Dissociation, transformation, and recombination of Si-H bonds in hydrogenated crystalline silicon determined by *in situ* micro-Raman spectroscopy

Y. Ma,* Y. L. Huang, R. Job, and W. R. Fahrner

University of Hagen, Chair of Electronic Devices (LGBE), Haldener Str. 182, P.O. Box 940, D-58084 Hagen, Germany
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In situ Raman measurements are applied on plasma hydrogenated Czochralski (Cz) silicon samples. The thermal evolutions of several hydrogen related defects, i.e., Si-H bonds (corresponding Raman peak at ~ 2095 cm^{-1}) at the thin surface layer of the sample, Si-H bonds (Raman peaks at ~ 2105 and ~ 2110 cm^{-1}) at the inner surfaces of the hydrogen induced platelets (HIPs), and H_2 molecules (Raman peak at ~ 4150 cm^{-1}) in the open space of the HIPs are investigated. We find strong evidence for an Si-H bond dissociation and recombination at elevated temperatures ($T \geqslant 350$ °C) and at room temperature (RT), respectively. The dissociation energies of about 2.2 and 2.4 eV (assuming a jump frequency of 10^{13} s^{-1}) for the Si-H bonds at the thin surface layer and at the inner surfaces of the HIPs are obtained, respectively. It is found that at RT the hydrogen atoms which are released at elevated temperatures are trapped again by the HIPs and passivate the silicon dangling bonds at the inner surfaces of the HIPs or form H_2 molecules in the open HIP volume, possibly relating to the basic mechanism of the hydrogen-induced exfoliation of the silicon wafer and the so-called "smart-cut" process.

INTRODUCTION

Hydrogen in silicon has been intensively studied for about three decades since it plays a major role for a lot of important processes in the semiconductor industry.[1,2] Infrared (IR) spectroscopy and Raman spectroscopy (RS) are powerful methods for the examination of hydrogen-related defects within silicon, such as Si-H bonds, V-H complexes, and H_2 molecules. Numerous IR-absorption investigations on the thermal evolution of various Si-H or V-H IR bands have been carried out since the late 1970s [see, e.g., Refs. 3–6]. However, definitive assignments for specific absorption peaks are still somewhat problematic, and some of them are even full of controversies.

Recently, due to the discovery of the HIPs, which play a basic role in the so-called "smart-cut" technology,[7] this issue has attracted an intense interest again. A lot of different structural models of the HIP have been suggested based on both, theoretical and experimental investigations (see, for instance, Refs. 6 and 8–11). Generally, it is suggested that the HIPs trap H_2 molecules, build up an internal pressure and finally lead to cracking.[7] RS is an effective method to investigate both the Si-H bonds and the H_2 molecules within silicon.[12] With applying RS on the beveled surface of the plasma hydrogenated Cz silicon wafers, the assignments for several specific Si-H peaks have been achieved, i.e., the peak at ~ 2095 cm^{-1} stemming from the Si-H bonds at the thin surface layer of the sample, and the peak at ~ 2110 cm^{-1} from those at the inner surface of the HIPs.[13] These recent works imply that the evolution of certain Si-H bonds, H_2 molecules and HIPs can be related to each other. The purpose of this paper is to investigate the thermal evolution of certain Si-H bonds and of the H_2 molecules in the hydrogenated crystalline silicon by the *in situ* μ-Raman spectroscopy, i.e., the measurement is carried out on the same position during the sample annealing process.

EXPERIMENTAL

The substrate wafers were the boron doped [100]-oriented Cz silicon wafers. The resistivities were $5-10$ Ω cm, the diameter 12 cm, and the thickness 400 μm. Plasma hydrogenations were done in a PECVD-setup. The applied plasma power was 50 W. The samples treated with a plasma frequency of 13.56 MHz were labeled sample #1. The samples treated with a plasma frequency of 110 MHz were labeled sample #2. The plasma hydrogenations were applied for 1 h at a substrate temperature of about 250 °C and a hydrogen flux of 200 sccm. After hydrogenation, the wafers were cut into square pieces with sizes of $\sim 1 \times 1$ cm^2. The samples were fixed on a small hotplate, which was mounted on the sample stage under the microscope of the μ-Raman system to keep the measurement spot on the same position of the sample.

The *in situ* μ-Raman measurements were carried out following two different procedures.

Procedure A: *in situ* Raman measurements at elevated temperatures. In this case only the Si-H stretch mode related Raman spectra were recorded. The measurements were done in several steps. (1) The Raman system was adjusted to an optimum status by maximizing the intensity of the Si phonon peak (at 520 cm^{-1}). This was done via adjusting the focus of the Raman laser on the sample surface. The first Raman spectrum was then measured on the as-plasma treated sample under ambient conditions (~ 27 °C). (2) The sample temperature was rapidly increased to a desired temperature (such as 450 °C) in about 3 min and maintained within ± 0.5 °C. Twenty minutes later the Raman system was refocused and the second Raman spectrum was measured at the desired temperature. Refocusing of the Raman system was necessary due to the change of the measurement temperature (from RT to elevated temperature). (3) A series of isochronal spectra was measured at the desired temperature every 20 min, until

the annealing duration reached 340 min. (4) Finally the sample was slowly cooled down to RT within about half an hour, the Raman system was refocused again (because of the temperature change) and the last Raman spectrum was measured at RT. The measurement spot was kept on the same local position of the sample surface for the series of Raman spectra obtained at every desired temperature.

Procedure B: *in situ* Raman measurements at RT. In this case the Raman spectra related to both Si-H bond and H_2 molecule stretch modes were recorded. The steps were as follows. (1) The Raman system was focused for an optimum status, and then the first Raman spectrum was measured on the as-plasma treated sample under ambient conditions ($\sim$27 °C). (2) The sample temperature was rapidly increased to a desired temperature in about 3 min and maintained within ±0.5 °C. The annealing duration was 5 min. (3) When the annealing step was finished, the sample was rapidly cooled down to RT in about 1 min. The Raman system was refocused and the second Raman spectrum was measured at RT. (4) The sample temperature was rapidly increased to the desired temperature again and maintained again for 5 min, so that the total annealing duration for this sample was 10 min. The sample was rapidly cooled down to RT again, then the Raman system was refocused and the third Raman spectrum was measured at RT. Step (4) was repeated until the total annealing duration reached 120 min. The measurement spot was kept on the same local position of the sample surface for the series of Raman spectra obtained at every desired temperature.

In both procedures A and B the collecting time of Raman measurements was set to 1 min, and the average factor 15 times. The center of the spectral window was set to 2100 cm^{-1} (for Si-H spectra) or 4000 cm^{-1} (for H_2 spectra), so the recorded spectra extended from $\sim$1300 to $\sim$2700 cm^{-1} (for Si-H spectra) or from 3400 to 4500 cm^{-1} (for H_2 spectra). The spectral resolution of the measured Raman spectra was $\sim$0.7 cm^{-1}. A special 50× objective, which was designed for high temperature measurements, was used. Due to the various configurations of the Si-H bonds in the H-plasma treated Cz silicon samples, the Raman spectrum related to Si-H bond stretch modes always showed a very broad and complex peak. Lorentz function fitting was employed to decompose the Si-H Raman peak into several Lorentz subpeaks, which originate from the corresponding vibrating species. The area which was enveloped by a subpeak is a measure for the concentration of the corresponding vibrating species. Consequently the total area underneath the whole peak represents the intensity of all kinds of Si-H bonds. Similar mathematical treatments were also employed for Raman spectra related to the H_2 molecules in HIPs.

RESULTS

In Figs. 1(a) and 1(b), the series of Raman spectra measured on samples #1 and #2 by procedure A at 350 °C is shown, respectively. The spectrum marked with "as plasma" is measured at RT on the as plasma treated sample (i.e., before annealing), while the spectrum marked with "RT" is also measured at RT but on the annealed sample (i.e., after
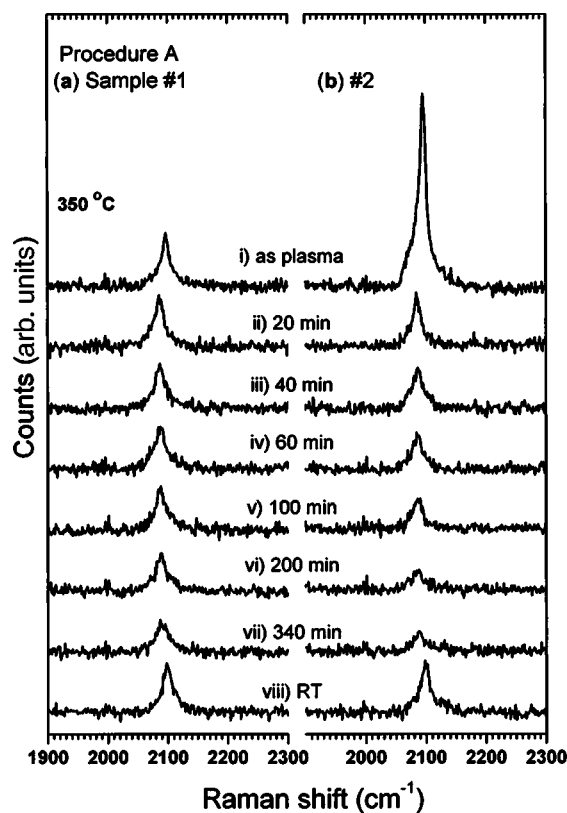

FIG. 1. Series of Raman spectra measured on sample #1 (a) and #2 (b) by procedure A at 350 °C. Spectra (i) and (viii) are measured at RT. Spectra (ii)–(vii) are measured at 350 °C.

annealing, for details see section "Experimental"). As can be seen in Fig. 1, for the spectra measured at RT [spectra (i) and (viii)], the peak is centered at $\sim$2095 cm^{-1}. For the other spectra, the Raman shift of the peak center is reduced by about 10 cm^{-1} to a value of $\sim$2085 cm^{-1} due to the measurement at higher temperature. The intensity of the Raman peak roughly decreases with the annealing duration [see Figs. 1(a) and 1(b), the tendency is even more evident on sample #2]. Since the concentration of the Si-H bonds is proportional to the peak intensity, one can conclude that the dissociation of the Si-H bonds occurs in both samples #1 and #2 at 350 °C. However, it is obvious that at the beginning of the annealing process the dissociation process of the Si-H bonds in sample #2 is faster than for sample #1.

The intensity of the Si-H bonds increases when the samples are cooled down again to RT upon annealing at elevated temperature [see the changes between spectra (vii) and (viii) in Fig. 1], hinting at the recombination of the Si-H bonds at RT. Figure 2 shows the Raman spectra measured on samples #1 and #2 by procedure A at 400 °C, 450 °C, 500 °C, and 550 °C. The recombination of Si-H bonds is even more evident at 400–500 °C for sample #1, and at 400 °C for sample #2, because the intensities of Si-H bonds at the desired temperatures are nearly zero before the samples are cooled down to RT, while the Si-H peak suddenly appears again at RT.

Figure 3 shows the Raman spectra measured by procedure B on sample #1, of both Si-H [Fig. 3(a)] and H_2 [Fig. 3(b)]
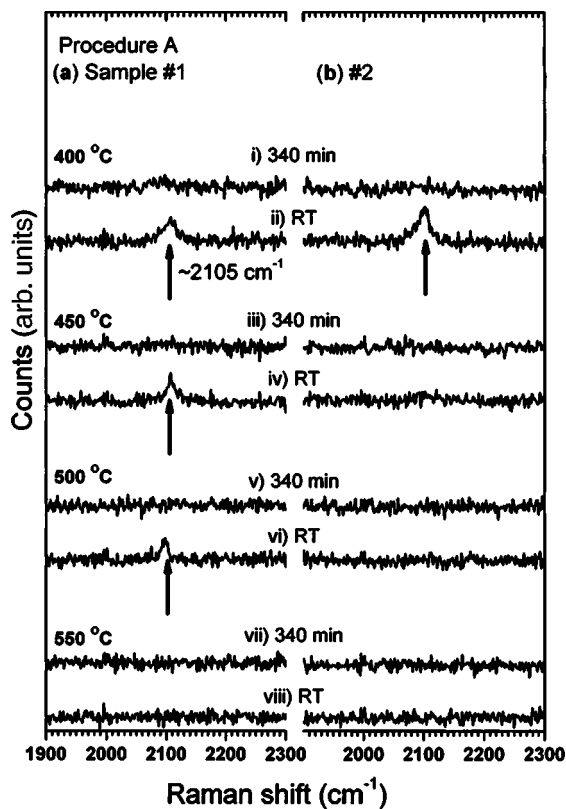
FIG. 2. Raman spectra measured on sample #1 (a) and #2 (b) by procedure A at 400–550 °C. Spectra (i), (iii), (v), and (vii) are measured on the sample during annealing. The annealing duration is 340 min. Spectra (ii), (iv), (vi), and (viii) are measured on the annealed sample at RT (i.e., after annealing).
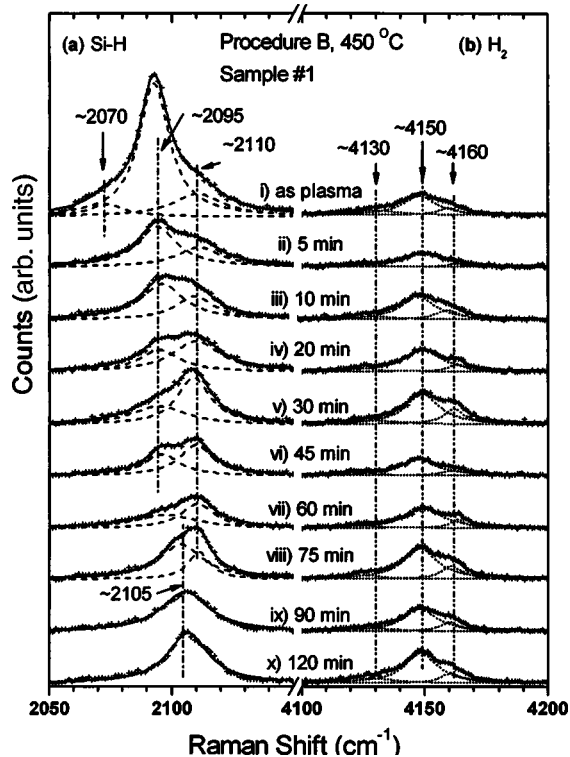

FIG. 3. Series of Raman spectra measured on sample #1 by procedure B. The sample is annealed at 450 °C; (a) shows the spectra related to the Si-H stretch modes, and (b) shows the spectra related to the H_2 stretch modes. The spectra are fitted with Lorentz function (plotted by the dashed and dotted lines). Several subpeaks at ~2070, ~2095, ~2105, ~2110, ~4130, ~4150, and ~4160 cm^{-1} are indicated by the vertical dash-dot or dash-dot-dot lines.

stretch modes. The annealing temperature is 450 °C. The annealing duration covers the range from 5 min to 2 h. The spectra are measured at RT and at the same local position on the surface of the sample. By Lorenz fitting the Si-H peaks can be decomposed into one, two or three subpeaks depending on the annealing duration. The subpeaks are centered at ~2070, ~2095, ~2105, or ~2110 cm^{-1}. In Fig. 3(b), based on the Lorenz fitting, all of the H_2 peaks can be decomposed into three subpeaks, i.e., ~4130, ~4150, and ~4160 cm^{-1}. It has been suggested that the subpeaks at ~4150 and 4160 cm^{-1} can be contributed to the ortho-H_2 molecules (with parallel nuclear spins) and para-H_2 molecules (with anti-parallel nuclear spins), respectively.[13,14]

DISCUSSION

Dissociation of Si-H bonds

According to the first order kinetic theory,[15] the concentration of Si-H bonds N can be expressed as

$$\ln(A) = \ln(A_0) - t \cdot \nu \cdot \exp\left(\frac{-E_d}{k_B T}\right), \qquad (1)$$

where A_0 is the initial concentration of Si-H bonds, t is the annealing duration, ν is the jump frequency, E_d is the dissociation energy, k_B is the Boltzmann's constant, and T is the

temperature. As an example, for the annealing temperature of 350 °C we plot ln (A) versus the annealing duration t in Fig. 4. Here we exclude the Si-H concentration of as plasma treated sample, because its Raman spectrum is measured at RT. Figure 4 shows that within the measurement error $-\ln (A)$ is proportional to t. For both samples #1 and #2 a
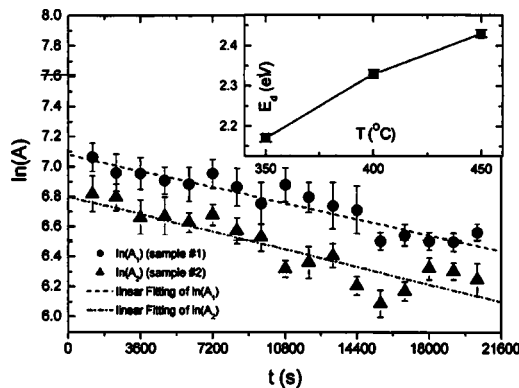

FIG. 4. Annealing duration dependence of the area of the Si-H Raman peaks measured on sample #1 (circle) and #2 (up triangle) at 350 °C by procedure A in the natural logarithmic scale. The inset shows the dissociation energy deduced from the Raman measurements at different temperatures.

slope of $b = -3 \pm 0.3 \times 10^{-5}$ s^{-1} is deduced. If we set the jump frequency ν to 10^{13} s^{-1},[16] the dissociation energy E_d is 2.17 ± 0.01 eV. This energy is much lower than the activation energy when the hydrogen atom is released from Si-H bond to the free space (~ 3.6 eV), but rather similar to the energy when the released H atom is trapped in the bond-center position in the crystalline silicon bulk (~ 2.5 eV), as was estimated by *ab initio* density-functional calculations[17]).

The dissociation energies deduced from the isochronal Raman spectra measured at 350, 400, and 450 °C by procedure A are compared in the inset of Fig. 4. The dissociation energy increases with the annealing temperature, implying different thermal stability of different Si-H species. This issue will be discussed again below, combined with the discussion of the transformation of the Si-H bond species.

Recombination of Si-H bonds

When the samples are cooled down to RT again, the peak intensities increase, both in samples #1 and #2, indicating the recombination of the Si-H bonds at RT upon the dissociation at elevated temperature. However, one can discuss whether the spectra obtained by the *in situ* Raman measurements at elevated temperature and RT are comparable or not. In general, the observed Raman intensity (Stokes scatter) can be expressed as[18]

$$I_R = A \frac{(\upsilon_0 - \upsilon_k)^4}{\upsilon_k}[1 - \exp(-hc\upsilon_k/k_B T)]^{-1}, \quad (2)$$

where υ_0 and υ_k are the wave numbers of the exciting radiation and the excited vibration. A is a constant without impact of the temperature T, and k_B is the Boltzmann's constant. In the case of Si-H stretch modes, the wave number is 2100 cm^{-1} at RT. It is several cm^{-1} lower at higher temperatures than at RT. The estimation shows that the change of the intensity due to the different measurement temperatures is less than 5% (i.e., if comparing the values for RT and 500 °C). Therefore, it is expected that the recombination of Si-H bonds can be investigated by *in situ* Raman measurements at RT and elevated temperature, at least qualitatively. So there is no doubt that Figs. 1 and 2 clearly reveal the recombination of the Si-H bonds at RT after they have been dissociated during annealing at elevated temperatures.

Transformation of Si-H bond species

As can be seen in Fig. 3, it is evident that the transformation of various Si-H bond species occurs during the annealing. For a quantitative comparison, in Fig. 5(a) we plot the time dependence of the sum of the areas of the peaks at ~ 2105 and ~ 2110 cm^{-1}, together with the time dependence of the area of the H$_2$ peak. The time dependence of the area of the individual Si-H Raman subpeaks and the time dependence of the area of the whole Si-H peak are plotted in Fig. 5(b).

The subpeak at ~ 2070 cm^{-1} only appears for the as plasma treated sample. Due to its frequency and thermal annealing behavior, we assign it to the vacancy-hydrogen complex (VH). After annealing the vacancies are probably an-
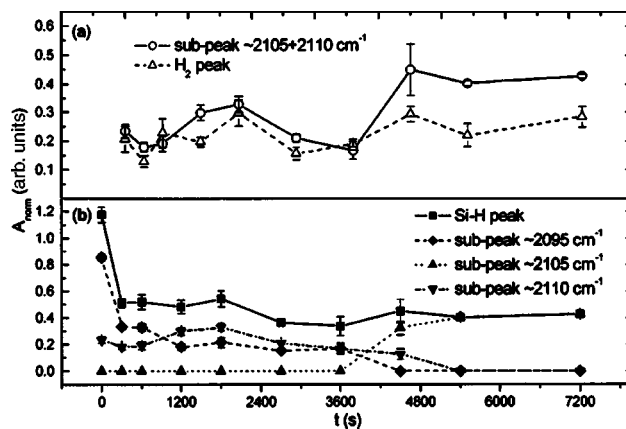

FIG. 5. The normalized area of the Si-H subpeaks and H$_2$ peak measured on sample #1 at 450 °C by procedure B. (a) Shows the area of the H$_2$ peak and the sum of the Si-H subpeaks at ~ 2105 and 2110 cm^{-1}. (b) Shows the area of the whole Si-H peak and several subpeaks at ~ 2095, ~ 2105, and ~ 2110 cm^{-1}.

nealed out or aggregated to voids so that the recombination of VH cannot occur after the sample is cooled down to RT again. Nielson *et al.*[19,20] have also reported that this defect is stable up to 200 °C in proton implanted material.

As shown in Figs. 3(a) and 5(b), it is evident that the intensity of the subpeak at ~ 2095 cm^{-1} decreases almost monotonously with the annealing duration. This peak has been assigned to the Si-H bonds which are located at the H-plasma damaged thin surface layer (extend from surface down to ~ 0.2 μm depth).[13] However, two other subpeaks, i.e., at ~ 2105 and ~ 2110 cm^{-1}, show different tendencies as compared to the subpeak at ~ 2095 cm-1. If the annealing is applied for a duration between 20 and 60 min, the subpeak at ~ 2110 cm^{-1} is dominant. If the annealing lasts longer than 90 min, the subpeak at ~ 2110 cm^{-1} disappears, while the subpeak at ~ 2105 cm^{-1} becomes dominant. The latter one appears for the first time after annealing for 75 min. It is found that the sum of the intensities of the Si-H subpeaks at ~ 2105 and ~ 2110 cm^{-1} is almost proportional to the intensity of the H$_2$ peak [see Figs. 3 and 5(a)]. This significantly proves that they stem from the Si-H bonds at the inner surfaces of the HIPs. The subpeaks at ~ 2105 and ~ 2110 cm^{-1} can be possibly assigned to the dihydride (SiH$_2$) at the (100) orientated smooth and rough surface of the silicon, respectively.[6] Based on the annealing dependence of the three Si-H subpeaks and the H$_2$ molecule peak, we conclude that the hydrogen atoms released from the hydrogen damaged surface layer at elevated temperatures are trapped by the HIPs, where they combine and form H$_2$ molecules. These newly formed H$_2$ molecules increase the internal pressure of the HIPs so that they can anisotropically grow along the $\langle 100 \rangle$ direction. In addition the inner surfaces which are created during the annealing are also passivated by hydrogen atoms. As a consequence, the intensity of the subpeak at ~ 2095 cm^{-1} decreases, while the intensities of both the H$_2$ molecule peak and the subpeak at ~ 2105 or ~ 2110 cm^{-1} increase with the annealing duration. The transformation of the subpeaks at ~ 2105 and ~ 2110 cm^{-1} after long time annealing is possibly due to the (2×1) reconstruction of the internal surface.[6]

The first order kinetic theory is also applied to deduce the dissociation energy of the Si-H bonds at the hydrogen plasma damaged surface layer (i.e., related to the subpeak at ~ 2095 cm^{-1}). The intensity of the subpeak at ~ 2095 cm^{-1} is measured by the above-mentioned procedure B at RT. The deduced dissociation energy is 2.30 ± 0.01 eV. Keep in mind that in this case the kinetic process indeed includes three steps: (i) the dissociation of the Si-H bonds, (ii) the diffusion of the hydrogen atoms, and (iii) the recombination of the Si-H bonds. The reported diffusion energy for the migration of the hydrogen atoms between bond-center sites is about 0.3 eV,[21,22] i.e., much less than the dissociation energy. Therefore, the diffusion of the hydrogen atoms is a fast process as compared to the dissociation of the Si-H bonds and can be ignored either at RT or elevated temperatures. The Si-H recombination can also be neglected at elevated temperatures. The Si-H dissociation energy obtained by procedure A at 350 °C is 2.17 ± 0.01 eV (see above), i.e., rather close to the dissociation energy obtained at RT (2.30 ± 0.01 eV). Therefore, we can conclude that the main dissociating Si-H species at 350 °C is the Si-H bond at the thin surface layer of the sample. It is also further proved that none or just a few of the hydrogen atoms released from the H-plasma damaged surface layer at elevated temperature will recombine with the silicon dangling bonds there again at RT; otherwise the dissociation energy deduced by procedure B for the subpeak at ~ 2095 cm^{-1} should be much lower than 2.3 eV.

As mentioned above, we find the dissociation energy deduced from the *in situ* Raman spectra measured by procedure A at higher temperature (such as 450 °C) is larger than the one deduced at lower temperature (such as 350 °C). This is evident due to the different thermal stability of various Si-H species. As shown in Figs. 3 and 5, at 450 °C the Si-H bonds at the hydrogen plasma damaged surface layer are dissociated very quickly. Therefore, it is reasonable to assign the dissociation energy deduced by procedure A at 450 °C (i.e., 2.43 ± 0.01 eV) to the Si-H bonds at the inner surface of the HIPs. This assignment fits very well with the results obtained by *Myers et al.* based on the nuclear-reaction analysis method (2.5 ± 0.2 eV).[23]

Several questions remain. First, the recombination of the Si-H bonds occurs at RT for the sample #1 which are annealed at 350 °C, 400 °C, 450 °C, and 500 °C, while for the sample #2, it only occurs at RT after annealed at 350 °C and 400 °C, as shown in Figs. 1 and 2. Second, the Si-H intensity of the as-plasma treated sample #2 is much higher than for sample #1, but the dissociation of the Si-H bonds at the beginning of the annealing process in sample #2 is also much faster than in sample #1. These questions can be ex-

plained considering the three-layer structure model of the H-plasma treated silicon, where a hydrogen plasma damaged (HPD) surface layer with a thickness of ~ 0.2 μm, a HIP sub-surface layer of ~ 0.5 μm, and a transition region of ~ 1 μm are defined.[13] The treatment applying a H-plasma with higher frequency (110 MHz) is "softer" for the silicon wafers as compared to a 13.56 MHz H-plasma exposure, so that fewer platelets are induced. The HIP plays the role of a trap center for the hydrogen atoms. Therefore, a smaller number of hydrogen atoms are trapped in the HIPs in sample #2 as compared to sample #1, and, as a consequence, a larger number of hydrogen are still remaining at the HPD surface layer. The penetration of the light from the Raman laser is limited to a depth of ~ 0.3 μm. Therefore, the Si-H intensity of the as-plasma treated sample prepared with higher frequency is higher than for the sample with lower frequency. As proved above, the Si-H bonds at the thin surface layer are less stable than those located at the inner surface of the HIPs, so that at the beginning of the annealing process the Si-H bonds dissociate faster in sample #2 than in sample #1. Sample #1 contains more HIPs, so that the recombination can still be found after higher temperature annealing.

SUMMARY

Two different *in situ* Raman measurement procedures are described in detail and applied on the H-plasma treated and annealed Cz silicon samples. It is found that the intensity of the Si-H bond Raman peaks decreases during annealing, however the intensity increases again when the sample is cooled down to RT. This is strong evidence for Si-H bond dissociation and recombination at elevated temperatures and at RT, respectively. The dissociation energy of the Si-H bonds at the thin surface layer of the sample deduced from both Procedure A and B is about 2.2 eV, while the dissociation energy of the Si-H bonds at the inner surface of the HIPs is about 2.4 eV. It is found that the released hydrogen atoms at elevated temperatures are trapped again by the HIPs at RT and passivate the silicon dangling bonds at the inner surfaces of the HIPs or form H_2 molecules in the open space of the HIPs. The results are possibe related to the basic mechanism of the hydrogen-induced exfoliation of the silicon wafer and the so-called "smart-cut" process.

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*Corresponding author. Email address: yue.ma@fernuni-hagen.de

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