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## LETTER TO THE EDITOR

# Vibrational wavenumbers of SiH<sub>x</sub> bonds in binary Si:H materials

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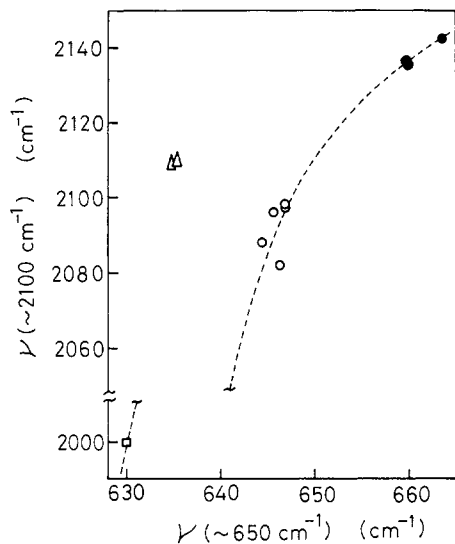
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**Abstract.** Vibrational wavenumbers of SiH<sub>x</sub> bonds in sputter-prepared Si:H materials are examined by the infrared absorption technique. The wavenumber of the SiH<sub>x</sub> stretching mode is greatly affected by the crystallographic structure of the host Si network as well as by the effective electronegativity sum of the nearest neighbour H atoms. The wavenumber for the SiH group attached to relatively large Si microcrystals takes the value 2100 cm<sup>-1</sup>. The wavenumber of the SiH<sub>3</sub> rocking mode is also different from those reported previously and our value is 660 cm<sup>-1</sup>. The origin of these shifts in the vibrational wavenumber is discussed on the basis of the structural change in the Si:H materials.

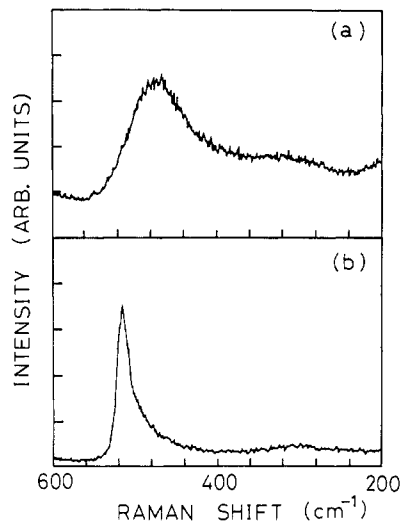
Many researchers have reported on topics concerning infrared spectra of binary Si:H materials. It is now generally accepted that two absorption peaks appear for the material containing the SiH group only, while four peaks appear for the material containing SiH<sub>x</sub> ( $x = 2, 3$ ) as well as SiH groups. In the former case, the vibrational wavenumbers are 630 and 2000 cm<sup>-1</sup> for the rocking and stretching modes, respectively. In the latter, they are respectively, 630, 845, 890 and 2100 cm<sup>-1</sup> for the rocking, wagging, bend–scissor and stretching modes of the SiH<sub>2</sub> or (SiH<sub>2</sub>)<sub>n</sub> groups; and respectively, 628, 848, 902 and 2144 cm<sup>-1</sup> for the rocking, symmetric deformation, degenerate deformation and stretching modes of the SiH<sub>3</sub> group (Lucovsky *et al* 1979, Furukawa and Matsumoto 1985).

In this paper, binary Si:H materials are prepared by the reactive sputtering method. As a result, various kinds of Si:H materials including microcrystalline Si:H ( $\mu\text{c-Si:H}$ ) are obtained. By measuring infrared absorption spectra of these materials, it is found that the stretching absorption wavenumber of the Si–H bond in a material containing relatively large Si microcrystals (about 2100 cm<sup>-1</sup>) becomes greater than that in a material containing amorphous or very small Si microcrystals (about 2000 cm<sup>-1</sup>). The former value is almost the same as that for the SiH<sub>2</sub> group in the latter material. It is also found that the wavenumbers of all vibrational modes are systematically increased by increasing the number of H atoms attached to one Si atom (or effective electronegativity), and the value of the SiH<sub>3</sub> rocking mode becomes about 660 cm<sup>-1</sup>.

The Si:H materials used in this study were fabricated by reactive sputtering in an atmosphere of pure hydrogen. The substrate temperature and RF power were varied from about 100 to 300 K and 50 to 300 W, respectively. The Si:H materials on the single-crystal Si substrates were observed using an infrared absorption technique (400–4000 cm<sup>-1</sup>), and the materials on the quartz glass substrates were observed using a



**Figure 1.** Relation between the stretching absorption wavenumber  $\nu$  ( $\sim 2100 \text{ cm}^{-1}$ ) and the rocking wavenumber  $\nu$  ( $\sim 650 \text{ cm}^{-1}$ ).

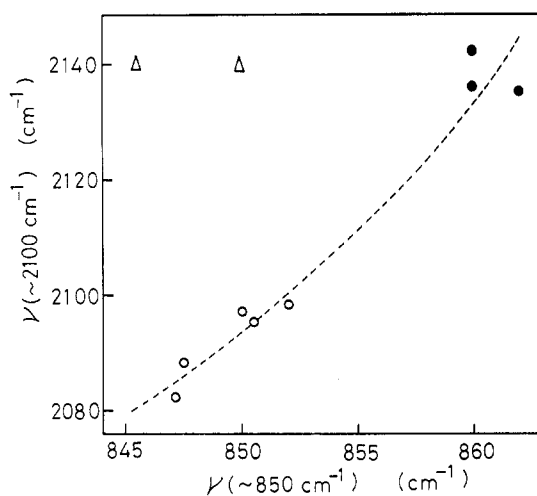


**Figure 2.** Typical Raman spectra for materials prepared at (a)  $\sim 100 \text{ K}$  and (b)  $300 \text{ K}$ .

Raman scattering technique ( $200\text{--}600 \text{ cm}^{-1}$ ). The details of these procedures have been published elsewhere (Furukawa and Miyasato 1989).

Figure 1 shows the relationship between the stretching absorption and the rocking wavenumbers. Both absorption peaks are not necessarily sharp, so those values are gravity centres of the absorption bands. The plots marked by circles and triangles are for the Si:H materials prepared at about 100 and 300 K, respectively. The variety of the plots for the  $\sim 100 \text{ K}$ -prepared materials are obtained by changing the hydrogen gas pressure and the RF power during the deposition. The plot marked by squares is for conventional hydrogenated amorphous silicon (a-Si:H).

From figure 1, it is seen that the plots for the  $\sim 100 \text{ K}$ -prepared materials and conventional a-Si:H are on the same curve, and the stretching absorption wavenumber increases with an increase in that for rocking absorption. From the previous assignment for the stretching mode, it is concluded that the H atoms are incorporated in the forms of  $\text{SiH}_2$  and  $\text{SiH}_3$  for the materials marked by open and full circles, respectively. The materials for the full circle plots ( $\text{SiH}_3$ -rich materials) were prepared under conditions where the hydrogen gas pressure was high. The result is consistent with the previous data (Komori *et al* 1989). The small deviation in the wavenumber is considered to be caused by the mixture of the plural groups (i.e. the mixture of  $\text{SiH}_2$ ,  $(\text{SiH}_2)_n$  and  $\text{SiH}_3$ ). These groups have a different value of effective electronegativity, which increases the ionic component of the Si-H bond force, producing a different value for the wavenumber. It should be noted that this effective electronegativity affects the rocking absorption wavenumber as well as the stretching absorption one, and the maximum rocking wavenumber becomes about  $660 \text{ cm}^{-1}$ . This value is larger by about  $30 \text{ cm}^{-1}$  than that reported previously. The discrepancy is probably caused by the mixture of the plural  $\text{SiH}_x$  groups in the previous material, or by the difference in the crystallographic structure of the host Si material as discussed below. The plots marked by triangles are



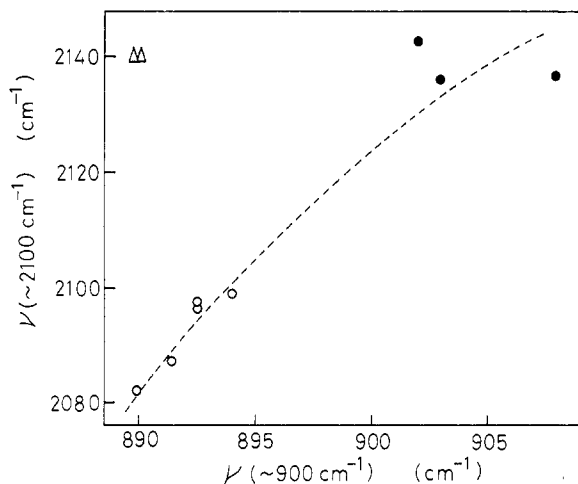
**Figure 3.** Relation between the stretching absorption wavenumber  $\nu$  ( $\sim 2100$  cm $^{-1}$ ) and the wagging or symmetric deformation wavenumber  $\nu$  ( $\sim 850$  cm $^{-1}$ ).

not on the broken curve in figure 1 and the reason for this will be discussed in the next paragraph.

Figures 2(a) and (b) show typical Raman spectra for the materials marked by circles and triangles, respectively, in figure 1. It is found that figure 2(a) has a broad peak near 480 cm $^{-1}$ , whereas figure 2(b) has a sharp peak at 520 cm $^{-1}$ . These indicate that the former material consists of amorphous or microcrystalline Si (less than a few tens of Å), and the latter one consists of relatively large Si microcrystals.

As shown in figure 1, the plots marked by circles and squares are on the same curve, whereas those marked by triangles are not. The most plausible origin of these results is that the former materials show a broad Raman peak near 480 cm $^{-1}$  while the latter do not. The triangle plots in figure 1 are above the broken curve indicating that the stretching absorption wavenumber for the apparent  $\mu$ c-Si:H becomes greater than that for a-Si:H and the Si:H material containing very small Si microcrystals. Therefore, it is concluded from the small rocking absorption wavenumber (about 635 cm $^{-1}$ ) that a large number of H atoms are incorporated in the monohydride form in the materials marked by triangles. The result is consistent with the quantitative analysis concerning the infrared absorption strength for the bending (845–905 cm $^{-1}$ ) and rocking (630–660 cm $^{-1}$ ) regions (Furukawa 1990). That is, the ratio of the bending absorption strength to the rocking one becomes reduced for the materials corresponding to the triangle plots due to the incorporation of monohydride groups.

Figure 3 shows the relation between the stretching absorption wavenumber and that of the wagging or symmetric deformation. The notation is the same as in figure 1. The wagging and symmetric deformation vibrations are caused by SiH $_2$  and SiH $_3$  groups, respectively. Therefore, the plot corresponding to conventional a-Si:H, in which H atoms are bonded in the monohydride form, is not indicated in figure 3. Similarly, care should be given to the data for the apparent  $\mu$ c-Si:H. The infrared spectrum of such a material also shows the bending absorption band, irrespective of its containing a large number of SiH groups (Furukawa 1990). Hence, a small number of SiH $_2$  groups are contained in the material, which cause wagging and bend–scissor vibrations. The stretching absorption wavenumber of these SiH $_2$  groups is expected to be increased from that of SiH groups in the  $\mu$ c-Si:H. In fact, the stretching band shows a main absorption peak



**Figure 4.** Relation between the stretching absorption wavenumber  $\nu$  ( $\sim 2100\text{ cm}^{-1}$ ) and the bend-scissors or degenerate deformation wavenumber  $\nu$  ( $\sim 900\text{ cm}^{-1}$ ).

at  $2100\text{ cm}^{-1}$  with a shoulder near  $2140\text{ cm}^{-1}$  (Furukawa 1990). This value of  $2140\text{ cm}^{-1}$  should be used for the vertical axis in figure 3, because the monohydride group does not have a wagging or a bend-scissor mode, so only the dihydride group determines the wavenumber for the horizontal axis. As shown in figure 3, the stretching wavenumber, rather than that of the wagging or symmetric deformation, is affected by the crystallographic structure of the host Si material.

Figure 4 shows the relation between the stretching wavenumber and that of the bend-scissor or degenerate deformation. The notation is the same as that in figures 1 and 3. In this case, the stretching wavenumber rather than that of the bend-scissor or degenerate deformation is also affected by the crystallographic structure.

From figures 1–4, it is concluded that the stretching force constant of the Si–H bond is affected by the crystallographic structure of the neighbouring Si atoms much more than is the bending force constant. A similar result for the bond force constants was obtained for varying the preparation method (i.e. the structure of the material) (Minomura 1984). From the peak wavenumber shift observed in the present Raman spectra, the stretching force constant of the Si–Si bond in the relatively large microcrystalline Si is greater by about 8% than that of the amorphous or microcrystalline Si. Therefore, the Si–H stretching wavenumber for the microcrystalline material is expected to be increased by about 6%, on the assumption that it is linearly affected by the three nearest neighbour Si–Si bonds. Thus the value of the Si–H stretching wavenumber obtained becomes about  $2120\text{ cm}^{-1}$ , because the conventional Si–H stretching wavenumber is  $2000\text{ cm}^{-1}$ . On the other hand, the experimentally obtained value is about  $2100\text{ cm}^{-1}$ , which is stated in the discussion concerning figure 3. The small discrepancy of  $20\text{ cm}^{-1}$  may arise from the softening of the stretching force constant at the microcrystal surface. Concerning the effect of the crystallographic structure on the bending force constant of the nearest neighbour bond, one cannot discuss the details at this stage. However, the present experimental result is similar to that obtained previously (Minomura 1984), in which the bending force constant (or the  $150\text{ cm}^{-1}$  Raman peak) was not so much affected by the preparation method.

As shown in figures 3 and 4, the stretching wavenumber of the SiH<sub>2</sub> group in the  $\mu\text{c-Si:H}$  is about  $2140\text{ cm}^{-1}$ , which is greater by about  $40\text{ cm}^{-1}$  than that of the SiH group

in such a material. This shift is caused by an increase in the effective electronegativity, which arises from an increase in the number of H atoms attached to one Si atom. Therefore, the Si–H stretching absorption wavenumber is determined from both the crystallographic structure of the neighbouring Si atoms (covalent component) and the number of H atoms bonded to the Si atom (ionic component).

In conclusion, various Si:H materials were prepared by reactive sputtering in an atmosphere of pure hydrogen, and their vibrational spectra were measured using an infrared absorption and a Raman scattering technique. As a result, it was found that the Si–H stretching absorption wavenumber increased with an increase in the force constants of the three nearest neighbour bonds, which contain both covalent and ionic components. The former effect increases the wavenumber from  $2000\text{ cm}^{-1}$  (SiH in a-Si:H) to  $2100\text{ cm}^{-1}$  (SiH in  $\mu\text{c-Si:H}$ ), and the latter from  $2100\text{ cm}^{-1}$  (SiH in  $\mu\text{c-Si:H}$ ) to  $2140\text{ cm}^{-1}$  (SiH<sub>2</sub> in  $\mu\text{c-Si:H}$ ). A value of  $2100\text{ cm}^{-1}$  is almost the same as that for the SiH<sub>2</sub> in a-S:H and  $\mu\text{c-Si:H}$ . On the other hand, the Si–H bending force constant is not affected so much by the change in the covalent component of the nearest neighbour bonds, but is affected by the change in the ionic one.

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