large values of [H] a similar mechanism may be reducing the low- and intermediate-frequency band intensities.

Predicting qualitative variations in the LA intensity is at present difficult as the origins of this band are unclear. A recent study by Nichols *et al.*³⁴ suggests that the LA feature is due to bending-rocking modes involving four Si atoms. Bermejo *et al.*,³⁵ on the other hand, have attributed this to rings. Lattice dynamical calculations for *a*-Ge and *a*-Si suggest that closed rings contribute to somewhat sharper structure than that seen in the LA region.³⁶ A dependency of the LA intensity on the bond-angle distribution has also been noted. The similar decrease in the

TA and LA bands at larger values of [H] suggest that the LA band is not due to rings alone, but suggests an influence of changes in the number of Si-host bond angles. The attribution by Nichols *et al.*³⁴ of the LA modes to bond-bending-rocking motions involving clusters of four Si atoms implies the possible importance of a joint bond-angle distribution. Further theoretical analysis of this spectral region is clearly required to determine to what extent changes in individual or neighboring bond-angle distributions may influence the Raman intensity.

Summary

The role of hydrogen in modifying the optical and vibrational properties of *a*- $\text{Si}_{1-x}\text{H}_x$ has been studied for homogeneous chemical-vapor-deposited and rf-sputtered films. The effects are seen to be very different for the two methods of sample preparation. Increasing the hydrogen content in the present initially highly disordered rf-sputtered samples is seen from the TO band to improve the short-range structural order considerably. Maximum structural order is obtained in these films with the incorporation of ~ 16 at. % hydrogen. For HMCVD films, which are more highly ordered initially, hydrogen influences short-range order only at low concentrations. A comparison of the correlation between Δ^{-1} , the structural order parameter, and E_0 , the optical gap, for hydrogenated and unhydrogenated *a*-Si films permits a first-order separation of the effects of hydrogen into those due to structural order and alloy electronic states. The latter effect is seen in RFS films at all H concentrations and in the HMCVD films at $x \gtrsim 0.06$. The change in the optical gap due to alloy electronic-state effects is seen to be larger for *a*- $\text{Si}_{1-x}\text{H}_x$ than for *a*- $\text{Ge}_{1-x}\text{H}_x$ films. Variations in low-frequency features in the Raman spectra with increasing x suggest that hydrogen, in addition to improving short-range order, modifies network bonding and topology as well. Theoretical analysis of the TA and LA Raman bands with [H] is required, however, to more precisely determine the separate role of dynamical correlations beyond second-bonded neighbors. The more rapid decrease in the spectral ratios of Figs. 7 and 8 with [H] $\gtrsim 20$ at. % suggests additional structural changes. As the TO width is approximately constant for the HMCVD spectra, this suggests that these changes are topological in character. This may be due to a substantial increase in the number of dihydride environments along with their increased effect on Si-network termination.

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