ASSOCIATION OF 2100 cm^{-1} INFRARED SPECTRA WITH MICROSTRUCTURE IN HYDROGENATED AMORPHOUS SILICON

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Various arguments are presented to show that the association of the silicon-hydrogen stretching mode at 2100 cm^{-1} observed in hydrogenated amorphous silicon with hydrogen bonding on inner surfaces of voids is questionable. It is suggested that the unique association of the 2100 cm^{-1} mode with poor photoelectronic properties may be flawed. We point out that the vibrational frequency shift due to the solid state effect caused by the surrounding dielectric medium is appreciably smaller than 100 cm^{-1} . Further experiment and theoretical studies of the local environment arising the 2100 cm^{-1} mode are still needed.

THE INCORPORATION of hydrogen into tetrahedrally coordinated amorphous semiconductors has been shown to lead to dramatic improvement in electronic and optical properties from those of the unhydrogenated material [1, 2]. Identification of the local environment of the H atom is important for the development of quantitative models for the electronic density of states and so of all the optical, electrical, and device properties. One of the most direct identifications of the role of H in the *a*-Si matrix comes from studies of the optical absorption in the infrared attributable to vibrations of the Si-H unit. The vibrational spectra of *a*-Si:H often exhibit a doublet structure at 2000 and 2100 cm^{-1} due to the silicon-hydrogen stretching mode [3–5]. The assignment of the 2100 cm^{-1} mode has been the subject of a long controversy. It is generally admitted that it can arise from Si-H bonds in the SiH_2 , $(\text{SiH}_2)_n$ or SiH_3 configurations [3, 5], or from interacting Si-H bonds on internal surfaces of microvoids [6]. The former has been questioned by several authors [4, 7, 8] who argued that the missing of a clear correspondence between the oscillator strengths of the 2100 cm^{-1} stretching vibration and the respective bending modes. Later on, H. Wagner *et al.* [6] pointed out that only small variations are expected to arise from the number of hydrogen atom attached to a single silicon atom, since the Raman spectra [9, 10] of the various well-isolated higher silanes show unambiguously that a frequency difference of at most 20 cm^{-1} occurs between the stretching modes of SiH and SiH_2 groups.

In this Letter we question the assignment of 2100 cm^{-1} mode to the arising from interaction Si-H bonds on internal surfaces of microvoids. Our argu-

ments are supported by results from infrared absorption and hydrogen evolution in samples under various treatments. We point out that the 2100 cm^{-1} mode cannot be used as an indication of poor photoelectronic properties. In addition we have shown that the solid state effect on the shift of vibrational frequency caused by the surrounding dielectric medium is appreciably smaller than 100 cm^{-1} . Thus the assignment of 2100 cm^{-1} is still an open question and needed further study. Due to many recent publications [11–15] using infrared measurements in the 2100 cm^{-1} range as a means of quantifying amorphous semiconductor materials, this kind of information is of great technological interest.

In a series of He bombardment and annealing experiments on samples of sputtered *a*-Si:H [16] it was found that the integrated intensities of the 2000 cm^{-1} mode is enhanced significantly after the bombardment, whereas the band at 2100 cm^{-1} shows little change. If the silicon-hydrogen stretching modes at 2000 cm^{-1} and 2100 cm^{-1} are attributed to hydrogen bonding within the amorphous network and to inner surfaces of voids [6], respectively, the above observation will be very difficult to explain since 200 KeV He^+ ions bombardment will break the network and introduce microvoids. The Harvard group [17] has also carried out experiments where they have sputtered *a*-Si:H films on substrates kept at different positions in the plasma between the target and the substrate platform. It was found that the ratio of the integrated intensities of the 2000 cm^{-1} and 2100 cm^{-1} bands varies rapidly as function of target to substrate distance, with the films closest to the target displaying a pure 2000 cm^{-1} mode. There is, however, a systematic

rapid decrease in the dark resistivity, photoconductivity and photoluminescence for films closest to the target. This deterioration is attributed to the increased bombardment of the films by energetic electrons and ions emitted from the target during sputtering, and the large 2000/2100 ratio is actually a result of the bombardment which is consistent with that of He bombardment experiments. Thus, these results provide evidence against the assignment of the 2100 cm⁻¹ mode to hydrogen bonding on inner surfaces of microvoids and also against the association of the 2100 cm⁻¹ mode with poor photoelectronic properties as shown in the recent publications [11–15].

Hydrogen evolution experiments are known to yield valuable information on the structure of the material, if the evolution rate is measured as a function of temperature. For *a*-Si:H two evolution processes are generally found. It is observed that the films are permeable to molecular hydrogen at low temperature (< 350°C) but not at high temperature (> 500°C) as the evolution is limited by diffusion of atomic hydrogen. This result can be explained by the fact that void-rich structure for the as-deposited material allows for rapid diffusion of molecular hydrogen, and upon hydrogen release, the voids collapse and a rather compact material is formed so that the diffusion of molecular hydrogen becomes impossible at high temperatures. Based on these results, Beyer *et al.* [18] have attributed the low temperature process to the desorption of hydrogen bound to internal surface followed by out-diffusion of H₂ through a network of voids. If this assignment is right and the 2100 cm⁻¹ mode is due to hydrogen bonding on inner surfaces of voids, the ratio of the intensity of the 2100 cm⁻¹ band relative to that of the 2000 cm⁻¹ mode will decrease after the annealing of material at the temperature where the low temperature evolution occurs. However, it was found that instead of decreasing, the ratio is either unchanged [19] or increased [8]. Thus, the association of the 2100 cm⁻¹ mode with hydrogen bonding on inner surfaces of voids may be questionable.

According to the observation of high resolution electron energy loss spectroscopy [20, 21] and infrared measurements [22] which prove the stretching frequencies of SiH and SiH₂ groups on crystalline silicon (1 0 0) and (1 1 1) surfaces are the same within 10 cm⁻¹ and are located at 2090 cm⁻¹, Wagner and Beyer [6] thus associated the 2100 cm⁻¹ infrared band in *a*-Si:H with SiH or SiH₂ species on the internal surfaces of microvoids. However, there is no physical foundation to make such a correspondence. Recently, the frequencies of the hydrogen vibrational modes on crystalline Si (1 1 1) surface have been calculated [23] and

the results are in excellent agreement with experiment. A surface-atom vibrational mode is compared to similar modes in the amorphous hydrogenated materials. The comparison predicts that internal surfaces (microvoids) in the amorphous network are locally softer than the corresponding crystalline surface configuration. The force constant *f* is smaller by a factor of two in the amorphous material, and hence the frequency (proportional to *f*^{1/2}) of vibrational mode on the inner surface of amorphous microvoid is smaller than that of the corresponding configuration on the crystalline surface. In addition, from recent infrared data and cluster calculations [24] it has been shown that the modes of H on crystalline Si surfaces with different structures can vary from 2070 cm⁻¹ to 2173 cm⁻¹. Based on these data, it appears that the general statement, the stretching frequencies of SiH and SiH₂ groups on crystalline silicon surfaces are the same within 10 cm⁻¹ and are located 2090 cm⁻¹, made by Wagner *et al.* [6] is not appropriate. These results, therefore, also against the association of the 2100 cm⁻¹ mode with hydrogen bonding on inner surfaces of microvoids.

It has been argued that a solid state effect [6, 8, 25] caused by the surrounding dielectric medium can account for the occurrence of the Si–H stretching vibration at both 2000 cm⁻¹ and 2100 cm⁻¹. It is based on the model that the Si–H bonds are distributed in the *a*-Si matrix a dilute assembly of harmonic oscillators that consist of two atoms with effective charges $\pm e_s^*$ and reduced mass μ . Then the contribution of a given i.r.-active vibration of a Si–H band of frequency ω_i to the complex transverse dielectric constant is [26, 27]

$$\Delta\epsilon(\omega) = \frac{4\pi N e_s^{*2} / \mu}{\omega_i^2 - \omega^2 - i\gamma\omega}, \quad (1)$$

where

$$\omega_i^2 = \omega_0^2 - \frac{4}{3} \pi \left(\frac{N e_s^{*2}}{\mu} \right),$$

$$\omega_0^2 = k_0 / \mu,$$

k_0 is the restoring constant, ω_0 the Si–H stretching frequency in the free molecule, γ a phenomenological transverse damping constant, N the number of oscillators per unit volume. The effective charge of the Si–H stretching mode in the free molecule e_G^* related to the absorption strength Γ is given by [3]

$$\frac{e_G^{*2}}{\mu} = \frac{c\omega_i}{2\pi^2 N_A} \frac{\Gamma}{\xi}, \quad (2)$$

where N_A is Avogadro's number, ξ the number of relevant bonds per molecule, and c the speed of light. Equation (2) cannot be used directly to determine e_s^*

because in the solid the local field differs from the applied field: a local-field correction must be made. There are two main approaches for the local-field correction. The first is the Onsager local-field approximation, which treats the absorber as a point dipole in a spherical cavity within the dielectric medium. For weakly polarizable bonds, the result is [3]

$$e_s^* \simeq \frac{3\varepsilon}{1 + 2\varepsilon} e_G^*, \quad (3)$$

where ε is the electronic dielectric constant of the medium. The second approximation uses the Lorentz local fields [27], which treats the absorption of the bonds embedded in a dielectric medium resulting in

$$e_s^* \simeq \frac{\varepsilon + 2}{3} e_G^*. \quad (4)$$

Using the value of Γ given by Brodsky *et al.* [3] (3.5 cm²/mmol bond), $N = 1.5 \times 10^{22}$ bonds/cm³ [3] which is contained in a glow-discharge film grown at 250°C and implies about 24 at % H for film density equal to 95% of the crystalline Si density of 5.0×10^{22} atoms/cm³, $\varepsilon \approx 12$, $\omega_0 = 2116$ cm⁻¹ the monohydride frequency for *i*-tetrasilane [6]

we obtain $\omega_i \approx 2113$ cm⁻¹ for the Onsager local-field approximation, and $\omega_i \approx 2106$ cm⁻¹ for the Lorentz local-field approximation. Comparing these values with the vibrational frequency in the free molecule ω_0 , the shift is appreciably smaller than 100 cm⁻¹. The above result is contrary to that of Wieder *et al.* [24]. We believe the difference coming from the fact that Wieder *et al.* [24] used the number of oscillators per unit volume $N = 6/\pi L^3$, where L is the length of the SiH bond ($L \approx 1.48$ Å), while we used $N = 1.5 \times 10^{22}$ bonds/cm³ taken from the result of Brodsky *et al.* [3]. Since the number of monohydride oscillators in hydrogenated amorphous silicon should be much smaller than the number of silicon atoms ($\approx 5.0 \times 10^{22}$ atoms/cm³), the data used by Wieder is too large to be believed. Thus the so-called solid state effect on the shift of the frequency of Si-H vibration cannot account for the occurrence of the Si-H stretching modes at both 2000 cm⁻¹ and 2100 cm⁻¹.

In conclusion, we do admit that microvoids exist in amorphous semiconductors because of the lack of surface mobility of the deposited atoms at low temperature deposition and the mechanism relieving the strain in the amorphous network. Their existence has

clearly been shown in several experiments [28–30]. Here, we just want to point out that the assignment of the silicon-hydrogen stretching mode at 2100 cm⁻¹ observed in *a*-Si:H to hydrogen bonding on inner surfaces of microvoids is questionable. We suggest that the association of the 2100 cm⁻¹ mode with poor photoelectronic properties may be inadequate. We point out that the vibrational frequency shift due to the solid state effect caused by the surrounding dielectric medium is appreciably smaller than 100 cm⁻¹. Thus the local environment arising the 2100 cm⁻¹ mode is still unclear and needed further study.

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