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We have found that hydrogen exists in molecular form in crystalline silicon treated with hydrogen atoms in the downstream of a hydrogen plasma. The vibrational Raman line of hydrogen molecules is observed at 4158 cm^{-1} for silicon samples hydrogenated between 180 and 500 °C. The assignment of the Raman line is confirmed by its isotope shift to 2990 cm^{-1} for silicon treated with deuterium atoms. The Raman intensity has a maximum for hydrogenation at 400 °C. The vibrational Raman line of the hydrogen molecules is broad and asymmetric. It consists of at least two components, possibly arising from hydrogen molecules in different occupation sites in crystalline silicon. The rotational Raman line of hydrogen molecules is observed at 590 cm^{-1}. The Raman band of Si-H stretching is observed for hydrogenation temperatures between 100 and 500 °C and the intensity has a maximum for hydrogenation at 250 °C. [S0163-1829(97)09235-7]

I. INTRODUCTION

Hydrogen in semiconductors has been examined extensively in various experimental and theoretical studies, which indicate there are several configurations of hydrogen in crystalline silicon. Hydrogen introduced in silicon terminates dangling bonds on the surface, and passivates deep-level impurities, as well as shallow acceptors and donors in the bulk.[1] An infrared-absorption experiment has shown that hydrogen introduced in to *p*- or *n*-type silicon forms complexes with acceptor or donor atoms.[2] Other experimental results and theoretical calculations have suggested that {111} platelets[3–8] and a metastable diatomic hydrogen complex[9–11] are formed in heavily doped *n*-type silicon.

Recent theoretical calculations have suggested that the hydrogen molecule is stable in crystalline silicon.[10–15] Chadi and co-workers have performed a calculation of the total energies and defect levels of various hydrogen-related defects using the *ab initio* pseudopotential method, and have suggested that the hydrogen molecule is stable at Si tetrahedral interstitial sites with its axis along a ⟨111⟩ or a ⟨100⟩ direction.[10,11] The bond length of a hydrogen molecule at the tetrahedral interstitial site is calculated to be 0.78 Å, about 0.03 Å longer than that in the gas phase. Van de Walle and co-workers have calculated the energy of hydrogen interacting with bulk silicon and defects in the silicon lattice, using density-functional theory in the local-density approximation and *ab initio* pseudopotentials.[12,13] They have predicted that a hydrogen molecule is stable at the tetrahedral interstitial site oriented along a ⟨100⟩ direction.

In hydrogenated amorphous silicon, hydrogen molecules are observed using infrared absorption[16] and nuclear magnetic resonance.[17] In crystalline silicon, there are several experimental studies suggesting the existence of hydrogen molecules.[18–21] However, all the results are indirect or controversial. Stutzmann and co-workers have studied the transformation of deuterium in *p*-type silicon using thermal desorption, Raman, and infrared-absorption spectroscopy. They inferred the existence of interstitial D_2 molecules after dissociation of *B-D* complexes by thermal annealing at 250 °C for 1 h,[18] although they did not detect any Raman spectrum associated with interstitial D_2 molecules. Johnson and Herring reported an immobile form of nonatomic hydrogen, which they have attributed to molecular hydrogen based on their secondary-ion mass spectrometry measurements.[19] Stallinga *et al.* have performed electron-paramagnetic-resonance experiments on silicon annealed at 250 °C for 30 min after implantation with hydrogen and deuterium.[20] They observed a trigonally symmetric defect center labeled NL52, which they associated with a negatively charged hydrogen molecule. However, they have not reported any isotope effect on implantation with deuterium[20] and Brower *et al.* have reported no level associated with negatively charged hydrogen molecules.[21]

Recently, we have confirmed the existence of hydrogen molecules in crystalline silicon by detecting their vibrational and rotational Raman lines in heavily doped *n*-type crystalline silicon treated with hydrogen atoms.[22–24] Hydrogen molecules have also been seen in GaAs.[25] In this paper, we report a detailed study on the hydrogenation-temperature dependence of the formation of hydrogen molecules by means of Raman measurements. Raman spectra of hydrogen molecules are observed not in only *n*-type silicon with P$^+$ implantation but also in *p*-type silicon without implantation.

The vibrational Raman band assigned to hydrogen molecules consists of at least two components, plausibly corresponding to two different occupation sites in crystalline silicon. The formation of hydrogen molecules is discussed in comparison with that of other hydrogen-related defects such as Si-H bonds and {111} platelets.

II. EXPERIMENTAL METHODS

We used p-type [100] floating zone (FZ) Si (80–100 Ω cm) wafers for our samples. Some of the samples were implanted with P^+ (phosphorus ions) at a dose of $5 \times 10^{14}/cm^2$ at an energy of 50 keV to obtain heavily doped n-type silicon. All the implanted P impurities were electrically activated by furnace annealing at 900 °C for 30 min in an atmosphere of flowing N_2 gas. Other samples were used without P^+ implantation to study the effect of ion implantation and thermal annealing.

A hydrogen atom treatment (HAT) was performed on all the silicon samples using a remote downstream flux of hydrogen atoms from an H_2 plasma for 3 h. The samples were placed in the quartz tube 60 cm from the plasma to suppress damage from the activated species. H_2O gas (0.05 Torr) was added to H_2 gas (0.95 Torr) to increase the amount of hydrogen atoms at the silicon surface. We also performed deuterium atom treatments (DAT) by using D_2 and D_2O instead of H_2 and H_2O, respectively. The substrate temperature during hydrogenation was measured accurately by interference using an infrared-laser ($In_xGa_{1-x}AsP$; $\lambda=1310$ nm) with both surfaces of the wafers mirror-polished, because conventional thermocouples react with hydrogen atoms and their use leads to overestimation of the sample temperature. The substrate temperature during HAT was controlled to an accuracy of ± 2.5 °C. Details of the method and hydrogenation conditions have been reported elsewhere.[26,27]

Depth profiles of hydrogen in the sample after HAT and DAT were obtained by means of secondary-ion-mass spectroscopy (SIMS) measurements using Cs^+ ion beams with a CAMECA IMS 4f system. The total amount of hydrogen is greatest for hydrogenation at 400 °C. For hydrogenation above 600 °C and below 100 °C the concentration of hydrogen is comparable to the background level. This is accounted for in terms of a very large diffusion of hydrogen during the hydrogenation above 600 °C and a very low efficiency in the introduction of hydrogen in the substrate below 100 °C. Figure 1 shows typical depth profiles of hydrogen in the silicon samples without P^+ implantation after HAT. The concentration scale was determined by comparison with a standard sample implanted with hydrogen ions (40 keV H_2^+, $1 \times 10^{15}/cm^2$). The depth profile of hydrogen has a maximum near the surface for the samples, and the penetration depth of hydrogen is larger for higher hydrogenation temperature. The profile for the samples with P^+ implantation is similar except for a slight shift of the concentration peak to a greater depth.

Raman scattering measurements were performed at room temperature and 90 K. A cw argon-ion laser (Coherent Model INNOVA 70) with a wavelength of 514.5 nm was used as the excitation source. Scattered light, collected at 90 °, was analyzed using a triple grating monochromator (JASCO TRS-600) with a wave-number resolution of up to
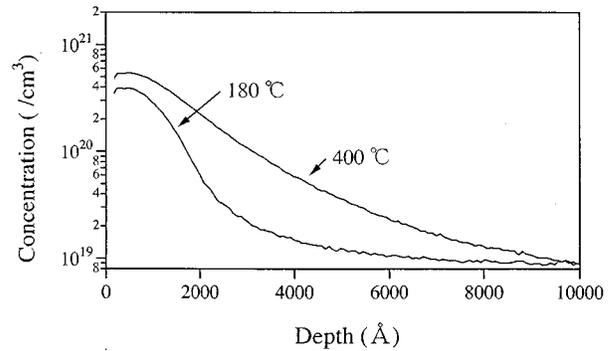

FIG. 1. Depth profiles of hydrogen for the silicon samples without P^+ implantation treated with hydrogen atoms at 180 and 400 °C.

0.2 cm^{-1} at best, and detected with a spectrometric multichannel analyzer (Princeton Instruments Inc. D/SIDA 700). Raman shifts ranging from 300 to 4300 cm^{-1} were measured.

III. RESULTS

Figure 2(a) shows a Raman spectrum for the sample with P^+ implantation after treatment with atomic hydrogen at 400 °C (HAT-400 °C). A Raman line observed at around 590 cm^{-1} after HAT is assigned to the $S_0(1)$ ($\Delta J=2$, $\Delta \nu=0$, and $J=1$; here J and ν are the rotational and vibrational quantum numbers, respectively) rotational line of H_2.[22,23] The rotational line of para-H_2 was not observed in the present study, because of the overlap with Raman lines of bulk silicon. A broad Raman band at 4158 ± 3 cm^{-1} is assigned to the Q_1 ($\Delta J=0$ and $\Delta \nu=1$) vibrational line of the hydrogen molecule in crystalline silicon.[22,23] The Raman shifts of the rotational and vibrational lines agree well with those of gaseous or solid hydrogen molecules, while the widths are much larger even compared with those in solid phase.[28–30] A broad and asymmetric Raman band observed at around 2100 cm^{-1} is assigned to the stretching band of Si-H bonds in crystalline silicon.[22] We also measured Raman spectra for the samples without P^+ implantation. The rotational and vibrational Raman lines of H_2 at 590 and
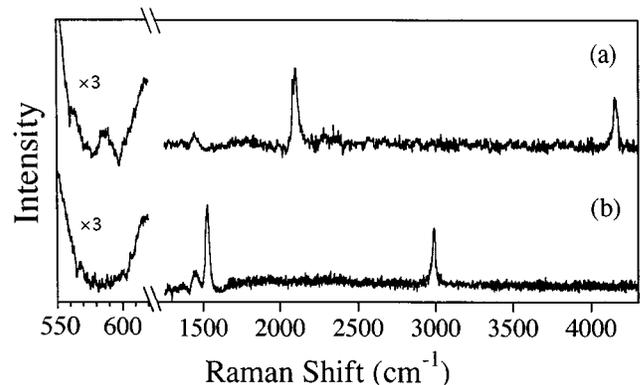

FIG. 2. Raman spectra of crystalline silicon (with P^+ implantation) (a) after treatment with atomic hydrogen at 400 °C and (b) after treatment with atomic deuterium at 400 °C.
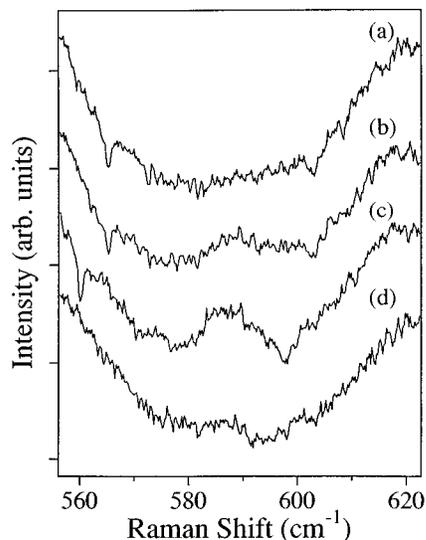
FIG. 3. The rotational Raman line of H_2 in crystalline silicon (with P^+ implantation) treated with hydrogen atoms at various hydrogenation temperatures: (a) 250 °C, (b) 350 °C, (c) 400 °C, and (d) 500 °C.

FIG. 4. The vibrational Raman line of H_2 in crystalline silicon with P^+ implantation (a) before hydrogenation, and after hydrogenation at (b) 180 °C, (c) 250 °C, (d) 300 °C, (e) 400 °C, and (f) 600 °C. The dashed lines are decomposed components using Gaussian shapes.

4158 cm^{-1}, respectively, were observed and have almost the same line shape as those for the samples with P^+ implantation. This indicates that hydrogen molecules are not trapped at defects remaining after annealing the P ion-implanted silicon. The Raman band assigned to Si-H stretching was also observed at around 2100 cm^{-1} for the sample without P^+ implantation. Figure 2(b) shows a Raman spectrum of the sample treated with deuterium atoms at 400 °C (DAT-400 °C). The Raman band at 4158 cm^{-1} was not observed for the DAT sample. A broad Raman line at around 2990 cm^{-1}, which was not observed for the HAT sample, is assigned to the vibrational Raman line of D_2.[22,23] This isotope shift confirms that the Raman band at 4158 cm^{-1} results from hydrogen molecules in crystalline silicon. The band at around 1530 cm^{-1} is assigned to the stretching band of Si-D bonds in crystalline silicon.[22]

To exclude the possibility that the Raman signals of H_2 arise from a very thin layer in the vicinity of the surface, which may be damaged by hydrogenation, we performed chemical etching of the surface layer with sequential rinses in HNO_3 followed by HF. Even after etching away about 100 Å, the vibrational Raman line of 4158 cm^{-1} showed no decrease in its intensity. We consequently conclude that hydrogen molecules exist not in damaged regions near the surface, but in bulk silicon crystal.

Figures 3 and 4 show the rotational and vibrational lines of H_2 for the sample with P^+ implantation treated with various hydrogenation temperatures. The vibrational line was clearly observed at the hydrogenation temperatures between 180 and 500 °C while the rotational line was visible only between 300 and 400 °C because of overlap with the intense Raman bands of bulk silicon. The intensities of the rotational and vibrational lines are largest at hydrogenation temperature of 400 °C. Figure 5 summarizes the intensity of the vibrational line as a function of hydrogenation temperature. The absence of the vibrational line for hydrogenation at 600 °C is consistent with the result of the SIMS experiments.[26,27] The
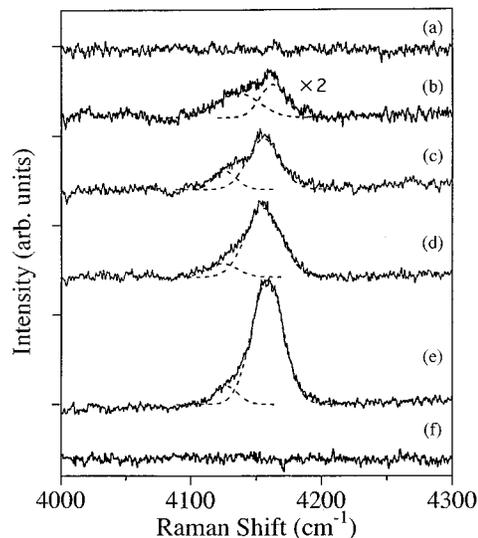
width of the vibrational line of H_2 decreases with increasing hydrogenation temperature, while the Raman shift was almost constant at $4158 \pm 3 \text{ cm}^{-1}$. Between the samples with and without P^+ implantation little difference was observed in the hydrogenation-temperature dependence of the intensity, the Raman shift, and the width.

Figures 6 and 7 show the Raman spectra of Si-H stretching for the sample with and without P^+ implantation, respectively. The Raman band of Si-H was observed for hydrogenation between 100 and 500 °C. The spectral shape of the Si-H stretching changes with hydrogenation temperatures for the samples with P^+ implantation, whereas it is almost constant for the samples without P^+ implantation. The line shape for hydrogenation at 180 °C is particularly different; the Raman band for the samples without implantation has a peak at around 2100 cm^{-1} with a shoulder at about 2130 cm^{-1},
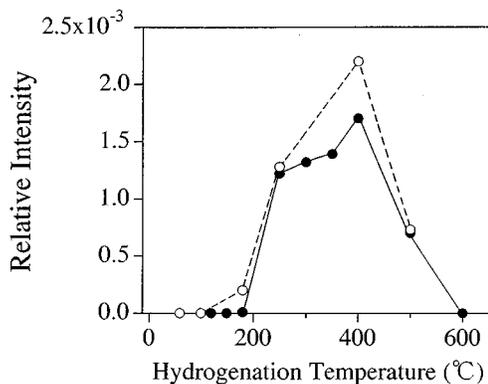

FIG. 5. The intensity of the vibrational Raman line of H_2 as functions of the hydrogenation temperature. The closed and open circles indicate the results for the samples with and without P^+ implantation, respectively. The Raman intensities are normalized by that of the optical-phonon line of silicon at 521 cm^{-1}.
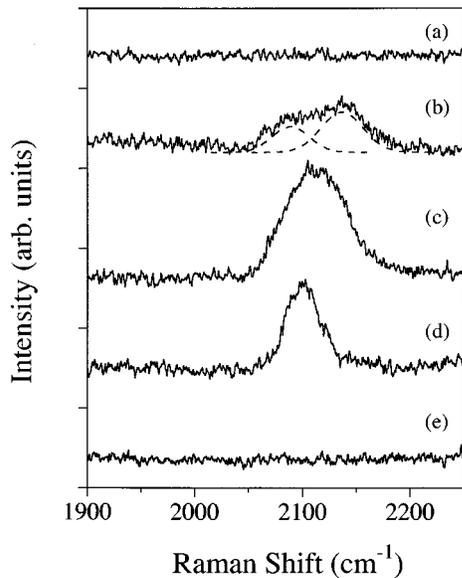
FIG. 6. Raman spectra of Si-H stretching for crystalline silicon with P$^+$ implantation (a) before hydrogenation, and after hydrogenation at (b) 180 °C, (c) 250 °C, (d) 400 °C, and (e) 600 °C. The dashed curves are decomposed components using Gaussian line shapes.

while for the samples with implantation treated at hydrogenation temperatures of 150–180 °C the peak is centered at around 2130 cm^{-1} with a shoulder peak at about 2100 cm^{-1}. Figure 8 summarizes the intensity of the Si-H stretching band as a function of the hydrogenation temperature. It has a maximum at 250 °C for the samples with and without P$^+$ implantation. The intensity maximum corresponds to the temperature above which {111} platelets are unstable.[4,27]

IV. DISCUSSION

The intensity of the vibrational Raman line of H$_2$ has a maximum at the hydrogenation temperature of 400 °C, while
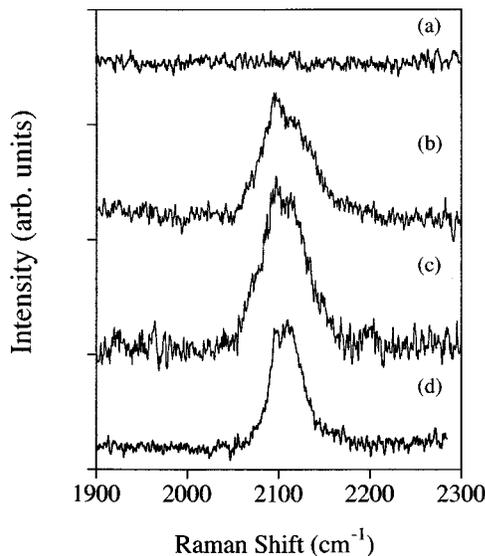

FIG. 7. Raman spectra of Si-H stretching for crystalline silicon without P$^+$ implantation (a) before hydrogenation, and after hydrogenation at (b) 180 °C, (c) 250 °C, and (d) 400 °C.
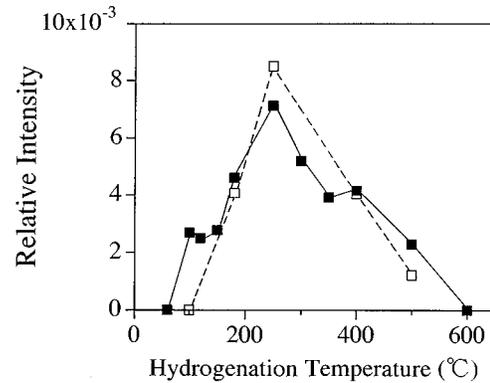

FIG. 8. The Raman intensity of the Si-H stretching line as a function of the hydrogenation temperature. The closed and open squares indicate the results for the samples with and without P$^+$ implantation, respectively. The Raman intensities are normalized by the Raman optical-phonon line of silicon at 521 cm^{-1}.

that of the Si-H stretching line occurs at 250 °C. The SIMS measurements show that the total amount of hydrogen introduced in silicon is greatest for hydrogenation at 400 °C. The hydrogenation-temperature dependence of the formation of H$_2$ and Si-H is consistent with that of the electron spin resonance (ESR) linewidth of the donor and/or conduction electrons at 4.2 K for HAT samples.[31] The ESR linewidth has two maxima at around 200 and 400 °C. The maximum at 200 °C is explained by the hyperfine interaction between electrons and nuclear spin of a single H atom such as H atoms in Si-H bonds, while that at 400 °C is predominantly by the interaction between electrons and nuclear spin of H$_2$. The maximum at 400 °C showed an isotope effect between H and D.[31] This shows that H$_2$ does not exist in voids or bubbles, where the wave function of donor and/or conduction electrons would not penetrate deep enough, but in the interstitial site in crystalline silicon.

The vibrational line of H$_2$ is very broad and asymmetric. We decomposed the spectra using two Gaussian line shapes, as shown with the dashed lines in Fig. 4. The two components have peaks at about 4160 and 4130 cm^{-1}. The intensities of the two components are shown in Fig. 9 as a function of the hydrogenation temperature. The intensity of the component at 4160 cm^{-1}, which is always much larger than
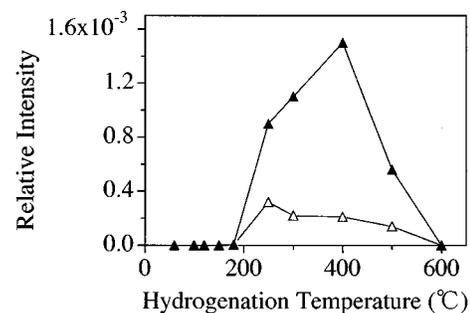

FIG. 9. The intensities of the components at 4130 cm^{-1} (open triangles) and 4160 cm^{-1} (closed triangles) of the sample with P$^+$ implantation as a function of hydrogenation temperature. These intensities are normalized by the Raman optical-phonon line of silicon at 521 cm^{-1}.

the other component, has a maximum at 400 °C, while the intensity of the component at 4130 cm^{-1} is largest at 250 °C. The components are assigned to H_2 in two different occupation sites in crystalline silicon. A tetrahedral interstitial (T_d) site has been proposed as one of the occupation sites of H_2 in crystalline silicon, according to recent theoretical calculations.[10–15] We attribute the component at 4160 cm^{-1}, which is the more intense, to H_2 in the T_d site. The hydrogenation-temperature dependence of the intensity of the component at 4130 cm^{-1}, especially the decrease above 250 °C, is similar to that of the Si-H stretching as shown in Fig. 8. Therefore, we tentatively, assigned the component at 4130 cm^{-1} to H_2 in a distorted T_d site where an Si-H bond is located as the nearest neighbor.

Each component of the vibrational line of H_2 after decomposition is still very broad compared with the vibrational line of gas, liquid, and solid H_2.[28–30] The present Raman measurements have a spectral resolution of 0.2 cm^{-1}, fine enough to distinguish the vibrational lines of para- and ortho-H_2 [$Q_1(0)$ and $Q_1(1)$] in gas or solid phase. Yet no fine structure due to para- and ortho-H_2 is observed in the Q_1 vibrational line in the present study. The broadening of the vibrational line of H_2 is too large to be explained by high-pressure gaseous H_2. The width of the vibrational Raman line of gaseous H_2 at room temperature is no more than 3 cm^{-1} at a pressure of 2000 atm,[29] which corresponds to the pressure of gaseous H_2 trapped in microvoids in heavily hydrogenated amorphous silicon.[16] On the other hand, for H_2 dissolved in vitreous silica, the width of the vibrational line of H_2 was about 20 cm^{-1} at room temperature and exhibited significant narrowing with decreasing measurement temperature.[32] The temperature-dependent part of the width is explained in terms of motional broadening including rotational relaxation while the temperature-independent width obtained by the extrapolation to 0 K results from the inhomogeneous broadening. In the present study the width of the vibrational line of H_2 in crystalline silicon does not change with the measurement temperature down to 90 K. We therefore attribute the broadening of the vibrational line not to motional broadening but predominantly to inhomogeneous broadening. A plausible explanation for the inhomogeneous broadening is orientational effect. Recently, Nakamura and co-workers calculated the potential of a hydrogen molecule in a silicon cluster ($Si_{10}H_{16}$) using the *ab initio* Hartree-Fock method.[14,15] They found that the most stable configuration of a hydrogen molecule in the cluster is at the tetrahedral interstitial site, oriented along a $\langle 100 \rangle$ direction with a bond length of 0.70 Å, about 0.04 Å shorter than in gas phase. The vibrational frequency of the hydrogen molecule is calculated to be 4470 cm^{-1}, which is in agreement with the present study. They also calculated the orientational effect on the vibrational energy of H_2 at the T_d site, and found that it has a distribution of about 30 cm^{-1}. This value is comparable to the width of the vibrational Raman line of H_2 in crystalline silicon observed in the present study. Thus the orientation of H_2 is a plausible origin of the inhomogeneous broadening of the vibrational Raman line of H_2 in crystalline silicon.

The Raman spectra of Si-H stretching for the HAT-180 °C sample is asymmetric, consisting of two components at 2100 and 2130 cm^{-1}. Deak *et al.* calculated the structure of hydrogen platelets using the self-consistent semiempirical MINDO/3 Hamiltonian, in which pairs of hydrogen atoms saturate the broken bonds between two adjacent Si atoms at the (111) surface.[5] According to their calculation, Si-H stretching has energies of 2095 and 2122 cm^{-1}. Heyman *et al.* reported local vibrational modes of hydrogen-induced platelets at 2065, 2095, and 2125 cm^{-1} in crystalline silicon after plasma hydrogenation.[6] The peak wave numbers of the two components in the present study are in agreement with the theoretical and experimental (2095 and 2125 cm^{-1}) values. However, the thermal stability of the two peaks is different in the present study: the peak at 2100 cm^{-1} persists for hydrogenation up to 500 °C, while that at 2130 cm^{-1} vanishes for a hydrogenation temperature above 250 °C. We attribute the peak at 2130 cm^{-1} to the Si-H bonds in platelets and 2100 cm^{-1} to isolated Si-H bonds other than platelets, since a TEM study showed that platelets are not stable above 250 °C.[4] The assignment is consistent with the intensity for the sample with P^+ implantation being larger than that for the sample without P^+ implantation, since platelets are known to be formed preferentially in heavily doped *n*-type silicon.[1] The higher wave number of the peak may be a consequence of the strains and stress given to the Si-H bonds in {111} platelets.

V. CONCLUSIONS

We have confirmed the existence of hydrogen molecules in crystalline silicon treated with hydrogen atoms at hydrogenation temperatures between 180 and 500 °C by means of Raman measurements. The vibrational and rotational Raman lines of hydrogen molecules in crystalline silicon are observed at 4158 and 590 cm^{-1}, respectively. The vibrational Raman line of deuterium molecules in crystalline silicon is observed at around 2990 cm^{-1}. The intensity of the vibrational Raman line of H_2 has a maximum for a hydrogenation temperature of 400 °C. The formation efficiency of hydrogen molecules is similar for samples with or without P^+ implantation. The broad and asymmetric Raman spectrum of H_2 suggests that the configurations for the hydrogen molecules are not unique in crystalline silicon. We decomposed the Raman spectrum into two components. The component at about 4160 cm^{-1} is assigned to H_2 in the tetrahedral interstitial site in crystalline silicon, which was predicted by the theoretical calculations, and the component at about 4130 cm^{-1} tentatively to H_2 in the T_d site having an Si-H bond as the nearest neighbor. The Raman spectrum of Si-H stretching was observed for hydrogenation temperatures between 100 and 500 °C. Its intensity has a maximum at 250 °C. The Raman peak at 2130 cm^{-1}, observed for the samples treated with hydrogen atoms at the substrate temperatures between 150 and 250 °C, is attributed to Si-H in {111} platelets.

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