



Reply to “Comment on ‘Infrared study of the Si-H stretching band in a-SiC:H’ ” [J. Appl. Phys. 69, 7805 (1991)]

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Citation: [Journal of Applied Physics](#) **71**, 4092 (1992); doi: 10.1063/1.350838

View online: <http://dx.doi.org/10.1063/1.350838>

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Reply to "Comment on 'Infrared study of the Si-H stretching band in α -SiC:H'" [J. Appl. Phys. 69, 7805 (1991)]

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(Received 4 November 1991; accepted for publication 27 November 1991)

We show that the theoretical arguments used in the preceding comment do not apply to our experiments, and that our interpretation of the behavior of the Si-H stretching band in α -SiC:H in terms of structural influences is correct.

Sacher objects¹ to our interpretation of the dependence of the stretching band of SiH bonds in α -SiC:H on carbon content.² In our work, we conclude that this dependence is mainly due to the presence of either voids or free volumes whose concentrations increase with the carbon content. Sacher¹ indicates that inductive effects cannot be neglected and tries to explain our results according to calculations which use equilibrium constants of the substituents. He also proposes an alternative interpretation of the results of our oxidation experiment. The validity of the prediction of inductive effects of substituted components based on empirical descriptions of the behavior of amorphous materials in terms of monomers is debatable and the results must be handled with care. First, in amorphous materials like α -SiC:H, neither the structure nor the carbon distribution are entirely known. The probabilities of existence of a Si-H bond having 1, 2, or 3 carbons as next nearest neighbors are different functions of carbon content.³ Something similar would be expected in the case of SiH₂ groups. Thus, the stretching band of SiH bonds should include more than three components, each of them having its own variation as a function of carbon content. The number of independent contributions would be larger if more distant neighbor substituents were considered. In fact, Lukovsky⁴ accounts for this through the "mean electronegativity of the host," which leads to a direct dependence of the inductive shift on the stoichiometry. One could expect the frequencies to be approximately independent of the amount of substituents in the case of surface contamination of porous α -Si:H with oxygen and carbon. In this case the mean effect of the host would be invariant and the variety of available substituent sites would be more limited. But in the case in which the carbon atoms are distributed in the bulk, inductive frequency shifts should depend on carbon content. An example to illustrate how the material behavior depends on structure and substituent distribution is embodied in the comparison of α -SiN:H prepared by glow discharge of ammonia⁵ (whose SiH stretching band frequency varies linearly with stoichiometry) and that prepared using nitrogen. A single calculation based on a generic model of the structure cannot account for these two materials. Our results from factor analysis show that, within experimental error, only two independent components contribute to the stretching band of SiH bond in our material.

Sacher¹ claims that his calculations⁶ predict that the theoretical peaks corresponding to the structures expected in α -SiC:H are exactly the same as those of the SiH and SiH₂ modes in α -Si:H. However, such a theoretical argument does not apply to our experiments, for the following reasons:

(a) Table 1 of Ref. 6 shows predictions for the case of contamination with oxygen and carbon of porous α -Si:H. Our samples do not contain oxygen in the bulk and, except for the largest carbon content, do not contain a void density high enough to cause the coalescence of the voids in an open pore network.⁷ Oxygen atoms cannot reach the bulk of the samples. Therefore the predictions in Table 1 of Ref. 6 for the structures labeled Si, O, H, and Si, H, O, C do not apply to our data. This constrains the frequency ranges to 2025–2040 cm⁻¹ for SiH₁, 2060–2070 for SiH₂ and 2100 for SiH₃. None of them contains the 2006 and 2085 cm⁻¹ values of the two components found in our work.² On the other hand, Table 1 of Ref. 6 contains neither predictions for substituents groups with carbon as second neighbor nor for effects of the whole host. One could expect that these groups and host effects lead to a broadening of the predicted frequency ranges, but in all cases, as explained above, the main frequency of the band should depend on the carbon content.

(b) In his calculations⁸ Sacher assumes that, although unknown, the σ_1 constant of the group (Si)₃Si- should be very similar to the constant of the group (CH₃)₃Si-, and he uses the value of the second instead of that of the first. A consequence of this assumption is that direct substitution of methyl groups instead of silicon atoms should keep the shape of the stretching band of SiH invariant, independent of the carbon content. However, the shape of the stretching band in our experiments does not remain invariant when the carbon content changes. Our material, as in all films of α -SiC:H prepared by glow discharge of methane, has carbon incorporated in the form of methyl groups. This fact was used to explain the presence of a void structure dependent on the carbon content.^{7,9} The only way to explain the increase of the 2085-cm⁻¹ peak and the vanishing of the 2006-cm⁻¹ peak when carbon content increases, using predictions based on the above mentioned hypothesis of σ_1 , is to assume an increase of the SiH₂ oscillator density in detriment to that of SiH as carbon content increases. How-

ever, the SiH_2 concentration should remain low, independent of carbon content.³

Therefore the predictions made by Sacher⁶ explain neither the peak positions themselves nor their invariant behavior in our material. On the contrary, his argument shows that inductive effects cannot explain the increase in intensity of the 2085-cm^{-1} peak and the decrease of that at 2006 cm^{-1} .

Conclusions from calculations in such complex systems as ours, therefore, must be made with care. In order to clarify the situation we performed an independent oxidation experiment,² which we now discuss.

Sacher indicates¹ that the growth of an oxidation peak can be explained in terms of an oxidized SiH structure.⁶ This affirmation led us to find a mistake in our definition of difference spectra, which was clarified in an erratum.¹⁰ The increase of a negative differential spectrum at 2085 cm^{-1} during oxidation cannot be interpreted as the growth of a new peak, but as the decrease of an already existing peak. Since the incorporated oxygen can only affect SiH and SiH_n groups near the surface of the pore network, our interpretation that the mode at 2085 cm^{-1} is related to SiH and SiH_n groups bonded near the surface of voids is quite reasonable. Since the microvoid density increases as the carbon content increases,¹¹ the correlation between carbon content and the height of the 2085-cm^{-1} peak is readily explained.

In conclusion, we show that inductive effects cannot explain the behavior of our spectra and that our hypothesis relating the 2006-cm^{-1} peak to that of bulk-bonded hydrogen and the 2085 cm^{-1} peak to that of void-bonded hydrogen is more reasonable.

This work was partially supported by the TWAS, grant RG MP 898-147, by the National Research Council of Brazil (CNPq) and SCTDE-SP (Brazil). The partial support of the Fundação de Amparo à Pesquisa de São Paulo is also acknowledge. R. R. Koropecski is a fellow of the CONICET, Argentina. The authors are indebted to Professor G. Kleiman for critical review of the manuscript.

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