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INFRARED AND FAR INFRARED ABSORPTION OF B- AND P-DOPED AMORPHOUS Si

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Abstract. - The infrared and far infrared absorption spectra of B- and P-doped a-Si(H) have been measured. The effect of annealing on these spectra has been studied. Three local modes of the B-H bond and a band of B-Si have been identified for the B-doped a-Si(H). The intrinsic infrared absorption of the Si-Si network is greatly enhanced by the presence of the dopants.

Introduction. - We present here measurements of the infrared and far infrared absorption spectra of B- and P-doped a-Si(H) and the effect of annealing. The infrared spectra of the B-doped samples show the characteristic vibrations of the B-H and B-Si bonds at the frequencies above the fundamental vibrations of the Si-Si network. Upon annealing, a new and weaker band emerges below the main band of the B-H bond stretching band. The wagging band of the Si-H in the weakly B-doped sample at 640 cm⁻¹ is swamped in the heavily doped cases by some broader band which can be attributed to the Si-B and B-H vibrations. After annealing at 560 °C, this broader band is resolved into two clear peaks and an absorption shoulder, centered at 620, 845 and 720 cm⁻¹, respectively. Besides these "local" modes the fundamental absorption in the region between 50 and 550 cm⁻¹ is strongly enhanced by the doping. From the magnitude of this absorption enhancement the effective dynamical charges for the Si-P and Si-B bonds can be derived and compared with the predictions based on Harrison's bond charge model.

Experiments and Results. - The samples used in these measurements were prepared on c-Si substrates (ρ > 400 cm-ohm) by glow discharge decomposition of SiH₄-PH₃ and SiH₄-B₂H₆ mixtures. Samples 101 to 103 are B-doped, the concentrations of B are 0.01, 0.09 and 0.29, respectively. The samples 104 to 106 are P-doped, the concentrations of P being 0.01, 0.1 and 0.20, respectively. The measuring methods including the infrared measurement and the determination of the B and P concentrations are described elsewhere (5).

The absorption spectra of the B-doped samples are shown in Fig. 1 for the spectral region above the fundamental absorption of the Si matrix (≪550 cm⁻¹). The spectra of the samples 101 and 104 are basically the same as those of undoped samples (6). With increasing B concentration, one notes in Fig. 1 the appearance and growth of a band at 2475 cm⁻¹. Upon annealing of these samples, another weaker band grows at 2370 cm⁻¹. Figure 3 shows the evolution of this band during isochronal annealing. After annealing at 510°C, the integrated intensity of this weaker band is about one third of that of the main band at 2475 cm⁻¹. The wagging band of the Si-H bond is clearly seen at 640 cm⁻¹ for sample 101, which is relatively rich in hydrogen and weakly doped with B. In the heavily B-doped cases, however, it is swamped by a broader absorption band. During the isochronal annealing, the broader absorption feature changes little up to 510°C. After annealing at 560°C, however, it changes dramatically and resolves clearly into two peaks and an absorption shoulder centered at 640, 840, and 720 cm⁻¹, respectively. The first of these peaks corresponds to Si-H wagging and that at 840 cm⁻¹ probably to B-Si bonds. The shoulder at 720 cm⁻¹ might be due to a B-H wagging mode, by comparison with the vapour, liquid
and crystalline diborane (7-8).

We did not find any features which could be associated with the stretching of the P-H bonds, although the concentration of P is as high as 20 (at)% . It should be pointed out, however, that the oscillator strength of the P-H bond stretching between 2100 and 2400 cm$^{-1}$ may be too weak to be observed. In the wagging mode region a peak is seen after annealing at 680 cm$^{-1}$. It probably corresponds to the wagging of P-H bonds. Fig. 3 shows the absorption spectra of B-doped a-Si samples in the region of the intrinsic vibrations of the Si-Si network. The absorption strength of the spectra increases as a whole with increasing doping. This happens also for P-doped samples: for sample 106, the integrated strength of the spectra is 7 times that of sample 104.

Fig. 4 shows the changes of the integrated strengths of some bands during the annealing for the B-doped sample 103. Different modes have quite different annealing behaviour. For the B-doped sample, the 2475 cm$^{-1}$ band and the intrinsic optical phonons centered at 480 cm$^{-1}$ have almost no change up to the annealing temperature of 510°C while the 1980 cm$^{-1}$ band has decreased by a factor of 4. For the P-doped sample, the peaks at 2000 cm$^{-1}$ and 640 cm$^{-1}$ decrease like for undoped a-Si(H) samples (4) while the peak of 480 cm$^{-1}$ remains very strong. The rapid weakening of all bands at T>550°C is most likely related to crystallization.

Discussion. - After annealing up to 510°C, the B-H peak at 2475 cm$^{-1}$ shows no decrease (see Fig. 4) but evolves into two peaks centered at 2475 and 2370 cm$^{-1}$, respectively (Fig. 3). In view of the fact that the stretching band of the B-H bonds in B$_2$H$_6$ occurs at 2609 cm$^{-1}$ and 2520 cm$^{-1}$ (7,8), we tentatively assign these two peaks to B-H bond stretching modes corresponding to the singlet (A$_1$) and the doublet (E) of BH$_3$ radicals. We can estimate the effective charge of the B-H bond from the integrated absorption $\int a(\omega) d\omega$ of this band if the density $N_{B-H}$ of B-H bonds in the sample is known. On the other hand, we can also estimate the density $N_{B-H}$ of the B-H bonds by using the following expression:

$$N_{B-H} = \frac{2n_{e2}}{\alpha_{B-H}^2} \frac{\mu}{\hbar} \int a(\omega) d\omega$$

The effective charge $\alpha_{B-H}^2 = 0.2$ can be estimated from the absorption spectra found in Ref. 7, thus we obtain for sample 103.
\( N_{B-H} = 22 \text{ at } \% \), which is somewhat lower than the value measured from the photoelectron spectra (29 at \%).

First order infrared absorption by lattice modes is forbidden by symmetry in c-Si. It becomes weakly allowed in a-Si due to the lack of long-range order which relaxes the crystal momentum and symmetry selection rules. It has been shown in reference 6 that the disorder-induced one phonon absorption is suppressed upon hydrogenation, partly because of relaxation of internal tensions and of the angular distortions responsible for the dipole moment. However, strongly electronegative impurities such as fluorine can highly enhance the infrared activity of a-Si(4). In Fig. 2 we can see that the disorder-induced one phonon absorption is remarkably enhanced by the dopants P or B. This enhancement is only weakly dependent on annealing and on the concomitant evolution of hydrogen from the sample as shown in Fig. 4. The P impurity will add an ionic component to the bonds. The additional absorption induced by the doping can be related to a dynamical effective charge for the Si-P bond with (5)

\[
e^2_{\text{Si-P,B}} = \frac{\mathcal{M}_S}{4\pi} \int |\alpha(\omega)|^2 d\omega
\]

For the samples doped with P we obtain \( e^2_{\text{Si-P}} = 1.8 \) which compares favourably with the transverse effective charge obtained from Harrison's bond-orbital model \( e^2_{\text{Si-P}} = 2 \). The analysis of the samples doped with B is more difficult as the atomic mass of B is much smaller than that of Si, a fact which leads to the Si-B local modes at \( 840 \text{ cm}^{-1} \). Harrison's model yields in this case \( e^2_{\text{Si-B}} = 0.8 \), a value which is unable to explain the observed enhancement of the Si-Si vibrations.

![Fig. 3: Evolution of the 2475 cm\(^{-1}\) peak after annealing at 510°C for the B-doped sample a-Si (103).](image)

![Fig. 4: Normalized intensities of the 2475, 1890 and 480 cm\(^{-1}\) bands versus annealing temperature for B-doped sample a-Si (103).](image)

References.
1. See, for instance, M.H. Brodsky (ed.), Amorphous Semiconductors, (Springer Verlag, Heidelberg, 1979)

For the samples doped with P we obtain \( e^2_{\text{Si-P}} = 1.8 \) which compares favourably with the transverse effective charge obtained from Harrison's bond-orbital model \( e^2_{\text{Si-P}} = 2 \). The analysis of the samples doped with B is more difficult as the atomic mass of B is much smaller than that of Si, a fact which leads to the Si-B local modes at \( 840 \text{ cm}^{-1} \). Harrison's model yields in this case \( e^2_{\text{Si-B}} = 0.8 \), a value which is unable to explain the observed enhancement of the Si-Si vibrations.