Infrared study of the Si-H stretching band in a-SiC:H

R. R. Koropecki, F. Alvarez, and R. Arce

Articles you may be interested in

Infrared study of the Si-H stretching band in a-SiC:H

R. R. Koropecki and F. Alvarez
Instututo de Física, Universidade Estadual de Campinas, C.P. 6165, Campinas S.P. 13081, Brazil

R. Arce
Instituto Para el Desarrollo de la Industria Química, Guemes 3450, 3000 Santa Fe, Argentina

Amorphous silicon carbide (a-Si$_{1-x}$C$_x$:H) samples having $x \leqslant 0.4$ were studied by infrared and visible spectroscopy. Treatment by factor analysis of the 2000–2100 cm^{-1} absorption band of the spectra allows us to interpret this particular vibrational mode in terms of only two independent contributions. The analysis shows that polarization inductive shifting is not significant. An IR study of the evolution of this band during oxidation of porous samples was also performed. All the experimental evidence indicates that the growth of free volumes induced by the presence of carbon plays the most important role in the behavior of the 2000–2100 cm^{-1} band upon stoichiometric variations.

I. INTRODUCTION

In a-Si:H and a-SiC:H the existence of two peaks (or more precisely one peak and one shoulder) in the 2000–2100 cm^{-1} range of the IR spectrum is well known. Although the whole band is generally attributed to stretching modes of Si-H bonds, the detailed assignment of the modes is still controversial, and there are two conflicting interpretations. According to one of these, the 2000 cm^{-1} peak corresponds to the stretching mode of Si-H bonds in the bulk.[1] This interpretation comes from infrared (IR) spectra of molecules of organosilicons, which show a vibration corresponding to the stretching mode of Si-H bond in mono, di, and trihydride groups between 2208 and 2050 cm^{-1}.[2] The observed shift to 2000 cm^{-1} of a-Si:H is attributed to a depolarizing effect produced by the vibrating dipole in the solid. In this model the interpretation of the 2080–2100 cm^{-1} feature is not so clear, however. Some authors attribute this mode to the presence of SiH$_2$ (dihidride) group,[3] while other authors[1,4] ascribe this mode to the contribution of two types of vibrations: one of them due to multiply hydrogenated groups like SiH$_2$ and SiH$_3$ and another due to the presence of Si-H bonds on the inner surface of microvoids (diameter $\geqslant 2$ Å). The first of these contributions is accompanied by bending modes around 900 cm^{-1}, whereas the second is not.

The other point of view,[5] however, challenges the above interpretation by suggesting that the splitting of the stretching band is exclusively due to structural effects. In this alternative model, the difference between the 2000 cm^{-1} and the 2100 cm^{-1} peaks is attributed to environmental effects produced by the existence of voids. In other words, the 2000 cm^{-1} mode corresponds to SiH in an amorphous network, and the 2100 cm^{-1} mode corresponds to SiH or SiH$_2$ in the inner surface of voids.

In the case of a-Si$_{1-x}$C$_x$:H, a global shift takes place in the stretching band of the Si-H vibration as the compositional parameter x increases. Lukovsky[6,7] assigns this shifting to modifications in the Si-H bond length due to the greater electronegativity of carbon atoms neighbors relative to silicon. In a similar way, Wieder et al.[8] attribute the shifting to a variation of polarizability due to the presence of neighboring carbon atoms. If no nucleations or preferential chemical order are present, these models predict a linear behavior of the shifting as a function of carbon content, x. Beyer and Mell,[9] however, find experimental evidence that the shifting is not linear for samples having low carbon content.

Mahan et al.[10] claim that the global frequency variation is due to the appearance of a "shifted" mode at ~ 2100 cm^{-1}, to the detriment of the 2000 cm^{-1} peak. They associate the shifted mode partially with the presence of SiH$_2$ and mainly with the existence of microvoids which correlate with the carbon content. Recently, small angle x-ray scattering results have been reported which support this hypothesis, showing that the microvoids number density increases when the carbon content increases.[11]

In this work, we report a systematic study of the influence of the carbon content ($x \leqslant 0.4$) on the 2000–2100 cm^{-1} absorption band. The factor analysis method[12] was applied to study the evolution of this absorption band and the existence of two phases related to the Si-H bonds environments was deduced. Also, the analysis showed that polarization inductive shifting is not significant in the studied range of x.

These conclusions, together with results from the evolution of the stretching mode during the oxidation of a-SiC:H porous samples, suggest that the most important effect on the behavior of the 2000–2100 cm^{-1} band is that of the growth of free volumes or voids induced by the presence of carbon in the material. The spectra vary continuously as would a linear combination of the two phases already present in pure a-Si:H, in agreement both with the Wagner-Beyer model[5] and the Mahan et al. results.[10]

II. EXPERIMENTAL DETAILS

The samples were prepared by rf glow discharge decomposition of gaseous mixtures of methane and silane. A parallel plate capacitively coupled reactor was used. In or-

der to get films with different carbon content, the gas mixing ratio $y = [CH_4]/[CH_4 + SiH_4]$ was varied from 0 to 0.87. For all the samples, the substrate temperature was 260 °C, the deposition chamber pressure 50 Pa., the total flow rate 10 sccm and the rf power density ~ 70 mW/cm^2. Film thicknesses were between 0.4 and 0.6 μm in all the samples.

Of the nine samples, two correspond to $y = 0.0$ (pure a-Si:H), and the others with the gas mixing ratio $y = 0.12$, 0.30, 0.40, 0.50, 0.60, 0.71, and 0.87. In all cases a variety of substrates were used to allow different measurements: high resistivity polycrystalline silicon for the IR analysis, Corning glass 7059 for the thickness and optical constants measurement and either stainless steel or crystalline silicon for Auger and XPS measurements of the carbon content. The IR spectra were taken with a Perkin Elmer model 580B double beam spectrophotometer connected to a PE3500 data station. The data were processed in a VAX 780/11 computer. All the measurements were performed using a bare substrate as a reference. The UV-Vis-NIR spectra were taken in the 350–2500 nm range using a Perkin Elmer 330 double beam spectrophotometer. An optical condenser was used in order to obtain a $\sim 0.7 \times 1$ mm^2 spot in the spectrometer beam. The optical constants were calculated following the procedure of Swanepoel.[13] To measure the compositional parameter x, results from the Auger, XPS and optical constants were used.

Sputter etching was performed to clean the sample surfaces before the Auger and XPS measurements. The etching was maintained until a uniform carbon signal was obtained, an indication of steady state in the preferential sputtering process. Then the C atomic concentration was derived taking into account the sputtering yield of Si and C. The results obtained by this method were compared with those obtained cleaning the samples with HF following the method of Y. Katayama et al.[14]

Finally the carbon content parameter x was also inferred using the correspondence between the refractive index n and x.[15,16]

The results for the compositional parameter x versus gas mixing ratio y are shown in Fig. 1, which shows that all these techniques give essentially the same results.

III. PRINCIPAL FACTOR ANALYSIS

In order to interpret the data, we use the Principal Factor Analysis (PFA) method. The PFA method is well described in the literature,[12] and we only describe it briefly here. The validity of this method follows from that of our assumption that the measured spectrum of any sample is a unique linear combination of the spectra resulting from n fundamental vibrations, each of which arises from a different physical environment which does not change from sample to sample. For measured spectrum $A_k(\lambda_i)$ (the absorbance of the kth sample at wavelength λ_i) we have:

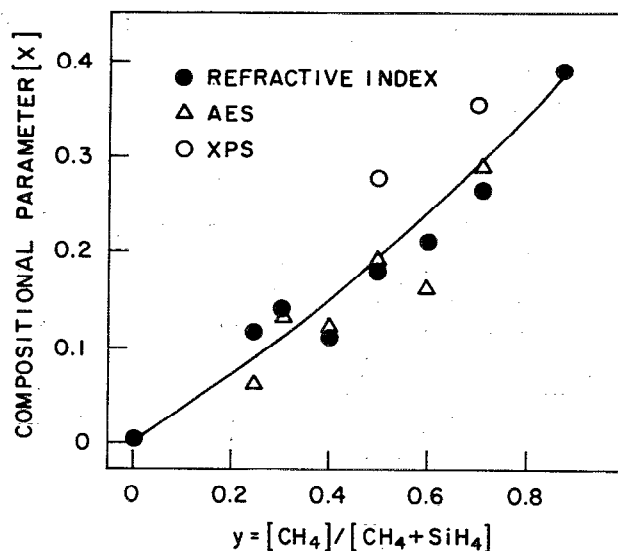$$A_k(\lambda_i) = \sum_{j=1}^{n} c_{kj} f_j(\lambda_i),$$ (1)

FIG. 1. Compositional parameter x as a function of the gaseous ratio mixture y measured by AES ($\triangle$), XPS ($\bigcirc$), inferred from the refractive index (Refs. 14 and 15) ($\bullet$). The solid line is to aid the eyes.

where $f_j(\lambda_i)$ is the unknown spectrum of fundamental vibration j at wavelength λ_i. c_{kj} is its concentration in sample k and n denotes the number of fundamental spectra. Defining "data" and "fundamental" matrices S and F by $S_{ki} = A_k(\lambda_i)$, and $F_{ji} = f_j(\lambda_i)$, respectively, we note that Eq. (1) can be viewed as one representation of S in a vector space. To be more specific, for l λ's and t samples, there are an infinite number of $t \times n$ matrices K and $n \times l$ matrices σ such that

$$S = K\sigma.$$ (2)

By hypothesis, the only physically meaningful such decomposition of S is that in Eq. (1), which remains to be determined.

The notion of an abstract vector space implies the existence of a set of basis vectors σ_i forming the columns of matrix σ in Eq. (2). One such set is furnished[17] by the eigenvectors Q_i of the Hermitian $t \times t$ covariance matrix $Z \equiv S^T S$ (S^T is the transpose matrix of S), such that

$$ZQ_i = \lambda_i Q_i.$$ (3)

Note that, from Eq. (1), there would be exactly n nonzero eigenvalues λ were there no experimental error and that t must be larger than n. The presence of error introduces unphysical additional eigenvalues. We describe below our criteria for eliminating these unphysical quantities.

A convenient form of Eq. (2) is:

$$\{K\}\sigma = \{SQ\}Q^T = \{SQ\}Q^{-1},$$ (4)

where the ith column of Q is Q_i. According to our criteria, we form matrix $Q^\pm$ from the n principal eigenvectors such that:

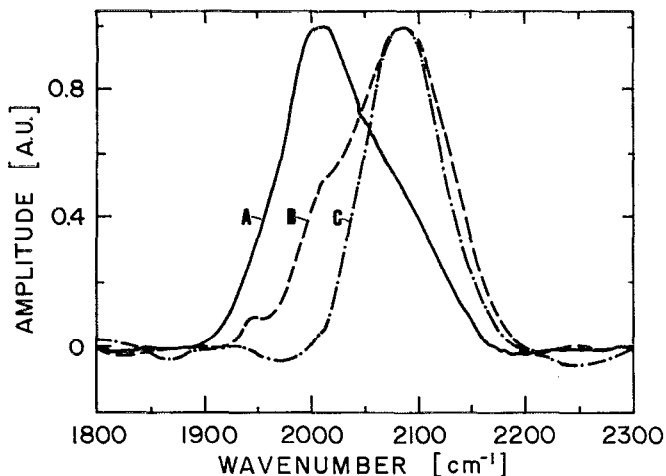$$S^\pm \equiv \{K^\pm\}[\sigma]^\pm \equiv \{SQ^\pm\}[Q^{\pm T}] \cong S.$$ (5)

FIG. 2. Three spectra of a-Si$_{1-x}$C$_x$:H samples normalized to the maximum height A: $x = 0$; B: $x = 0.12$; C: $x = 0.39$.

j	λ_j	FI ($\times 10^{-4}$)	RE
1	162.38	16.50	0.105
2	25.38	5.32	0.026
3	0.76	5.37	0.019
4	0.34	5.93	0.014
5	0.12	8.09	0.012
6	0.10	11.60	0.010
7	0.04	22.80	0.009
8	0.03	84.20	0.008

$S^{\pm}$ has less experimental error than the original data in S, even though the quantities in Eq. (5) are abstract. Physically meaningful values are derived from the target transformation method, which exploits physical hypothesis by assuming a transformation T such that Eq. (1) becomes:

$$S = \{C\}\{F\} = \{K^{\pm}T\}[T^{-1}\sigma^{\pm}]. \qquad (6)$$

The expression for transformation T is derived through least squares fitting to measured spectra whose decompositions are assumed known.

It is necessary to know the values of the concentrations c_{kj} for at least $n - 1$ components for some spectra, according to the physical hypothesis tested.[12] Application of T produces predicted values of c_{kj} ($k = 1,2$) in agreement with the target. Because of the vector space formulation PFA automatically performs the following steps: (1) it determines the F_{ji} for amorphous Si, and (2) derives the c_{kj} for the other samples from knowledge of the F_{ji}.

In Sec. IV we perform the abstract factor analysis determining the number of independent components. In Sec. V we discuss possible hypotheses to explain the existence of two independent components, and perform the target transformation using a model in accord with one of the hypothesis and in Sec. VI we present results of an oxidation experiment which support the validity of the hypothesis made for the PFA target transformation, discarding the other ones.

IV. ABSTRACT FACTOR ANALYSIS

Figure 2 shows the behavior of the spectra of the 1600–2600 cm^{-1} Si-H stretching mode for three samples with different carbon contents. The rest of the spectra are similar and are not displayed.

The data matrix S was constructed with the absorbance spectra of the nine samples, for 300 wavelengths between 1800 and 2300 cm^{-1} seven of them having dif-

ferent carbon content and two with $x = 0$. As it is explained later on, these last are necessary for accuracy of error estimation.

Results of factor analysis are summarized in Table I, where we show the eigenvalues λ_j of the covariance matrix, the real error RE, and the factor indicator function FI. RE is a measure of the difference between the "pure" data and the raw experimental data defined as:[12]

$$RE(i) = \left(\sum_{j=i+1}^{l} \lambda_j \right)^{1/2} \bigg/ \left(t(l-n) \right)^{1/2}. \qquad (7)$$

Here t is the number of rows in the data matrix (i.e., 9 samples), i is the number of eigenvectors considered for the data reproduction, and l is the number of channels, i.e., the number of columns in the data matrix (i.e., 300 columns). The factor indicator function FI was empirically defined by Malinowski and Howery[12] as:

$$FI(i) = RE/(l - i)^2. \qquad (8)$$

It is expected[12] that, if the experimental error is uniformly distributed during the measurement, the FI function will present a minimum for i equal to the true number of significant factors n.

In order to get the number of significant factors, we take into account four different criteria. The first criterion considers that the number of independent components is equal to the minimum number of eigenvalues which makes the RE lower than the experimental error of the data matrix S. To estimate the experimental error, we performed factor analysis for two samples of pure a-Si:H prepared in nominally identical conditions. In this case, there is only one independent component and the experimental error coincides with the RE obtained using only one eigenvector to reproduce the data matrix. The experimental error turns out to be 2.5×10^{-2} and comparing it with the RE of Table I, we observe that including only two components reduces RE to less than or approximately equal to the experimental error.

The second criterion establishes that the FI function presents a local minimum when the number of eigenvalues considered coincides with the true number of significant factors.[12] From Table I, it can be seen that this criterion leads to the existence of two factors.
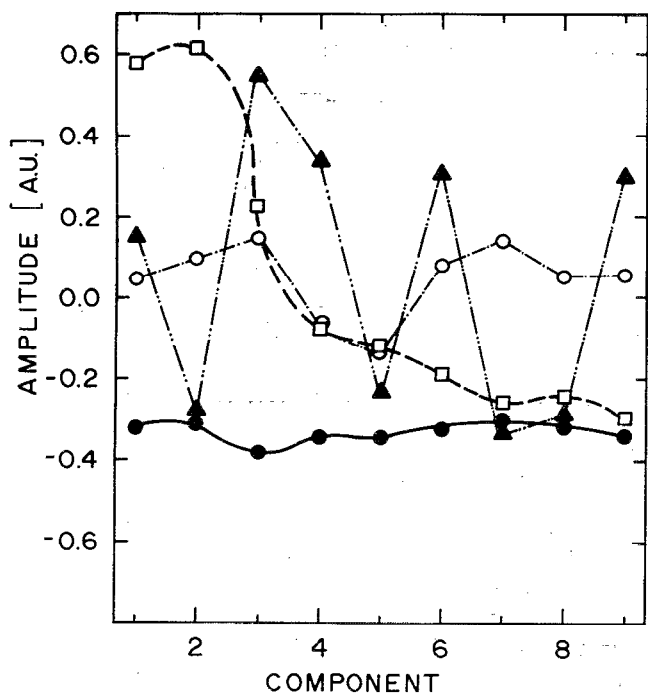
FIG. 3. Plot of the components of the 1st to 4th eigenvectors obtained from the factor analysis.

The third criterion involves the study of the plots of the eigenvector Q_i of matrix Z. In Fig. 3 it can be seen that the third and following components give very scattered plots. This scattering was attributed[18] to the statistical indistinguishability of the eigenvalues from zero.

Finally, the statistical test of the chi-squared function[19] resulted in two independent components.

Therefore, all our criteria agree in giving two significant factors for the Si-H absorption band. These results imply that there is no significant inductive shifting of any portion of the studied spectrum, as a function of x. Were such the case, we would have found a number of components equal to the number of spectra considered because the shifted modes are independent of each other. To summarize, within the experimental errors the factor analysis until this point indicates the existence of only two different components.

The existence of two factors imply limitations to the nature of the structure of the material, allowing us to establish some conclusions, even though the two physically significant spectra remain unknown as yet. As is well known, the silicon carbide alloy could have a strong polar structure,[6,7] which could account for the shifting of the stretching band through the dependence of frequencies on the bonding chemistry of the Si-H oscillators next nearest neighbors,[6] and, less strongly, by effects produced by the host.[7] In other words, the effect of electronegativity of carbon atoms (or radicals involving carbon atoms), which is larger than those of the substituted silicon atoms, produces an inductive shifting of the vibrational peak. Both the Lukovsky[6,7] and the Wieder et al.[9] models attribute the frequency shift entirely to inductive effects. Both models,

which consider that no nucleation or chemical order is present in the structure, lead to a linear behavior of the frequency shift as a function of the carbon content x. In such models the PFA would lead to a number of components equal to the number of spectra of samples with different x. Three possibilities remain:

(a) The shift is due to inductive effects but nucleation takes place. So independent of the carbon content, the Si-H bonds have only two alternative environments: the a-Si:H environment or the carbon altered environment.

(b) When carbon is present, the hydrogen prefers sites which have a definite type of environment during the deposition process, creating two phases.

(c) Inductive shifting due to substituting carbon is not significant and the two fundamental spectra are associated with another phenomenon.

Taking into account the Wagner-Beyer model[5] which suggests that the bands in ~2000 and ~2080 cm^{-1} in pure a-Si:H are exclusively due to structural differences in the environment of the Si-H oscillators, and the Mahan et al.[10] results for low carbon content a-SiC:H, we formulate the following model to test hypothesis (c):

In both pure a-Si:H and a-Si$_{1-x}$C$_x$:H with x up to ~0.4, the SiH and the SiH$_2$ oscillators have two different environments. The differences are exclusively structural: the band at 2000 cm^{-1} corresponds to modes related with SiH bonds in the bulk, whereas the mode in 2080 cm^{-1} corresponds to the stretching vibration of Si-H bonds or SiH$_2$ groups on the inner surface of voids or free volumes. The only effect of the carbon content increment is to increase the fraction of free volume in the material, and no significant inductive effect take place.

It remains to identify the physically significant components, compatible with the formulated hypothesis. As we have shown in Sec. III, from the point of view of the factor analysis method, the target transformation provides a way to reach this goal. It is necessary to know the weight of at least $n-1$ components for some spectra in order to perform the target transformation[12] (these weights are the so-called "target values"). Taking into account our hypothesis, the spectrum of the pure a-Si:H was decomposed into two Gaussians, which were assumed as the fundamental spectra for PFA. After this procedure, it was found that there is a 58% contribution of the Gaussian curve corresponding to the 2000 cm^{-1} vibration frequency, related to the total area of the whole band. Therefore a value of 58% was taken as the target value for the pure a-Si:H samples. The resulting two components are illustrated in Fig. 4 and their relative weights in all the spectra in Fig. 5. These components deviate very little from the Gaussians used in the decomposition, indicating the consistence of the procedure. In order to reconstruct each one of the measured spectra it is necessary to perform linear combinations with both components, i.e.:

$$S(x) = c_1(x) \times f_1 + c_2(x) \times f_2, \qquad (9)$$

where $S(x)$ is the spectrum to be reconstructed, f_1 and f_2 are the first and the second components shown in Fig. 4 and $c_1(x)$ and $c_2(x)$ are appropriate weights provided by
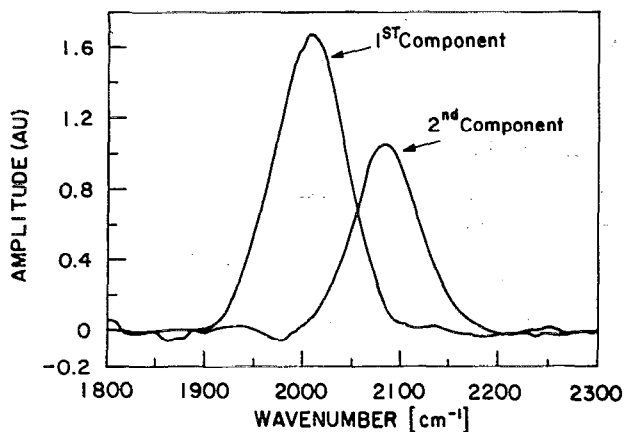
FIG. 4. First and second components obtained assuming the hypothesis that both components are present in the pure a-Si:H.

FIG. 6. Negative band in the differential spectrum of an oxidized a-SiC:H sample with high carbon content. The abscissa was obtained by subtracting the spectrum of the oxidized sample from the spectrum of the as-deposited sample.

the target transformation process. The weights c_1 and c_2 are plotted as a function of the compositional parameter x in Fig. 5.

Therefore, considering as mentioned in Sec. III the measured spectra as vectors belonging to a vectorial space (the "factor space"), we have found a basis with physical meaning in the frame of the proposed model.

The resulted components, shown in Fig. 4 were fitted by Gaussian curves using a Levenberg-Marquardt algorithm.[20] The Gaussian curves are centered at 2006 and 2085 cm^{-1} and their respective widths are 72 and 68 cm^{-1}. Therefore, according to our model, the band with shape approximately Gaussian, centered at 2006 cm^{-1} is due to stretching vibrations of Si-H oscillators embedded in a bulk environment, and the band at 2085 cm^{-1} is associated with SiH or SiH$_2$ groups on the inner surface of voids.
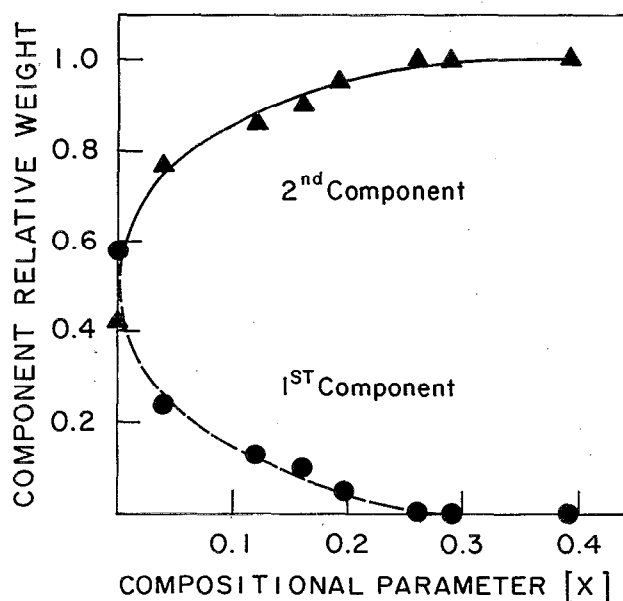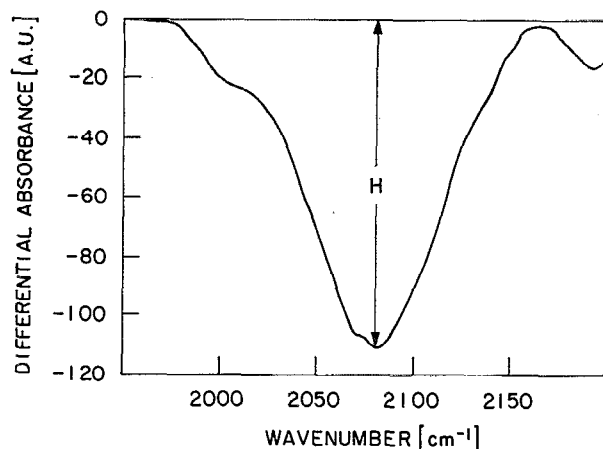

FIG. 5. Relative weight of the first and second components.

Up to this point we have shown that the individual bands at 2006 and 2085 cm^{-1} are good targets for the a-Si:H and low x a-Si$_{1-x}$C$_x$:H spectra. However, the above mentioned hypotheses (a) and (b) are possible. It is, therefore, necessary to perform independent experiments that allow us to confirm the assignments of the 2006 cm^{-1} band to a "bulk environment" and the 2085 cm^{-1} band to "void environment." To confirm these assignments we studied the behavior of the stretching band of Si-H bonds in a-SiC:H samples, during an oxidation experiment. Oxidation experiments[21] have been useful to elucidate the porous nature of the structure of the a-SiC:H, and, as we will show in the next section, they are a good tool for the analysis of the nature of the Si-H stretching band behavior. Moreover, the results of the oxidation experiment support the validity of the hypothesis made for PFA target transformation, discarding hypotheses (a) and (b).

V. OXIDATION EXPERIMENT

In a previous paper,[21] we showed that samples with high carbon content ($x > 0.4$) incorporate oxygen when exposed to air. We attributed the diffusion-like behavior of the oxygen incorporation to the existence of a porous network connected to the atmosphere. This work was performed by studying the behavior of the 1500–300 cm^{-1} region in the differential spectra of a sample with different exposure times to air. These differential spectra result by subtracting the spectra obtained after different exposure times from the spectrum of the as-prepared sample.

Here we report results for the 2000–2100 cm^{-1} range in the differential spectra of high carbon content oxidized samples ($x \sim 0.4$).

Considering the differential spectrum for a sample with $x \sim 0.4$, exposed six months to atmosphere at room temperature we get a sharp negative band peaking at 2080 cm^{-1} (see Fig. 6). On the other hand, samples having a smaller carbon content do not present evolution in their spectra.
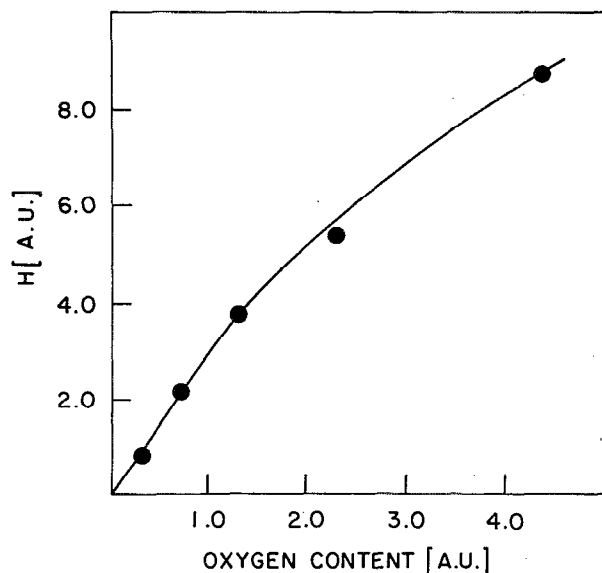
FIG. 7. Evolution of the height of the negative band in the differential spectra as a function of oxygen content.

As we pointed out in the cited work,[21] a long period is needed to detect significant variations in the IR spectrum. A series of isothermal annealings at 200 °C in air were performed in order to speed-up the oxidation process. Under these conditions, no aging effects were detected in the low carbon content samples, whereas the differential spectra of high carbon content samples have the same shape of those obtained during room temperature oxidation. The differential spectra of the annealed samples also present a band peaking at 2080 cm^{-1}, suggesting the same evolution mechanisms.

Figure 7 shows the height of the 2080 cm^{-1} peak as a function of the integrated area of the absorption band at 1030 cm^{-1}, which corresponds to the stretching mode of Si-O-Si bridges.[21] Although the strength of the Si-O-Si oscillator is unknown, the silicon-oxygen bond density is proportional to the area under this absorption band. Therefore, Fig. 7 shows that the negative band in 2080 cm^{-1} increases monotonically as the oxygen content increases. Note that the oxygen is attached only to the inner walls of the porous network.

The nature of the 2080 cm^{-1} negative band is not clear, although there is no doubt that is related with the stretching mode of the Si-H bonds. The negative band might mean either that hydrogen is displaced by the oxygen incorporated during the air exposure or that the environment of the same Si-H bonds is affected by the presence of oxygen.

Whatever the nature of the negative band, we want to point out that whenever we have displacement of hydrogen during oxidation or local modification of the environment by the oxygen, only the Si-H bonds connected with the surface of the porous network can be affected. Therefore the band peaking in ~2085 cm^{-1} must be assigned to the stretching of Si-H bonds in the inner surface of voids or free volumes. However, this result is clearly incompatible with the alternative hypotheses (a) and (b), mentioned in Sec. IV, therefore we must conclude that inductive effects are negligible.

VI. CONCLUSION

PFA was applied to the a-Si$_{1-x}$C$_x$:H IR spectra for $0 < x < 0.4$. The results indicate that the Si-H stretching spectra have two independent contributions. To identify these contributions a model was tested using the target transformation technique. As a result we identify the contributions as a band peaking in 2006 cm^{-1} due to the stretching of SiH bonds in the bulk, and a band at 2085 cm^{-1} due to the stretching of the same oscillators (or a mixture of SiH and SiH$_n$) in the inner surface of free volumes or voids. The latter are probably due to either the preparation conditions and/or as a consequence of limitations in the mechanisms of aggregation in the presence of CH$_3$ groups. In order to confirm the model, an experiment was performed showing that during the oxidation of carbon rich porous samples, a band in ~2080 cm^{-1} decreases which must be associated to SiH or SiH$_n$ oscillators located in the inner surface of the porous structure. This result supports the model made to perform the target transformation and discard hypothesis based on inductive effects. The oxidation experiment and the PFA results indicate that the Si-H bond stretching bands has a continuous behavior from $x = 0$ to $x = 0.4$ obeying a unique structural model. This model supports both the Wagner–Beyer model[5] and the Mahan et $al.$ results.[10]

[1] M. Cardona, Phys. Status. Solidi B **118**, 463 (1983).
[2] L. J. Bellamy, *The Infrared Spectra of Complex Molecules* (Chapmann & Hall, London 1975).
[3] E. C. Freeman and W. Paul, Phys. Rev. B **18**, 4288 (1978).
[4] H. Swanks, C. J. Fang, L. Ley, M. Cardona, F. J. Demon, and S. Kalbitzer, Phys. Status. Solidi B **100**, 43 (1980).
[5] H. Wagner and W. Beyer, Solid State Commun. **48**, 585 (1983).
[6] G. Lucovsky, Solid State Commun. **29**, 571 (1979).
[7] G. Lucovski, Journal de Physique, Colloque C 4, C4-741 (1981).
[8] H. Wieder, M. Cardona, and C. R. Guarnieri, Phys. Status. Solidi B **92**, 99 (1979).
[9] W. Beyer and H. Mell, in *Disorder Semiconductor* edited by M. A. Castner, G. A. Thomas, and S. R. Ovshinsky (Plenum, New York, 1987) p. 641.
[10] A. H. Mahan, P. Raboison, D. L. Williamson, and R. Tsu, Solar Cells **21**, 117 (1987).
[11] D. L. Williamson, A. H. Mahan, B. P. Nelson, and R. S. Crandall, Appl. Phys. Lett. **55**, 783 (1989).

[12] E. R. Malinowski and D. G. Howery, *Factor Analysis in Chemistry* (Wiley, New York, 1980).

[13] R. Swanepoel, J. Phys. E **16**, 1214 (1983).

[14] Y. Katayama, K. Usami, T. Shimada, Philos. Mag. B **43**, 283 (1981).

[15] M. P. Schmidt, I. Solomon, and H. Tran-Quoc, J. Non-Cryst. Solids **77-78**, 849 (1985).

[16] J. Bullot and M. P. Schmidt, Phys. Status Solidi B **143**, 345 (1987).

[17] H. H. Harmann, *Modern Factor Analysis*, 3rd ed. (The University of Chicago Press, Chicago, 1976).

[18] S. W. Gaarenstroom, Appl. Surf. Sci. **7**, 7 (1981).

[19] Z. Z. Hugus and A. A. Elawady, J. Phys. Chem. **175**, 2954 (1971).

[20] K. M. Brown and J. E. Dennis, Numerische Math. **18**, 289 (1982).

[21] R. Arce, R. R. Koropecki, R. H. Buitrago, F. Alvarez, and I. Chambouleyron, J. Appl. Phys. **66**, 4544 (1989).