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Phys. Rev. B **83**, 045204 — Published 28 January 2011

DOI: 10.1103/PhysRevB.83.045204

Reconfiguration and dissociation of bonded hydrogen in silicon by energetic ions

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Abstract

We report in-situ infrared measurements of ion-induced reconfiguration and dissociation of bonded hydrogen associated with various defects in silicon at low temperatures. Defect associated Si-H complexes were prepared by low temperature proton implantation in silicon followed by room temperature annealing. As a result of subsequent low temperature ^{3}He ion irradiation, we observed 1) ion induced dissociation of Si-H complexes; 2) a notable difference in the dissociation rate of interstitial type and vacancy type defects; and unexpectedly, 3) the growth of bond-center hydrogen (BCH) which had previously been observed only in association with low-temperature proton implantation. These findings provide new insight into the mechanisms responsible for the dissociation of hydrogen bonds in silicon and thus have important implications for bond-selective nanoscale engineering and the long-term reliability of state-of-the-art silicon semiconductor and photovoltaic devices.

PACS numbers: 61.72.uf, 61.82.Fk, 71.55.Ak, 78.55.Ap
Key words: Si-H complexes, Passivation, Bond-center hydrogen, Defects in silicon.

1. Introduction

The behaviour of hydrogen in silicon is of great importance both scientifically and technologically. For example, hydrogen plays a crucial role in the growth of single crystal silicon, amorphous silicon and nanocrystalline silicon [1]. In addition, hydrogen passivation of dangling bonds is an essential processing step in the state-of-the-art semiconductor and photovoltaic device technology [2]. Hot-electrons or electron-hole pairs, introduced inevitably during device operation, can deteriorate device performance by breaking Si-H bonds resulting in a) the hot-carrier deterioration of metal-oxide-semiconductor field-effect-transistors [3,4] and b) the photodegradation of hydrogenated amorphous silicon (a-Si:H) solar cells, i.e. the Staebler–Wronski effect [5]. Radiation exposure can further deteriorate the performance of Si-H containing devices used in space electronics. On the other hand, non-thermal processes offer selectivity to tailor material properties at nanoscale [6-10]. A critical challenge is to understand the effect of energetic particles and various kinds of radiation on the stability of bonded hydrogen in semiconductors.

Up to now, the only known way of creating observable bond-center hydrogen (BCH) in Si was by low-temperature implantation of protons [11-14]. Here it is important to note that low-temperature proton implantation in silicon results in only one observable infrared absorption peak that corresponds to bond-center hydrogen. In addition, with increased temperature, BCH decays irreversibly and other known infrared active Si-H complexes begin to appear. Although several calculations and experiments describe the possible role of BCH as an intermediate stage in the dissociation of various Si-H bonds [1, 15], direct experimental observation is not available.

To address these issues, we have initiated a program to utilize energetic beams of ^{3}He ions to irradiate silicon containing non-BCH Si-H complexes at low temperatures. New experimental studies, presented here, incorporating site-specific infrared spectroscopy combined with the capability to expose the material to directed beams of energetic ions and electromagnetic radiation at cryogenic temperatures reveal the complex sequences involved in the dissociation of Si-H bonds. Specifically, here we report on our observations of 1) ^{3}He ion induced dissociation of Si-H complexes; 2) pronounced differences in the dissociation rate of interstitial type and vacancy type defects; and unexpectedly, 3) the growth of bond-centered hydrogen (BCH) which had previously been observed only in association with low-temperature proton implantation. Here we demonstrate that low-temperature ion irradiation (with a ^{3}He beam) of silicon containing non-BCH Si-H complexes produces BCH. Our unique capability of combined low-temperature irradiation and *in-situ* infrared spectroscopy has made this observation possible.

2. Experimental

Silicon samples used in this study were cut from a high resistivity (16-23 kΩ-cm), 1.5 mm thick, double side polished, float zone Si (100) wafer. Hydrogen implantations and subsequent ion irradiations were performed at 80 K in a specially designed cryostat using a 2 MV Van-de-Graaff accelerator. *In-situ* infrared absorption measurements were performed at ~ 7 K using a Bruker-IFS 66v Fourier transform infrared spectrometer (FTIR) with a nominal spectral resolution of 2 cm^{-1}. Unless otherwise specifically mentioned the sample was never warmed up beyond 80 K.

Energetic protons (800 keV, 750 keV and 700 keV at doses of 7.5×10^{15} H/cm^2 at each energy) were implanted through an 8 μm Al foil into silicon to create BCH sites close to the surface. The intense characteristic infrared peak around 1998 cm^{-1} shown in Figure 1 confirms the formation of BCH in silicon. The peak is lost irreversibly upon increasing the sample temperature above 200 K. Concurrently, new infrared lines appear corresponding to other known H-related defects as shown in Fig. 1 (and Fig. 2a) [11-14]. These defect associated Si-H complexes are of principle interest in our present study. This defect containing sample then was irradiated with 1.8 MeV ^{3}He ions at 80 K and infrared spectra were recorded (7 K) at various dose intervals to study the effect of ion irradiation on the stability of these defects. A similar sample was irradiated by 1.8 MeV ^{3}He ions at 300 K to study the influence of temperature on the rate of ion induced dissociation of Si-H bonds. The incident beam current is kept constant at around 40 nA (~200 nA/cm^2 for ^{3}He) in all of our experiments (including ref. [14]) as a control parameter to avoid simultaneous influence of vibrational, electronic and heating effects. The ^{3}He flux is kept very low to minimize local heating effects. Further details of experimental procedures, including the estimated profiles of H and ^{3}He ions, are available in ref. [14]. The influence of above bandgap optical illumination is also reported here.

3. Results

3.1 ^{3}He induced dissociation of defect associated Si-H complexes:

Figure 2a shows the measured FTIR spectrum associated with various known Si-H complexes in the silicon sample prior to the low temperature ^{3}He radiation. The ^{3}He ion-induced modified distribution of Si-H complexes is shown in Fig. 2b. Comparison of Figs 1, 2a and b shows that, we have observed the decay of various Si-H bonded defect states and created the BCH state.

Note that Ref 14 reports the decay of BCH under ^{3}He ion irradiation from a low temperature implantated sample containing predominantly BCH. Thus the amount of BCH observed under any specific ion irradiation process involves both creation and annihilation.

Figure 3 summarizes the rates of decay of the Si-H defect complexes and the growth of the BCH signal as a function of ion dose. Also shown is the data of ^{3}He ion-induced decay of BCH from Ref. [14]. The ion-induced decay rate of the infrared intensity of Si-H defects as a function of ion dose can be modelled by two different rate equations as proposed earlier [14]. The dashed lines show pure exponential decay where the rate of decay of each defect is proportional to its concentration and the ion dose. The solid lines in Fig. 3 show second-order fits where the rate of decay of each defect is proportional to the square of its concentration and the ion dose. The second-order process imposes concentration dependence in the rate of decay and is based on a simple model which assumes that H_2 formation is the "sink" for the decay process. [14, 16]. In the following discussion, we assume an exponential decay for convenience

Figure 4 shows the dose dependence of ^{3}He induced dissociation of H_2^* defect measured as a function of irradiation temperature. It is clear that the observed ion-induced dissociation is slower at room temperature as compared to that of 80 K irradiation.

3.2 Difference in the dissociation of vacancy and interstitial type defects:

As shown in Fig. 3, the dissociation rate of Si-H bonds associated with vacancies is markedly lower than that of interstitial related defects. To illustrate this point more explicitly, Figure 5 shows a comparison of the ion-induced decay of an interstitial-type defect (IH_2) and a vacancy-type defect (VH_2), two defects with approximately the same initial infrared intensity and thermal annealing temperature. This difference in the dissociation probability depending on the nature of the defect - interstitial type or vacancy type is discussed below.

3.3: Creation of bond-center hydrogen by ^{3}He irradiation:

Figure 2a shows the measured FTIR spectrum associated with various known Si-H complexes in the silicon sample prior to the ^{3}He radiation. The ^{3}He ion-induced modified distribution of Si-H complexes can be seen in Fig. 2b. Note the formation of a new peak around 1998 cm^{-1} following ^{3}He irradiation of the Si(H) sample. An infrared peak at this frequency was observed earlier in silicon only after low-temperature implantation of protons [11-14]. Budde [12] assigned this peak to the positive charge state of bond-center hydrogen in silicon ($H^+_{[BC]}$ or BCH). BCH is known to decay irreversibly and produce several other H-related defects upon 200 K thermal annealing [11-14]. The present experiment provides a first observation of this Si-H complex formed without direct implantation of protons at low-temperature. Characteristic of the known BCH behaviour, the associated peak disappears upon annealing at 200K and results in the slight increase of other H defects (see Fig. 2c) further confirming the BCH identification. Fig. 2d shows the infrared spectrum of this sample after a low-temperature implantation of ^{3}He ions into the rear of the sample where the sample thickness (1.5 mm) is such that the ^{3}He range does not overlap the front-side implanted hydrogen. This spectrum does not show any intensity at 1998 cm^{-1} indicating that this feature is not generated by ^{3}He ions alone or by any possible hydrogen contamination in the irradiating beam. This further confirms the identification of the peak around

1998 cm^{-1} as BCH in silicon resulting from the low temperature ^{3}He irradiation of hydrogen containing silicon. The growth of BCH as a function of incident ^{3}He dose is shown in fig. 3.

4. Discussion

Energetic ion irradiation of a solid initiates a wide variety of processes including defect creation, a high density of excited carriers, and knock-on processes of both electrons and atoms of the solid. Furthermore the shower of energetic electrons can cause multiple molecular excitations. An additional possibility is the creation of shock waves. Here we examine the role of some of these processes on the observed ion-induced reconfiguration and dissociation of Si-H complexes.

4.1. Ion induced dissociation of Si-H complexes:

4.1.1 Local heating:

The stability of Si-H complexes is sensitive to the local temperature and each defect is characterized by a thermal annealing temperature for disassociation. Hence sample temperature increases associated with the irradiation could induce transformations in the hydrogen containing defect distribution. However the measured increase in the sample temperature was never more than 1 K during the implantations. The lack of a conventional thermal process is further verified by comparing the characteristic annealing temperatures of the various defects with the ion induced decay rate and the defect binding energy. Table 1 shows: i) the cross-sections for ^{3}He induced dissociation of various Si-H bonds measured in this work (from Fig 3, exponential decay model). ii) the thermal annealing temperatures and iii) minimum energy values of these configurations obtained from the existing literature [17]. The table clearly suggests that the ion-induced decay does not correlate with the thermal annealing temperature but does follow minimum energy considerations. In particular the H_2^* dimer is thermally stable up to 435 K whereas the BCH decays at 190 K. Hence the simultaneous formation of low-temperature-stable-defect like BCH and the dissociation of high-temperature-stable-defect like H_2^* indicates that the observed process is distinctly different from thermal annealing process. Further, the fact that two defects such as IH2 and VH2, with the same thermally induced decay temperature, have very different ion-induced decay rates indicates that local heating is not playing a role.

4.1.2. Electron-hole (e-h) pairs:

Earlier experiments showed that e-h pairs generated by photons or electrons can enhance the low-temperature diffusion of intrinsic defects and impurities and dissociation of hydrogen bonds in silicon [18]. Hence it is reasonable to expect a similar effect arising from electron-hole pairs generated by energetic ions. We have investigated this by subjecting one of our samples to 890 nm light from a Ti-Sapphire laser. Eight hours (~ 0.2 W/cm^2) of laser illumination at 80 K (and at 300 K) did not cause any observable decay of any of the <u>room-temperature</u> stable defects (ie H^{2*}). This behaviour is markedly different than the ion induced rate of dissociation of H_2^* which is substantial at 80K. This suggests that the light induced decay and its generation of e-h pairs is quite different from the ion-induced decay and is not responsible for the observed effects. However, we note that the BCH did decay for both optical illumination and ion irradiation at 80 K [14].

4.1.3. Migration of defects:

The presence of defects is expected to influence the stability of some of the Si-H bonds [18]. As a test we have implanted ^{4}He ions at about a micron before the region of hydrogen so as to create intrinsic defects in the close vicinity of Si-H bonds, without creating ionization / e-h pairs in the region of hydrogen. The smallest distance that can be obtained between defects and the hydrogen is limited by the straggling of both H and ^{4}He beams. However the defects generated by He ions are expected to have a broad distribution of about few microns as the sample is a high-resistive / un-doped (16-23 kΩ-cm) float-zone silicon [18-20] and defects are known to diffuse substantially under such conditions. Both isolated vacancies and interstitials are highly mobile in pure silicon even at cryogenic temperatures and they diffuse macroscopic distances until trapped by impurities or other defects. Hence the ^{4}He ion injected defects are expected to diffuse through the region of Si-H defects. ^{4}He implantations at 80 K followed by 300 K thermal anneal, as well as implantation at 300 K do not cause any observable change in the infrared intensity of any of the defects. Hence the influence of defect migration on the stability of any of the infrared-active defects could not be observed within the experimental limits.

4.1.4. Secondary electron induced vibrational excitation and ionization:

The breaking of Si-H bonds can occur either by direct electron ionization or by multiple vibrational excitation processes [6-10]. Foley et. al [6] showed that the electron-induced dissociation process of Si-H surface bonds is independent of temperature in the direct ionization regime. Here we report the temperature dependence of the ion irradiation measurement at room temperature in order to explore the similarity to the Foley observations. As shown in fig. 4, the measured rate of ion induced dissociation of H_2^* defect is found to be lower at higher temperatures suggesting that electron-induced direct ionization does not play a significant role in this case.

However, the multiple vibrational excitation mechanism is temperature dependent as the vibrational lifetime of the local modes of Si-H complexes decreases with increase in temperature [21-23], reducing the efficiency of this "vibrational state- ladder climbing" process. Hence our temperature dependence data suggests that secondary electron induced multiple vibrational excitation may be responsible for the observed site changes and dissociation of defect associated Si-H complexes.

Here it is important to note that the incident beam current is kept constant at around 40 nA (~ = 200 nA/cm^2 for ^{3}He) in all of our experiments (including [ref. 14]) as a control parameter to avoid simultaneous influence of vibrational, electronic and heating effects. The ^{3}He flux is kept very low to minimize local heating effects. More critically, at 40 nA the time interval between two incident ions is around 4 ps, which is close to or less than the vibrational lifetime of some Si-H complexes. However, the beam spot is relatively large, ~ 1 mm (scanned over an area of 5 mm x 5 mm), compared to the size of the electron cloud created by a single ion (<1 micron). Thus multiple ion effects are very improbable. The picture of vibrational excitation described here is associated with the intense, excited, many-electron cloud created by a single ion.

4.2. Differences in vacancy and interstitial type defects - influence of local structure:

The second major finding in this report is the observation that ion-induced dissociation of Si-H bonds in vacancy type defects is less probable than those associated with interstitial type defects. As can be seen in table 1, the ion-induced dissociation of hydrogen in these defects does not correlate with the thermal annealing temperature but it does follows minimum energy considerations. Table 1, clearly suggests that potential wells associated with vibrational excitation of vacancy-type defects are deeper than that of interstitial-type defects. Therefore the probability to break vacancy-type defects by multiple vibrational excitation process is less when compared to interstitial-type defects. Hence the proposed multiple vibrational excitation model explains the observed differences in dissociation rates of vacancy-type and interstitial-type defects.

4.3. Creation of bond-centered (BCH) hydrogen by ^{3}He irradiation:

One of the most surprising results of the present study is the formation of BCH during the low-temperature irradiation. Possible mechanisms are discussed below.

4.3.1 Knock-on Mechanisms

One mechanism that can produce BCH could be the simple low-temperature recoil implantation of H (from non-BCH sites into Si) by the incident ^{3}He ions. We evaluate this possibility by considering simple cross-section calculations and SRIM simulations [24]. From ref. [14], the total implanted hydrogen concentration is about 2 x 10^{16} H / cm^2. The maximum dose of 1.8 MeV ^{3}He ions used in this study is 1 x 10^{15} cm^{-2}. The standard SRIM [24] simulation estimates about 1 x 10^{12} cm^{-2} H recoils for the above sample-beam configuration. Similar numbers are obtained by a manual calculation where the cross-section to transfer 10 eV[1] to an H atom by 1.8 MeV ^{3}He ion is estimated using simple kinetics. Such recoiled H could be re-implanted into Si at 80 K and form 1 x 10^{12} cm^{-2} BCH centres. Some of these centres may again dissociate due to continued ^{3}He irradiation as per ref. [14]. However the intensity of the observed new BCH line corresponds to 2 x 10^{15} cm^{-2} (i.e about 10% of the total implanted hydrogen) which is at least three orders of magnitude larger than that of the recoiled hydrogen yield. Hence the recoil implantation is not sufficient to explain the formation / regeneration of BCH in silicon. We thus attribute the observed growth of BCH to the electronic excitations caused by the incident ^{3}He ions and not to recoil implantation.

4.3.2 Possible mechanisms involving electronic excitations

A likely hydrogen complex responsible for the newly created BCH is the H_2^* complex. It consists of two hydrogen atoms, one located close to the bond-center site (BC) and the other close to the anitbonding site (AB) [25, 26]. Theory reveals that the Si-H bond at the BC site is stronger than that of AB site and is characterized by a higher vibrational frequency [25, 26]. Molecular dynamics calculations of Zhang et al. [27] showed that the microscopic mechanisms for the dissociation of these two bonds are different based on the carrier type. Estreicher et al. [26] suggested that the H in AB site may break first leaving H at BC site. Such a process at low temperature can be responsible for the observed growth of BCH. This reduction of H_2* to BCH can neither be observed in thermal annealing nor in any room temperature dissociation processes as BCH is only stable below 200K. The dissociated H(AB) atom might form a H_2 molecule by recombining with another such H atom or it could be trapped by a pre-existing dangling bond or

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[1] The displacement energy of H in Si as per SRIM data [24]. The recoil cross-section will increase only by one order of magnitude even if this energy is considered as 1 eV (less than the binding energy of any Si-H bond).

at a BC site by a strained Si-Si bond. Some support for this process can be found in Fig. 3, where the decay rate of H_2* (~1.19 x 10^{-15} cm^2) is shown to be comparable to the growth rate of BCH (~1.13 x 10^{-15} cm^2), although the rate of BCH formation is a net result of growth and decay. The growth rate of BCH is estimated by fixing the rate of ^{3}He-irradiation induced decay of BCH to previously observed value (~8.71 x 10^{-16} cm^2) [14] and by assuming that the decay of a particular defect is responsible for the observed growth of BCH.

The observed growth of BCH is interestingly related to recent experiments and calculations which suggest that BCH plays an intermediate role in the athermal dissociation of Si-H bonds [1, 15]. These reports, directed at explaining the instability of hydrogen containing amorphous Si, address such processes as the Staebler Wronski effect [5]. In these mechanisms, solely electronically driven, an intermediate non-stable state, is envisioned as the BCH configuration. Since the process occurs at room temperature it is clear that BCH can only be a short lived intermediate state. For the experiments reported here the ion-irradiation may create sufficient excitation to break Si-H complexes and allow the formation of stable BCH. Thus the present result may correspond to the first direct observation of this intermediate stage.

5. Conclusion:

We report new experiments which demonstrate: 1) ion induced dissociation of Si-H complexes consisting of Si defects and hydrogen; 2) a notable difference in the dissociation rate of interstitial type and vacancy type defects; and surprisingly, 3) the simultaneous growth of bond-centered hydrogen (BCH) in hydrogen containing silicon. Temperature dependent data suggests a significant role of multiple vibrational excitations in the observed dissociation process, and possibly the BCH formation process. The ion induced dissociation of vacancy associated Si-H bonds is found to be considerably less probable than that of interstitial associated Si-H bonds. This vacancy-interstitial difference correlates with minimum energy considerations. A first and direct experimental evidence for the formation of BCH during the athermal annealing of Si-H bonds is reported and possible mechanisms discussed. It is suggested that the formation of the BCH is fed from the decay of the H2* defect. Most importantly, is a signature of the BCH intermediate state envisioned as a transient step in the chain of reconfigurations of H-Si bonds in materials such as hydrogen containing amorphous Si.

Acknowledgements

This work was supported by DOE through Grant DE-FGO2-99ER45781. We are thankful to W. Augustyniak, Anthony B. Hmelo and John Kozub at Vanderbilt University for discussions and technical support. SVSN thanks Pondicherry University, Pondicherry and Department of Science and Technology (DST), India for international travel support.

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Table Captions:

Table 1: Measured cross-sections for ^{3}He induced dissociation of various Si-H bonds by fitting the dose dependence data shown in Fig. 3 in an exponential decay model. Also shown are the thermal annealing temperatures and minimum energy values of these configurations obtained from the existing literature [17].

Figure Captions:

FIG. 1: Infrared spectra measured at 7 K in the region of Si-H stretch mode vibrations immediately after low temperature implantation of H into Si and after a thermal annealing at 280 K.

FIG. 2: Infrared spectra, measured at 7 K, of a) pre-irradiated, defect and H containing Si sample, showing the existence of various defect associated Si-H complexes. b) after ^{3}He irradiation (at 80 K), showing the reconfiguration of Si-H complexes. c) after room temperature annealing of above sample and d) after irradiating by ^{3}He ions from the rare side of the sample.

FIG. 3: Dose dependence data of the ^{3}He induced dissociation of various Si-H complexes and the corresponding growth of BCH (H^+_{BC}(G)). Also shown is the ^{3}He induced decay of BCH (H^+_{BC}(D)) from Ref. [14]. Dashed lines show exponential decay and the solid lines shown the second-order decay. The decay of vacancy-type defects (VH_2 and VH_4) is found to be slower as compared to that of interstitial-type defects (H^*_2, IH_2 and BCH: H^+_{BC}(D)). [y-axis (left): I/I_0 where I_o is the initial infrared intensity of a particular defect and I is the intensity of that particular defect as a function of dose.]

FIG. 4: Dose dependence data (I/I_0) of ^{3}He induced dissociation of H_2^* defect as a function of irradiation temperature (80 K and 300 K) showing that the decay is slower at room temperature.

FIG. 5: Dose dependence data of one interstitial defect (IH_2) and one vacancy type defect (VH_2) who's initial infrared intensity and the thermal annealing temperature are almost the same. This clearly shows that the IH_2 decays much faster than the VH_2 even though they have same thermal annealing temperature.

Table 1.

		Thermally induced decay	Ion induced decay	Energy per H (eV)
Defect Type	Defect	T_{ann} (K)	k (10^{-16} cm^2)	Van de Walle et. al. [17]
Interstitial	H^+_{BC}	190	8.71 ± 1.2	-1.05
	H_2^*	435	11.9 ± 1.3	-1.65
	IH_2	485	16.2 ± 1.9	-
Vacancy	VH_2	485	3.07 ± 0. 4	-3.15
	VH_4	775	0.99 ± 0.4	

T_{ann} : Temperature at which the corresponding infrared line disappears.

k : ^{3}He - decay constant in exponential model.

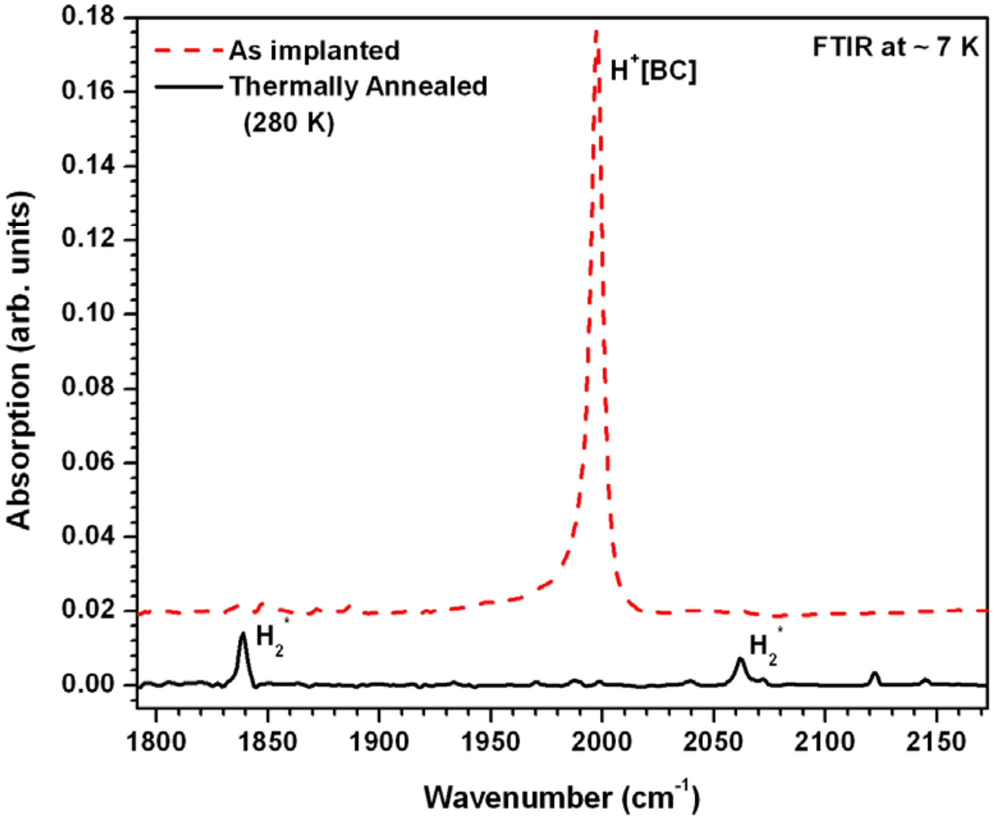

0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
Absorption (arb. units)
As implanted
Thermally Annealed
(280 K)
$H^+[BC]$
FTIR at ~ 7 K
H_2^*
H_2^*
1800
1850
1900
1950
2000
2050
2100
2150
Wavenumber (cm^{-1})

Fig. 1

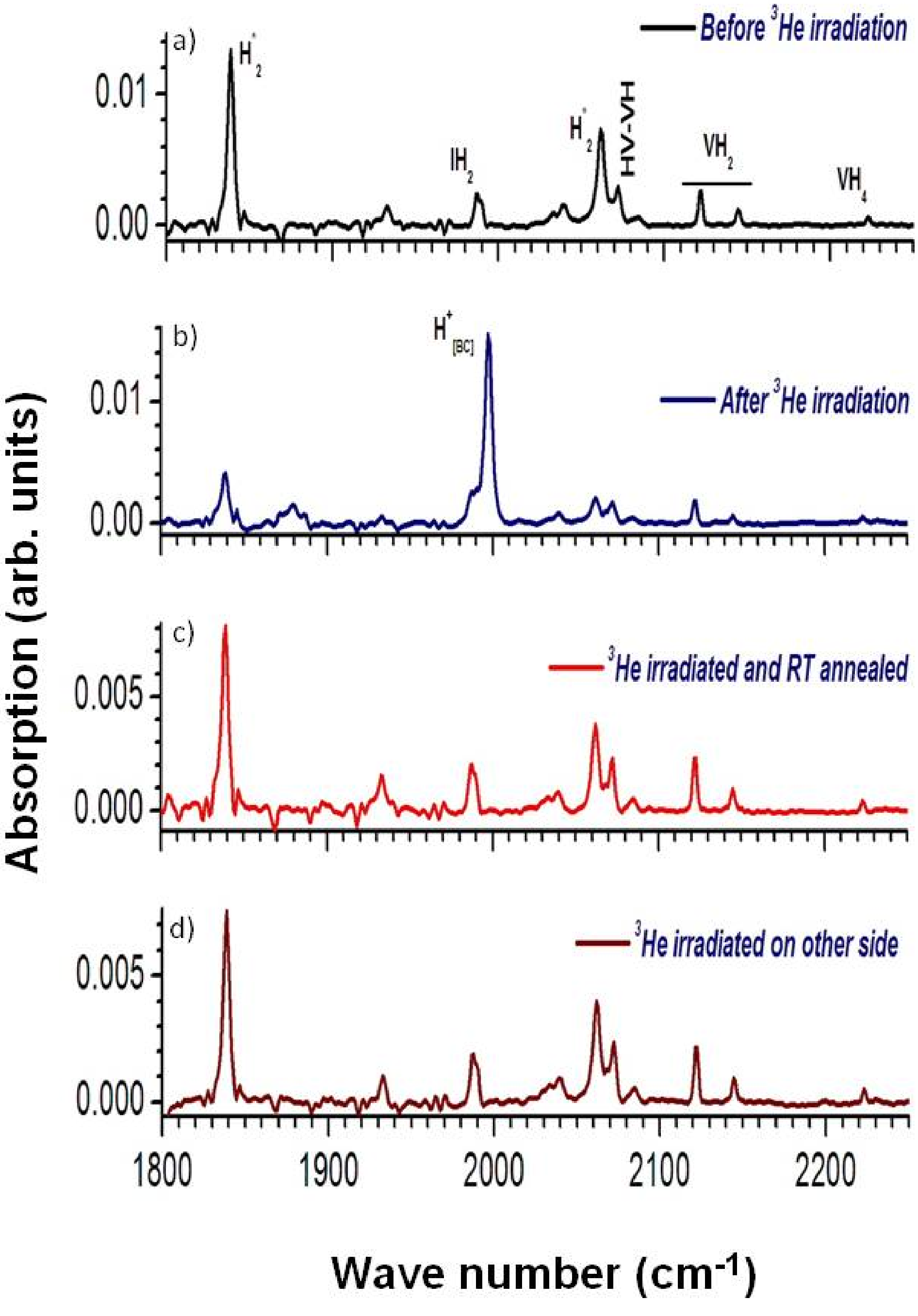
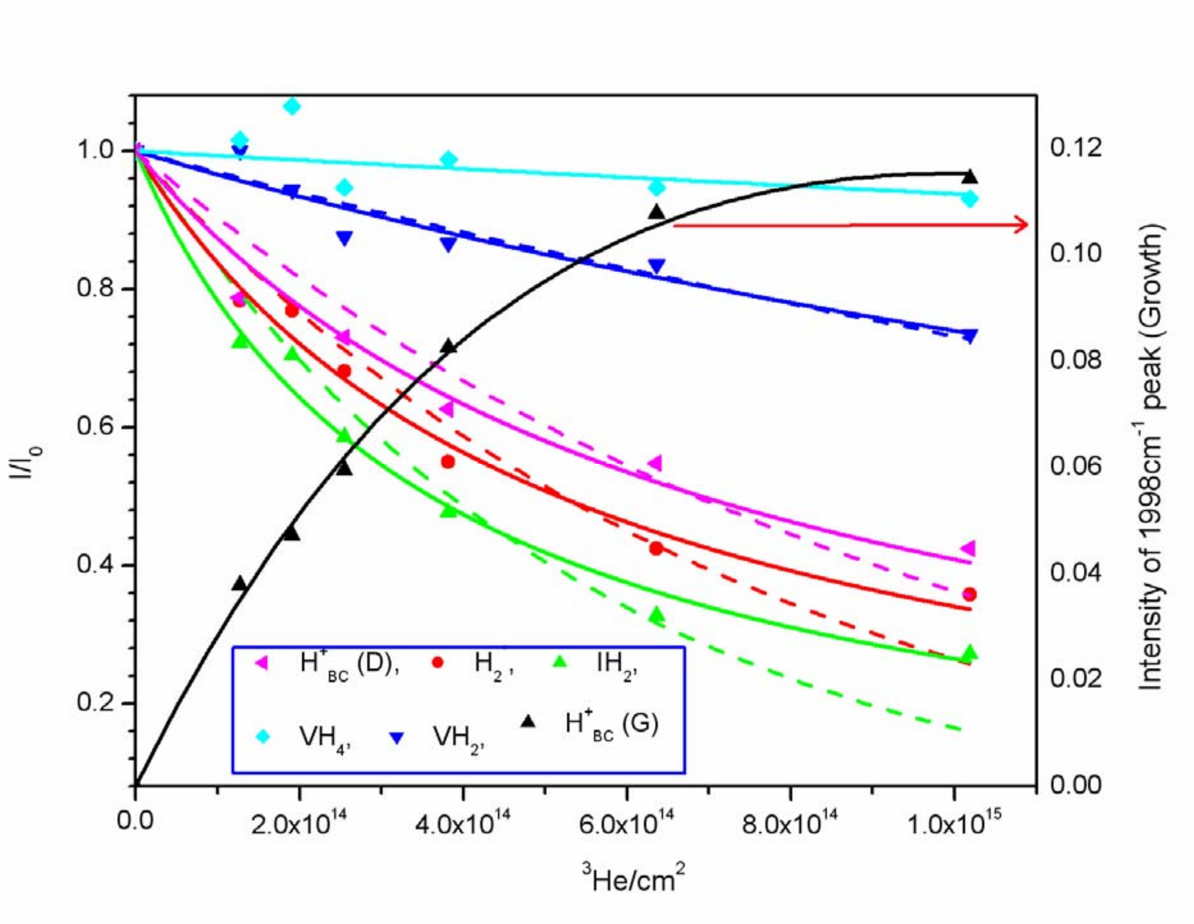
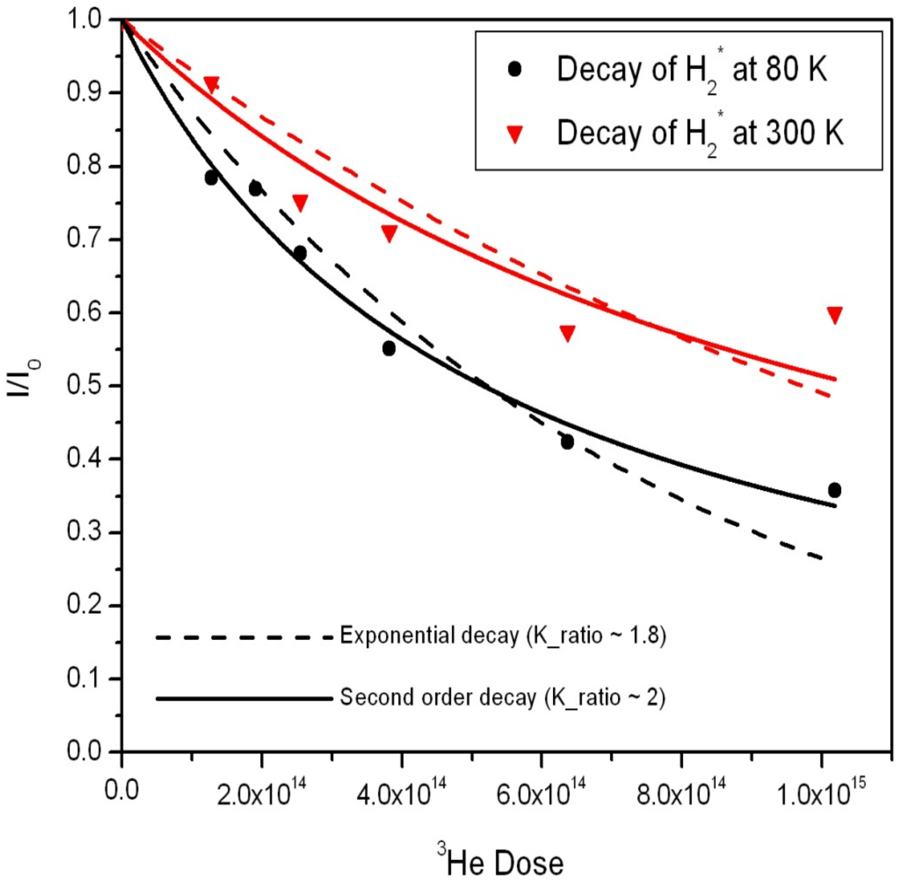

a)
Before ^{3}He irradiation
H_2^*
IH_2
H_2^*
HV-VH
VH_2
VH_4
b)
$H^+_{[BC]}$
After ^{3}He irradiation
c)
^{3}He irradiated and RT annealed
d)
^{3}He irradiated on other side
0.01
0.00
0.005
0.000
Absorption (arb. units)
1800
1900
2000
2100
2200
Wave number (cm^{-1})

Fig. 2



I/I$_0$
1.0
0.8
0.6
0.4
0.2
0.0
2.0×10^{14}
4.0×10^{14}
6.0×10^{14}
8.0×10^{14}
1.0×10^{15}
^{3}He/cm^2
Intensity of 1998cm^{-1} peak (Growth)
0.12
0.10
0.08
0.06
0.04
0.02
0.00
H^+_{BC} (D),
H_2,
IH_2,
VH_4,
VH_2,
H^+_{BC} (G)

Fig. 3



1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
I/I_0
0.0
2.0×10^{14}
4.0×10^{14}
6.0×10^{14}
8.0×10^{14}
1.0×10^{15}
^{3}He Dose
● Decay of H_2^* at 80 K
▼ Decay of H_2^* at 300 K
Exponential decay (K_ratio ~ 1.8)
Second order decay (K_ratio ~ 2)

Fig. 4

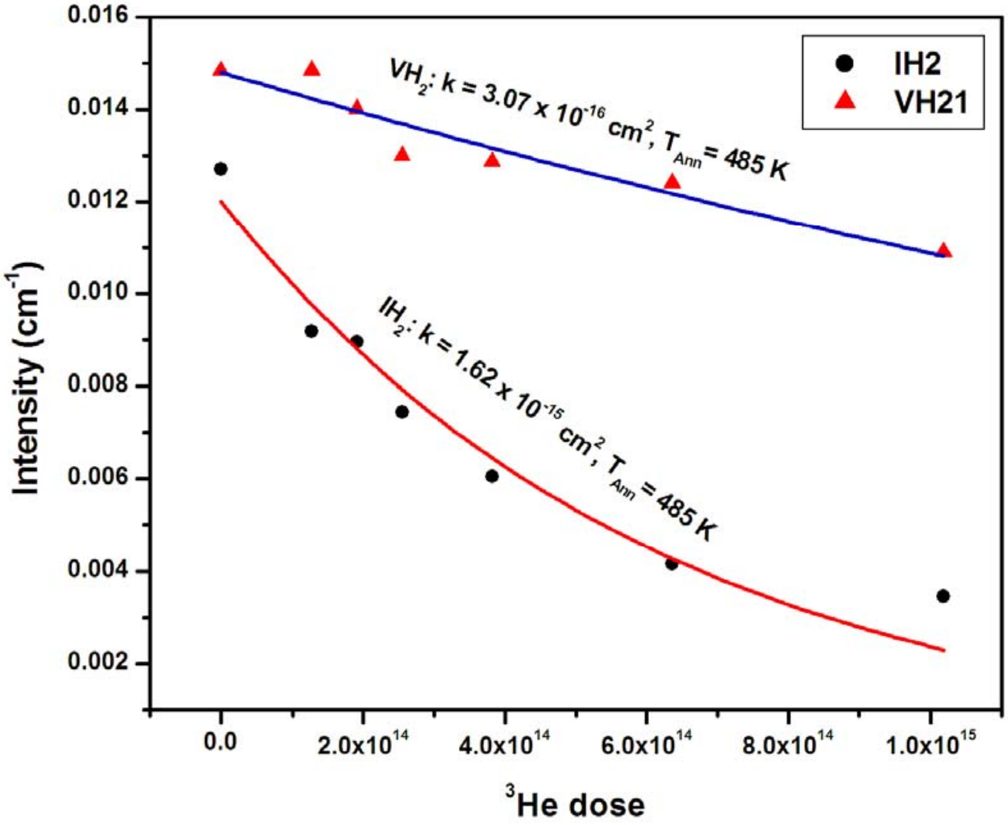

0.016
0.014
0.012
0.010
0.008
0.006
0.004
0.002
Intensity (cm^{-1})
0.0
2.0x10^{14}
4.0x10^{14}
6.0x10^{14}
8.0x10^{14}
1.0x10^{15}
^{3}He dose
IH2
VH21
VH$_2$: k = 3.07 x 10^{-16} cm^2, T$_{Ann}$ = 485 K
IH$_2$: k = 1.62 x 10^{-15} cm^2, T$_{Ann}$ = 485 K

Fig. 5.