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Hydrogen passivation of boron acceptors in silicon: Raman studies

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Raman scattering is used for an investigation of the passivation of substitutional boron acceptors in crystalline silicon by atomic hydrogen. The disappearance of free holes in the passivated samples can be observed via the changes of the zone-center optical-phonon line shape (Fano broadening). Parallel to the disappearance of the free holes, the localized vibrational modes of substitutional boron vanish, providing direct evidence for pair formation between B and H. A new boron mode at 650 cm^{-1} is observed in the spectra of passivated samples.

In recent years, the phenomenon of hydrogen passivation of shallow donor and acceptor levels in crystalline semiconductors has attracted a great deal of attention. First reported for the case of the boron acceptor state in silicon,[1] an increasing number of experiments has demonstrated that a large variety of shallow impurity states in different materials can be rendered electronically inactive in a reversible way by exposure to atomic hydrogen.[2–5] However, boron-doped crystalline silicon has remained the model substance for experimental and theoretical investigations of the hydrogen passivation mechanism.

Experimentally, it is observed that hydrogen passivation leads to an increase in the resistivity of the passivated region, together with an increase in the mobility of the free charge carriers.[1,6] This indicates that hydrogen passivation decreases the density of electronically active acceptors, thereby decreasing the concentration of free holes and of charged Coulomb scattering centers. These results have also been confirmed by optical studies of the free-carrier infrared absorption[6] and the boron-bound exciton luminescence.[7] On a more microscopic level, secondary-ion mass spectroscopy profiles of the passivated regions in B-doped Si have shown that the hydrogen concentration in the material closely follows the local boron concentration, indicating a spatial correlation between the boron impurities and hydrogen atoms.[8,9] Also, it has been shown that compensation of the p-type Si with shallow donors or the reduction of the free-hole concentration in a reverse-biased p-n junction can affect the diffusion of the atomic hydrogen into the sample and destroy the spatial correlation between the boron and hydrogen profiles.[9–11] Finally, several investigators have observed an infrared absorption band at ≈ 1875 cm^{-1}, which has been attributed to a vibrational mode of hydrogen in the vicinity of a passivated boron acceptor.[6,8,9]

Based on these experimental results, several microscopic models for the hydrogen passivation of shallow acceptors in crystalline silicon have emerged. Pankove, Zanzucchi, Magee, and Lucovsky[8] have suggested that hydrogen breaks one of the four equivalent bonds between a substitutional, fourfold-coordinated boron atom and the four surrounding Si atoms, forming a bridging B-H-Si site. This leaves the boron atoms effectively threefold coordinated and, thus, electronically inactive. The infrared absorption at 1875 cm^{-1} in this model is due to a Si-H stretching mode modified slightly by a small interaction with the boron dopant. A more quantitative discussion of this model has been given by DeLeo and Fowler.[12] A quite different approach has been taken by Assali and Leite,[13] who argued that hydrogen will occupy a nearest-neighbor interstitial site and form a fifth covalent bond with the group-III boron atom. Again, such a fivefold-coordinated boron atom would be electronically inactive, and it was argued that the infrared-active hydrogen mode at 1875 cm^{-1} is due to a B-H covalent bond modified by coupling to the three silicon atoms around the interstitial site.[14] Finally, a third model was proposed by Sah, Sun, and Tzou[15] and Pantelides.[16] These authors suggest that hydrogen passivation of boron in silicon is due to direct electronic compensation between substitutional, fourfold-coordinated boron and interstitial hydrogen. In this model, it is assumed that interstitial hydrogen has a donor level in the gap of silicon. Then, charge exchange between the hydrogen and boron atoms can occur, resulting in the formation of Coulomb-bound H_i^+-B_s^- pairs, without significant covalent bonding. In this model, hydrogen passivation would be microscopically equivalent to the well-known compensation of acceptors in silicon (or germanium) by the interstitial donor Li.

So far, only one experimental result has been reported which is directly linked to the structural processes involved in hydrogen passivation. This is the hydrogen-related mode at 1875 cm^{-1} (1360 cm^{-1} for the case of deuterium[9]) that appears after passivation. In this article, I will report on Raman investigations of hydrogen passivation in boron-doped silicon. It will be shown that Raman scattering can provide detailed information about three aspects of the passivation phenomenon, namely (i) the effect of hydrogen on the concentration of free holes, (ii) the characteristic vibrational modes of hydrogen in the passivation region, and most important, (iii) a direct observation of the effects of hydrogen on the localized vibrational modes of boron-dopant atoms in the silicon crystal.

For the present Raman studies, silicon crystals with boron concentrations between 1×10^{19} and 2×10^{20} cm^{-3} were used. For each boron concentration, several samples were cut from the same region of a silicon ingot with a (111)- or (110)-oriented surface. Half of the samples

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were passivated by exposure to atomic hydrogen for typically 6 h at temperatures around 130 °C; the remaining samples were kept for control purposes. Raman spectra were obtained in conventional backscattering geometry with a scanning double monochromator and with an optical multichannel analyzer (OMA) at room temperature. In most cases, the 514.5-nm line of an Ar^+-ion laser was used for excitation, but equivalent results were also obtained with other laser wavelengths. In order to suppress second-order features due to silicon vibrations in the Raman spectra, perpendicular polarization between exciting and scattered light was usually chosen. In the following, only data for a boron concentration of 6×10^{19} cm^{-3} will be shown, but samples with different dopant concentrations gave qualitatively similar results.

The Raman spectra of an Si sample with a boron concentration of 6×10^{19} cm^{-3} before (control, solid line) and after hydrogen passivation (hydrogenated, dashed line) are shown in Fig. 1 for the spectral region between 450 and 700 cm^{-1}. In the control sample, the presence of a large concentration of free holes causes a significant shift and broadening of the silicon zone-center optical phonon, which has been described in detail by Cerdeira, Fjeldly, and Cardona[17] and Chandrasekhar, Chandrasekhar, Grimsditch, and Cardona.[18] As can be seen from Fig. 1, hydrogen passivation leads to a narrowing of the phonon line and to a shift toward the optical-phonon position of 520 cm^{-1} in undoped silicon, thus indicating the disappearance of a large fraction of the free holes present in the control sample. A quantitative estimate of the free-hole concentrations in the control and passivated samples can be made by fitting the observed Raman line shape in Fig. 1 to the Fano expression[19]

$$I(\omega)\propto(\Gamma q+\omega-\Omega_0-\Delta\Omega)^2/[\Gamma^2+(\omega-\Omega_0-\Delta\Omega)^2] \ , \quad (1)$$

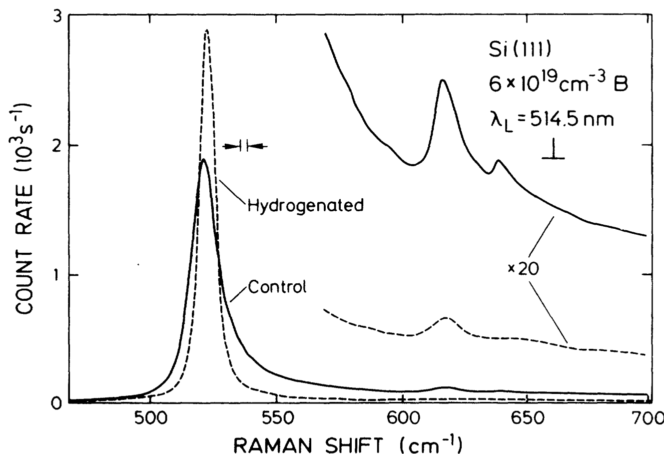

FIG. 1. Raman spectra of boron-doped Si before (control, solid line) and after hydrogen passivation (hydrogenated, dashed curve). The spectra were taken with the 514.5-nm line of an Ar-ion laser and perpendicular polarization between incident and scattered light. The region of localized vibrational modes of ^{11}B (620 cm^{-1}) and ^{10}B (643 cm^{-1}) is also shown magnified.

where ω is the Raman shift, Ω_0 the zone-center optical-phonon frequency in undoped Si, and $\Delta\Omega$, Γ, and q are the parameters describing the frequency shift, broadening, and asymmetry introduced by the presence of free holes. By comparing the line-shape parameters deduced from the spectra in Fig. 1 to those reported in Ref. 18 for samples with different boron concentrations, it can be concluded that hydrogen passivation caused a reduction of the free-hole concentration from 6×10^{19} cm^{-3} ($q=8$, $\Gamma=6$ cm^{-1}) to about 1×10^{19} cm^{-3} ($q=40$, $\Gamma=3$ cm^{-1}) in the case of Fig. 1.

The same conclusion can also be reached by comparing the intensities of the Raman signals due to the localized boron vibrations in the unhydrogenated and hydrogenated samples. These vibrations lead to the two peaks at 620 and 643 cm^{-1} in Fig. 1 (solid line), which correspond to substitutional ^{11}B and ^{10}B atoms at lattice sites with tetrahedral symmetry. The intensity ratio of the two peaks reflects the natural abundance of the two boron isotopes (80% ^{11}B and 20% ^{10}B). After hydrogen passivation, the smaller ^{10}B peak can no longer be resolved, and the intensity of the ^{11}B peak decreases by about a factor of 5. [In fact, most of the remaining peak at ≈620 cm^{-1} in the passivated samples is due to two-phonon Raman scattering (2 LA), which can also be observed in undoped Si with similar intensity.] The disappearance of the localized boron modes proves directly that hydrogen passivation changes the microscopic environment of the substitutional dopant atoms (hydrogen-boron pairing).

Thus both the changes of the Si optical-phonon line shape and the decrease in the local-boron-mode scattering intensity provide a quantitative measure of the effects of hydrogen passivation with Raman scattering. For an independent confirmation of these results, we have also measured the infrared reflectance of the doped and passivated samples in the spectral region of the free-carrier plasma edge shown in Fig. 2. From the shift of the plasma edge upon hydrogen passivation, a decrease of the free-hole concentration from 6×10^{19} cm^{-3} to 7×10^{18} cm^{-3} can be calculated.[20] Moreover, the interference pattern observed in the ir spectra of the hydrogenated specimen allows us to

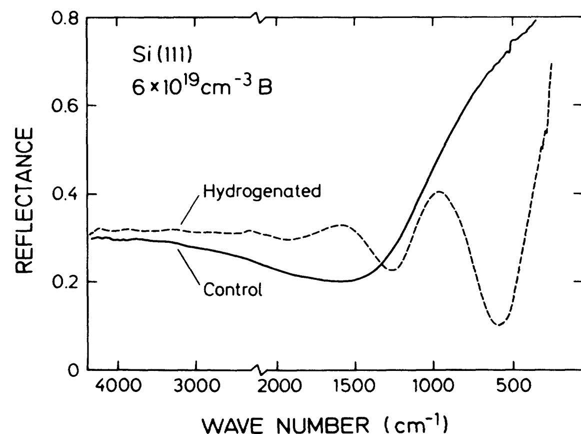

FIG. 2. Infrared reflectance spectra of the samples in Fig. 1.

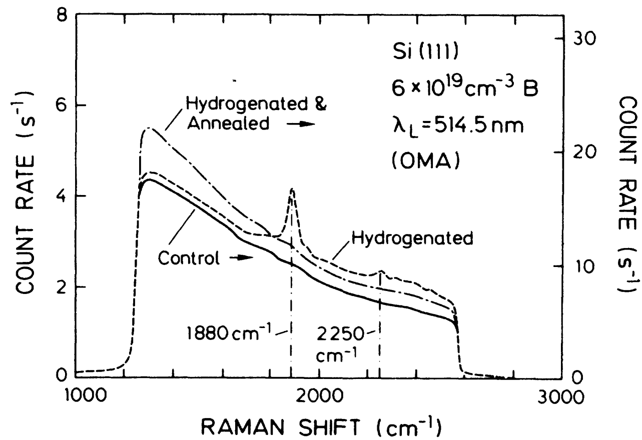

FIG. 3. Raman spectra in the spectral region between 1200 and 2600 cm^{-1} obtained with an optical multichannel system (OMA). Solid line: control sample (no passivation); dashed curve: after hydrogen passivation; dashed-dotted curve: after anneal at 200 °C for 30 min.

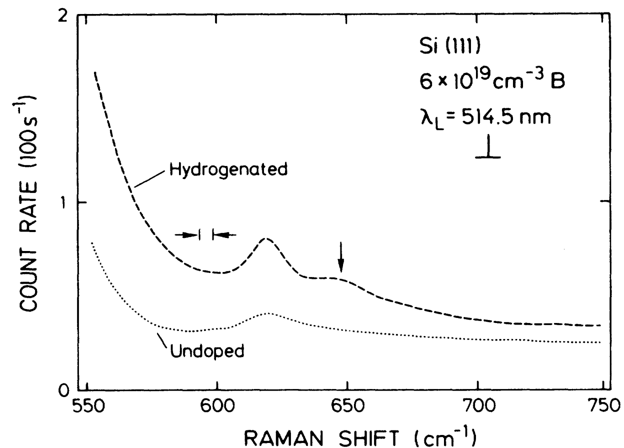

FIG. 4. Raman response of a passivated specimen between 550 and 750 cm^{-1}. The arrow marks the new peak at ≈ 650 cm^{-1}. The Raman spectrum of an undoped Si sample (1600 Ω cm) is shown for comparison.

estimate the thickness of the passivated surface region (about 2.5 μm).

Coming now to the more microscopic aspects of the boron-hydrogen passivation mechanism, I show in Fig. 3 the Raman spectra of unpassivated and passivated silicon samples in the spectral region between 1200 and 2600 cm^{-1}, i.e., the region of hydrogen-related modes. The main feature in Fig. 3 is the appearance of a new Raman peak at 1880 cm^{-1} with a full width at half maximum of ≈ 50 cm^{-1} in the spectrum of the passivated sample. Position and width of this peak are similar to the infrared-active modes in hydrogenated Si(B) samples reported previously.[6,8,9] In addition, a small Raman signal at 2250 cm^{-1} can be resolved, which is tentatively ascribed to OH vibrations in a thin ($\approx$100-Å) surface oxide of the plasma-treated sample. Further experimental evidence for such an oxide layer was provided by spectroscopic ellipsometry measurements performed on the material before and after hydrogen treatment.[21] The third (dashed-dotted) curve included in Fig. 3 exemplifies the reversible nature of the changes in the Raman spectra induced by hydrogen passivation. After isothermal annealing of a passivated sample at a temperature of 200 °C for 30 min, the Raman response of the original, untreated boron-doped silicon was recovered in the whole spectral range between 400 and 2600 cm^{-1}.

In contrast to the appearance of the hydrogen-related vibration at 1880 cm^{-1} as seen in Fig. 3, which has also been observed in previous investigations of the infrared response, a unique aspect of the present Raman studies is the observation of a new vibrational band at ≈ 650 cm^{-1} in passivated specimens shown in Fig. 4. This band is distinctively different in position and intensity from the boron-related Raman peaks in unpassivated silicon (Fig. 1), or the second-order Raman features of undoped crystalline silicon shown in Fig. 4 for comparison (dotted line). One may conclude, therefore, that this additional peak is due to a vibrational mode of boron in the B-H pairs formed during the passivation process. Such pair formation will reduce the tetrahedral symmetry of substitutional boron atoms to axial symmetry with respect to the B-H axis, thereby causing a splitting of the triply degenerate boron mode with T_d point symmetry into a doublet with C_{3v} symmetry. In this respect, boron passivation by atomic hydrogen resembles the well-studied mechanism of lithium compensation of p-type crystalline silicon. Interstitial lithium possesses a donor level in crystalline silicon, so that charge exchange between the B acceptors and the Li donors results in the formation of Coulomb-bound Li^+-B^- pairs with C_{3v} symmetry. For the more abundant ^{7}Li and ^{11}B isotopes, the nondegenerate and doubly degenerate vibrational modes of these pairs lie at 570 and 650 cm^{-1}, respectively.[22,23]

On the basis of the 1880 cm^{-1} hydrogen vibration alone, a definitive decision in favor of any of the three models described in the beginning has not been possible so far. The present results concerning the effect of hydrogen passivation on the local boron modes, therefore, can provide additional criteria which need to be met by a realistic microscopic model. Thus, preliminary calculations suggest that the boron modes will behave quite differently for a bridging versus an interstitial site of the hydrogen atom.[24] In addition, a mechanism similar to the Li compensation appears to be a possible alternative. These questions should provide interesting perspectives for future research.

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