Chapter 1

Chapter 1

Introduction

Hydrogen-Si surface interaction has been the subject of very active research for a long time because it covers a great variety of interesting surface phenomena. The interest in this system is mainly twofold. On one hand, hydrogen is in principle the simplest possible adsorbate and thus, chemisorption of H on Si surface can be regarded as an ideal prototype system for understanding chemisorption phenomena. On the other hand, it has many practical importances in silicon device processing which includes adsorption and desorption of hydrogen on the Si surfaces.[1] The strong Si-H bond can passivate the surface and resist against further reaction. Adsorbed H atoms limit the Si growth rate at low temperature regime below 770 K in chemical vapor deposition (CVD)[2,3,4] and alter the morphology of epitaxially grown film.[5,6] This hydrogen-silicon interaction can contribute to surface cleaning,[7,8] removal of halogens,[9] etching,[10,11] etc.

When silicon surface is exposed to atomic hydrogen, various types of interactions would be possible. The schematic diagram shown in Fig.1.1 (ref.12) illustrates possible elemental reactions from adsorption to etching when hydrogen atoms are admitted to clean Si surfaces. These interactions are: (1) Sticking: Si dangling bonds on the surface can be passivated by gas phase H atoms. (2) and (4) Adsorption-induced desorption: Admission of H on H/Si surface can induce recombinative desorption of H adatoms to form H_2 from monohydrides and dihydrides species. (3) Diffusion: adsorbed H atoms can diffuse to the adjacent Si atoms over the surface. (5) Reflection: Gas phase incoming H atoms can reflect directly without any loss of energy to Si substrate. (6) Bulk diffusion: If the surface is rough, H atoms can diffuse to the bulk. (7) Direct abstraction: Gas phase H atoms can abstract surface H adatoms directly. (8) Etching: Over exposure of Si substrate to H atoms can accelerate the etching of surface Si through the SiH_4 formation.

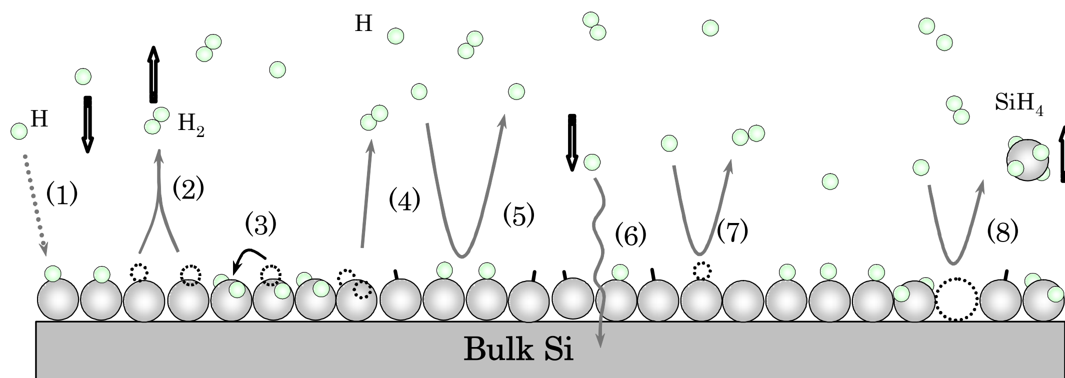

Fig. 1.1 H-Si surface interactions: (1) H adsorption on the dangling bond of surface Si atom; (2) and (4) associative desorption of H_2 from the monohydride and dihydride phase, respectively. This processes could be initiated by adsorption of H atoms at the adjacent sites; (3) diffusion or hopping of H adatom to the neighboring Si atom; (5) direct reflection of H without reacting with the surface; (6) H diffusion to the bulk Si; (7) H-induced H adatom abstraction on the surface; (8) etching of the surface Si atom via SiH_4 formation. [Ref. 12]

In addition to such H-Si interactions, oxygen interaction with H(D)-terminated surfaces has become important in wide research field such as space science and material science. It is known that H-terminated Si surfaces are inactive towards oxidation with O_2 molecules, but can be easily oxidized with O atoms.[13,14] Atomic oxygen may be a promising agent to prepare oxide layers on the hydrogen terminated Si surfaces,[15,16] particularly, in preparation of gate oxide of MOSFET[17,18,19,20] or Si nanowires.[21] It has been argued that O atoms can be inserted either into Si–Si bonds to form Si–O–Si species or in Si–H bonds to form Si–OH (Si–OD) species.[22,23] In the more applied fields, oxygen interactions with the solar panels or other peripheral Si based devices of space crafts as well as with dust grains in the far space, are also investigated.[24,25] The aims of research in those fields are to protect the space crafts from ambient oxygen effects and to reveal the mechanism of water formation on the dust grain, respectively. However, to date, the reaction mechanisms of O atoms on H/Si surfaces are yet to reveal.

1.1 D abstraction by H on Si surfaces

When D/Si surfaces are exposed to H atoms, surface D adatoms can be abstracted quite efficiently and HD molecules are formed. This process is known as direct abstraction (ABS). Along with this ABS, recombinative desorption of D adatoms to form D_2 molecules can also occur. This process is known as adsorption-induced desorption (AID). Thus, the D abstraction by H can be categorized into following two reaction pathways:

$H + D/Si_{(s)} \rightarrow HD$ (Direct abstraction or ABS)

$H + D/Si_{(s)} \rightarrow D_2$ (Adsorption-induced desorption or AID)

Kinetics of H reactions on Si(100) surfaces has been investigated by many groups from an uptake point of view. In order to explain the unexpected first-order kinetics in thermal desorption of hydrogen, Sinniah et al.[26] proposed a mechanism, in which H adatom was promoted to excited state (H*) and could react with another adjacent H adatom to form a H_2 molecule. They anticipated that a mechanism which was a combination of Eley-Rideal (ER) and hot atom (HA) idea was involved in the thermal desorption of hydrogen. Naitoh et al.[27] suggested that during H (D)-irradiation on D(H)/Si(100) surfaces, substitution between two H or D adatoms was found to occur. Koleske et al.[28] abstracted the H(D) adatoms by incident D(H) atoms on Si(100) surfaces and reported a first-order HD desorption with respect to surface D coverage. They proposed a generalized ER mechanism. In contrast, Widdra et al.[29] proposed a hot-precursor mechanism for the adsorption of atomic hydrogen on Si surfaces. According to the hot precursor mechanism, incident H atoms were initially trapped in the chemisorption wells. However, they were in still energetically hot to move laterally over the surface with several bounces before adsorption. On the other hand, Flowers et al.[30] criticized that the uptake of H could be explained neither by a Langmuir model nor by the hot-precursor model. They proposed a quasi-equilibrium model, in which dihydride species were formed upon H-sticking on the monohydride surface by breaking Si dimer bonds. So formed

dihydrides migrated over the surface by an isomerization reaction between monohydride dimers and dihydrides. When two of such migrating dihydride units met each other, H_2 desorbed leaving behind a monohydride surface. This is actually the thermal desorption (TD) of dihydrides (β_2 TD).

By exposing the D/Si(100) surface to atomic H to induce HD and D_2 desorption, several groups studied these reactions from the desorption point of view.[31,32,33,34,35,36] Dinger et al. reported that the first- and second-order kinetics were operated for HD and D_2 desorptions, respectively. They proposed that both the HD and D_2 desorptions could be explained in terms of the HA mechanism. Buntin, for the first time, measured the kinetic energy distributions of H-induced HD molecules on D/Si(100) using time-of-flight (TOF) technique. By using a H beam of 1.1 eV, generated by laser photolysis of HI, he measured the kinetic energy of HD to be 1.2-1.3 eV. He also observed a broader energy distribution of the desorbing HD molecules with increasing incident H beam energy. This might be due to energy dissipation to the surface phonons during the abstraction process. These finding motivated him to propose the adatom abstraction on Si(100) surface was less ER like.

Almost at the same time, Shimokawa et al. reported the fourth-order kinetic of recombinative desorption of D_2 induced by H as a function of momentary D coverages for the first time. They explained the fourth-order AID reaction with the kinetics model proposed by Flowers et al. They also reported a nominal reaction cross section for direct abstraction of HD as ~ 7Å^2. Later on, Khanom et al. proposed rate equations for HD and D_2 desorptions from Si(100) surface at 573K. They reported that HD desorption was a combination of two process, one was direct abstraction (HD ABS) and another was adsorption-induced desorption of H and D adatoms (HD AID). The measured HD rates for ABS obeying the first-order kinetics for low θ_D ($\leqslant$ 0.5ML) and the second-order kinetics for high θ_D. For the adsorption-induced desorption of HD and D_2, an isotope effect was also reported for the first time by Rahman et

al.[37]. Hayakawa et al. reported a second-order HD desorption and showed a strong Ts dependence of D_2 AID. Based on these findings, they ruled out the HA mechanism for HD ABS and proposed a new model named as hot-complex (HC) mechanism (will be discussed in the section 1.2.3) for the first time. Kubo et al. also investigated the H-induced processes on Si(100) surfaces and reproduced the second-order HD ABS and the fourth-order D_2 AID on Si(100) surfaces. Recently, Inanaga et al.[38] studied the angular distributions of H-induced HD and D_2 desorptions from Si(100) surfaces. They found the HD and D_2 angular distributions were different suggesting different mechanisms were operative. Along with this, they reported that HD desorption occured along the direction of dangling bond, which was nearly 20^{0} with respect to surface normal. Recently, Rahman et al.[39] revealed two types of D_2 desorption on D/Si(100) surface by employing a modulated H beam. According to them, D_2 desorbed not only at H-beam on-cycles but also at H-beam off-cycles. Based on this finding, Inanaga et al.[40] determined the reaction lifetimes of four D_2 desorption components and reported their T_s dependence on Si(100) surfaces.

Dinger et al.[41] extended the kinetic investigation on the Si(111) surface and reported the first-order HD and second-order D_2 desorption kinetics, supporting the hot atom model again. Later on, Khanom et al.[42] replotted the HD and D_2 rate curves obtained by Dinger et al. and found that their fitting curves deviated from the kinetics predicted in the HA mechanism. They elaborately studied the same subject and found that HD ABS followed the first-and the second-order kinetics for low and high θ_D, respectively, while D_2 AID followed the third-order kinetics. A strong Ts dependence on the D_2 rates even on Si(111) surfaces was also reported. They were confident on the point that the hot-complex (HC) model was indeed capable of explaining the H-induced ABS and AID on the D/Si(111) surfaces ruling out the HA mechanism.

1.2 Possible abstraction mechanisms

As mentioned in the first paragraph of section 1.1, when D/Si surfaces are exposed to atomic H beam, two types of abstraction reactions can take place, one reaction is the direct abstraction (ABS) and the other is the indirect abstraction or adsorption-induced desorption (AID). Various mechanisms have been proposed so far to reveal the abstraction reactions.

1.2.1 Eley-Rideal (ER) mechanism

Surface adatoms could be abstracted directly by a gas phase atom within a femto second (fs) period without any interaction with the surface. Such a direct abstraction has been referred as the Eley-Rideal (ER) mechanism after Eley and Rideal since 1940.[43] According to this mechanism, the impinging H atoms, with a certain energy and orientation, react directly with D adatoms on the first impact. More distinctively, the ER reaction proceeds within the time duration less than an oscillation period of surface-adatom vibration, which is not long enough to dissipate the reaction energy to the surface. The reaction rate typically shows a weaker dependence on T_S and the reaction cross-section (σ) is expected to be less than 1Å^2. In principle, this abstraction reaction cross section is independent of surface coverages (θ_D) as well as of temperature (T_S).

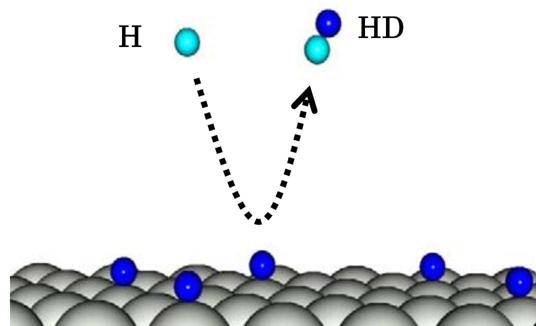

Fig. 1.2 Schematic diagram of HD desorption via Eley-Rideal mechanism.

A dynamical study on H(D) + D(H)/Cu(111) → HD at 100K , done by Rettner[44], explained the direct abstraction in terms of the ER mechanism. However, afterward, Rettner and Auerbach reported a HD reaction cross section of ~5Å^2 for the same reaction system[45,46] which contradicted seriously with theoretical evaluation of the ER cross section (σ <1Å^2).[47,48] Then they turn to believe a hot-atom mechanism.

1.2.2 Hot-atom (HA) mechanism

Harris and Kasemo[49], in 1981, proposed an idea to explain the H interaction with the adsorbed oxygen on platinum surface named as Hot Atom (HA) mechanism. According to the HA model, hot H atom (H*) can move laterally over the surface without dissipating its energy to the substrate. When this hot atom approaches adatom, it can interact with them to form a molecule followed by desorption. In this process, H* is denoted as a primary hot atom. H* can abstract surface D adatoms to form HD molecules following a first-order kinetics with respect to θ_D. Together with this, incident H atoms can also dissipate energy to nearby D adatom to produce a secondary hot atom, D*. Thus, newly formed D* can react with another nearby D adatom to induce D_2 desorption following a second-order kinetics with respect to θ_D.[50,51,52,53,54,55,56,57] According to them, the larger reaction cross-section (σ ~3Å^2) is evidence for this HA model. The following picture (Fig. 1.3) illustrates the HA model.

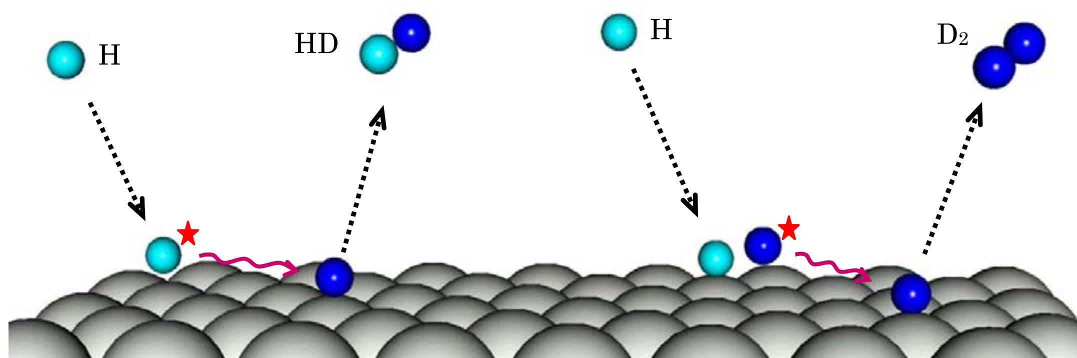

Fig. 1.3 HD desorption (first-order) via primary hot-atom mechanism (left) and D_2 desorption (second-order) via secondary hot-atom mechanism (right).

Based on the experimental results of H interaction with adspecies on metal surfaces, the HA model has been proposed. It must be mentioned here that the chemisorption potential is weakly corrugated on metal surfaces and hot atoms can migrate over the surface. Therefore, the HA picture is a widely accepted model for the H-induced D adatom abstraction on metal surfaces. However, interaction potential of silicon surface is highly corrugated[58]. Moreover, H induced HD and D_2 reaction order is found to be second- and forth-order with respect to adatom coverages. Based on this fact, the HA mechanism on silicon surface is no longer an effective model and must be ruled out. Instead, recently proposed hot-complex model can explain the ABS and AID reactions on Si surfaces successfully.

1.2.3 Hot-complex (HC) mechanism

While hot atom (HA) idea was accepted by many scientists working on Si surfaces, Shimokawa et al. reported that H induced D_2 desorption on Si(100) surfaces is of fourth-order rather than second-order with respect to D coverage. Later on, Hayakawa et al. proposed that HD desorptions obeyed second-order kinetics on the same surfaces. They explained that result with a new mechanism named as Hot Complex (HC). According to HC model, incident H atom is first trapped in the chemisorption potential on the doubly occupied Si dimer (DOD) of Si(100)-2x1 surface and formed a short lived energetic complex (H + D-Si-Si-D)*. This HC can dissipate energy through two channels. One way is the direct abstraction. In this way, H atom abstracts one of the two D adatoms to form a HD molecule, leaving behind a singly occupied dimer (SOD). In this circumstance, the second-order kinetics for ABS can be explained successfully. The second-order HD desorption is also confirmed by Kubo et al.. On the other way of energy dissipation is H sticking on the Si dimer by breaking Si-Si bond. The schematic diagram shown in Fig.1.4 can illustrate the HC model. Sticking of H by breaking Si dimer is also reported by Flowers et al.[59] On the other hand, H-induced D_2 desorption, which

is fourth-order with respect to D coverage, is also explicable by a transiently formed dihydride which is initiated from the HC. According to Rahman et al. (3x1) phase on Si(100) surface is the precondition for such D_2 desorption. Incident H atoms form a hot complex on the doubly occupied Si dimer (Fig.1.4). If sticking process is most plausible in HC, adjacent four dihydrides or local (1x1) domain is formed onto (3x1) phase. Such a local (1x1) domain on (3x1) phase is thermodynamically unstable. This instability compels the dihydrides to induce D_2 desorption and thus the system returns back to (3x1) phase. In this situation, one incident H atom interacts with four D adatoms, thus, the reaction order is four with respect to D coverage. H induced HD and D_2 desorptions from the Si(111) surface was also studied by Khanom et al. According to their experiments, at the high coverage, HD and D_2 desorptions were of second- and third-order with respect to θ_D, respectively. They also explained their results based on the hot complex model.

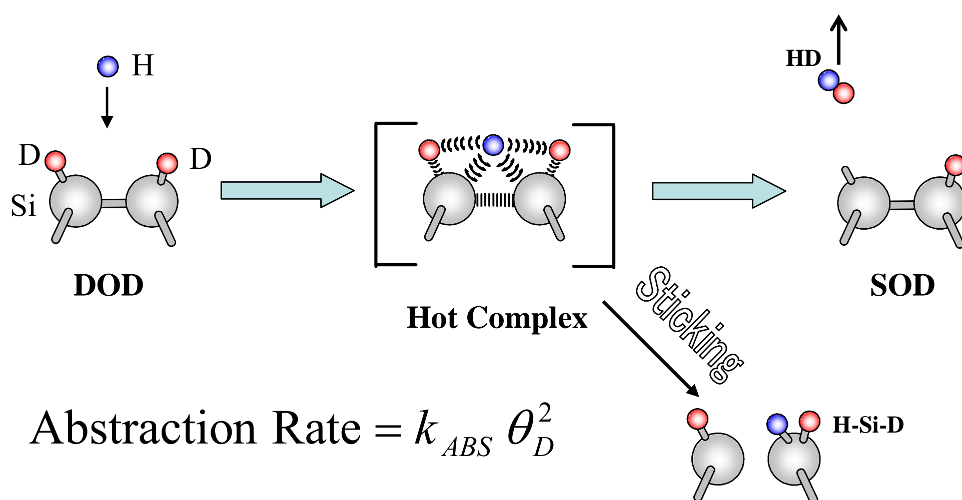

Fig. 1.4 Schematic diagram of hot-complex mechanism

1.3 Oxygen interactions with Si surfaces

As was mentioned in section 1.1, when Si surfaces are exposed to O atoms, it can be inserted either into Si–Si bonds to form Si–O–Si species or in Si–H bonds to form Si–OH (Si–OD) species. Adsorption energy (1 eV) is theoretically evaluated for both reactions.[22,23] Weldon et al.[60,61] also studied the initial oxidation structure by means of surface infrared absorption spectroscopy and density functional cluster calculations. They demonstrated that Si-Si dimer bond was the preferred target for the initial insertion of oxygen on Si(100) surfaces. They also reported that Si-OD or Si-OH species were stable only at room temperature and went through a rearrangement leading to the incorporation of O atoms into Si-Si backbonds even at moderate temperatures above 400 K. Recently, by analyzing the O uptake curves obtained on clean Si surfaces, Kinefuchi et al.,[62] reported the same results mentioned above. According to them, as the O-coverage was increaseed, the oxygen uptake curve gradually deviated from the Langmuir kinetics. Fig. 1.5 shows possible structures of Si(100)–2×1 surfaces before and after O-insertion reported by Kinefuchi et al.

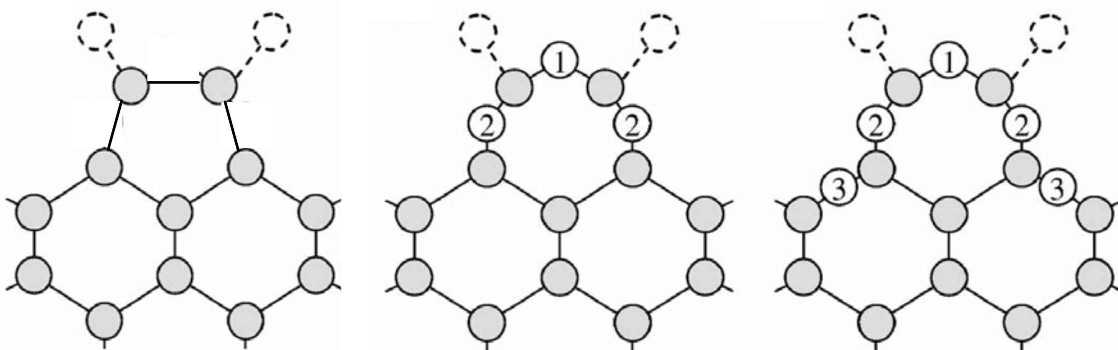

Fig. 1.5 Clean Si(100)-2x1 surface (left). Accessible reaction sites at 673 K for the pure O_2 (middle) and 5.1 % O_3/O_2 (right): (1) dimer bridge, (2) dimer backbond and (3) subsurface backbond. Circle with dashed lines show dangling bond site.

The adsorption and decomposition of water (D_2O) on Si(100) and Si(111) surface were studied using temperature-programmed desorption (TPD)[63] and static secondary ion mass spectroscopy (SSIMS).[64] They found that peaks of the D_2 TPD spectra were shifted to the higher temperature region on already oxidized Si surfaces. Quite the same TPD result was reported by Shimokawa et al.[33] The reason of this peak shift in the TPD spectra was explained by Kato et al.[65] when they studied the oxidation of dangling bond at the single occupied dimer (SOD) on Si(100) surface by the first principles calculations. They revealed that Si-H bond energy became stabilized by back bonding oxygen atoms. Shimokawa et al.[66] exposed D/Si(100) surfaces to atomic O beam and found, for the first time, the D_2O formation and D_2 desorption occurred at various D precovered surfaces. Similar results were also reported on Pt(111) surface by Kan.[67] On the monolayer D covered Si(111) surfaces at various *T*s, the same experiments were done by Rahman et al.[68]. The desorption kinetics of D_2 and D_2O molecules exhibited a feature characterized with a quick rate jump at the very beginning of O exposure followed by a gradual increase with a delayed maximum and then an exponential decay. They also reported that O-induced D_2 and H-induced D_2 spectra as a function of *T*s appeared to be very similar. Based on these findings, they discussed the possible reaction mechanisms on the Si(111) surfaces. In the same year, Tsurumaki et al.[69] reported the details of the incorporated oxygen effect in H adsorption, desorption and abstraction processes on the partially oxidized Si(100) surfaces by *in situ* mass spectroscopic study.

However, the works mentioned above are related to the O-incorporated Si surface structures, the influence of already incorporated oxygen atoms on D/Si surfaces and possible reaction mechanism of O induced D_2O formation and D_2 desorption on D/Si(111) surfaces. Although, D_2O and D_2 desorptions induced by O atoms was reported on the Si(100) surfaces, no reaction mechanism has been proposed.

1.4 Structures of Si surfaces

To understand the kinetics and dynamics of hydrogen adsorption and desorption at Si surfaces, the detailed knowledge of the geometric and electronic structure of Si crystalline surface is required as foundation for interpretation of experimental results. The structures of Si surfaces have been a subject of numerous investigations. Si(110) surface has been studied for over 50 years and proposed several superstructures on Si(110) surfaces. They are summarized in the table 1.1.

Table 1.1 Various surface structures of Si(110)

Authors	Structures	Technique	Ref.
F. Jona	Initial, 5x4, 2x1, 5x1, 7x1, 9x1 ,X		[70]
T. Sakurai et al.	5x1	UPS, LEED	[71]
Y.Yamamoto, et al.	16x2	RHEED	[72]
P. Martensson et al.	5x1	LEED, AR-UPS	[73]
T. Ichinokawa	16x2	LEED, AES	[74]
H. Ampo et al	16x2	LEED, AES	[75]
Y.Yamamoto, et al.	16x2	RHEED	[76]
E.J.van Loenen et al.	16x2 and (17,15,1)2x1	STM	[77]
Y.Yamamoto, et al.	16x2	STM	[78]
H. Sakama et al.	16x2	STM	[79]
G.Shimaoka	16x2	RHEED, LEED, XPS	[80]
Y. Yamamoto	16x2	RHEED	[81]
W. E. Packard et al.	16x2, 5x1	STM	[82]
T. An. et al.	16x2	STM	[83]

Jona[70], in 1965, for the first time, reported seven superstructures on Si(110) surface named as ‘Initial’, ‘5x4’, ‘2x1’, ‘5x1’, ‘7x1’, ‘9x1’ and ‘X’. Martensson et al.[73] described the electronic structure of Si(110)-5x1 by LEED and AR-UPS in 1985. Yamamoto et al.[72,76,78,81] for the first time, proposed 16-structure. They also revealed that the 16-structure transformed reversibly to 1x1 structures at 1033 K. Ichinokawa et al. ascertained by LEED-AES that 16-structure was formed on a clean Si(110) surface. They also reported that ‘5x4’, ‘2x1’, ‘5x1’ structures were induced by Ni deposition on clean Si(110) surface. In 1986, atomic configuration of hydrogenated and clean Si(110) surfaces were studied by Ampo et al.[75] The step structures were described as periodically up and down sequence of terraces along the direction $[\bar{1}12]$ determined by LEED. They also reported that the number of Si atoms across the width on each terrace is 8±1. Loenen et al.[77] illustrated for the first time by STM experiment that the 16-structure and the (17,15,1) vicinal plane coexisted on the clean Si surface. These findings were also confirmed by high temperature STM image done by Yamamoto et al.[84,85] Based on STM images, Packard et al.[82] informed the surface reconstruction of ‘16x2’ and ‘5x1’ on Si(110) surface and proposed a model named Stretch-hexagon face-centered adatom model in 1997. Most recently, An. et al.[83] investigated the Si(110) surface by STM images taken both on filled-state and empty-state bias voltage at room temperature and reconfirmed the ‘16x2’ reconstruction. Based on these images, they proposed several possible models including pair of pentagons (PP), among which a tetramer-interstitial model could be the most possible structure. Recently, surface phonons of clean and hydrogen terminated surface were analyzed by HREELS and LEED by Eremtchenko et al.[86] A Si(110)-1x5 reconstruction was reported as the most stable surface phase. Most recently, on Si(110) surface at room temperature, 16x2, (17,15,1)2x1, 1x1 and zigzag reconstruction were re-reported by a technique named non-contact atomic force microscopy for the first time by Miyachi et al.[87] A metastable ‘5x8’ reconstruction was

identified by Ohira et al.[88] at 603 K which returned to clean '16x2' phase after prolonged annealing at the same temperature.

Quite a few researchers completed their simulation, based on first-principle total energy calculations on Si(110) surfaces. Takeuchi,[89] based on first principles total energy calculations, showed that the Si(110) surface gained 0.67 eV/[(1x1)cell] energy with respect to the ideally bulk terminated surface. He also concluded that adatom structure was energetically more favorable and each adatom was bonded with four first layer atoms. Based on *ab initio* and first-principles calculations, Stekolnokov et al.[90,91] also informed that adatom reconstruction gained energy and adatom-rest atom electron transfer was more favorable. Their simulated STM images confirmed the pentagon structure observed on Si(110)-16x2 surface. They also reported that edge atoms and surface chains were rebonded in the antiphase and the steps along the $[\bar{1}12]$ direction yielded a trench, which was lower in surface energy.

Several researchers performed different reactions on reconstructed Si(110) surfaces. In 1976, Sakurai et al.[71] performed chemisorption of atomic hydrogen on Si(110)-5x1 surface and discriminated two distinct 1x1 phases (adsorbed H on tetrahedral site and non-tetrahedral site) during H exposure as a function of surface temperature detected by LEED and UPS. Different surface species of hydrogenated Si(110) surface in solutions were detected by IR spectroscopy. Watanabe,[92] in 1995, reported the ordered monohydride chains along the $[\bar{1}10]$ with some defects of strained dihydrides, found in acidic and water solutions. Effect of hydrogen plasma on Si(110) surfaces at room temperature was investigated by Shinohara et al.[93] According to their *in situ* real-time IRAS experimental result, at the initial stages of H-plasma treatment, surface hydride species (SiH_x, x = 1-3) were removed from the surface. A long-term H-plasma treatment of Si(110) surface reproduced monohydride species and created H-terminated Si vacancies at the subsurface regions. It was also reported that

monohydrides were relatively stable against the attack of hydrogen radicals as compared to higher hydrides species (SiH_2, SiH_3,etc.). Surface structure of H-saturated Si(110) surface after wet cleaning was studied by Arima et al.[94] by STM and FTIR-ATR. According to their findings, after rinsing with HF solution for a short period, a long terrace of 1x1 structure along the $[\bar{1}10]$ direction was formed. Atomic arrangement around the step edges were determined based on atomic images and first-principles calculations. Based on the results, they proposed the mechanism of H-terminated surfaces during the wet cleaning process.

Structure of the Si(110)-16x2 surface and hydrogen desorption kinetics were investigated by Kim et al.[95] using temperature-programmed desorption (TPD). According to their report, D_2 TPD spectra exhibited three second-order desorption peaks (denoted as β_2, β_1* and β_1) originated from dihydrides, adatoms and surface Si dimer species, respectively. Abstraction and adsorption of atomic hydrogen on Si(110) surfaces were also studied. Lottherloh et al.[96] performed the subsurface deuterium abstraction by atomic hydrogen. According to their experiments, when specially prepared highly rough surface (enriched with defects due to the use of high energy Ar sputtering) was exposed to H beam, α-deuterium (located underneath the surface) was abstracted by atomic hydrogen. Reaction cross sections were also measured in the order of 1 $Å^2$ ignoring any strong comment to the possible reaction mechanism. Atomic defects generated by adsorption of atomic hydrogen on Si(110)-16x2 surface were also reported by Yoshimura et al.[97] in 2002. According to their STM images taken at room temperature, atomic hydrogen was adsorbed preferentially on the specific site at the pentagons. Recently, oxidation of Si(110)-16x2 surfaces were done by Suemitsu et al.[98,99] and analyzed the data obtained by real-time XPS and room-temperature STM. They reported that pentagon pairs (PP) present on the reconstructed surface were most vulnerable for oxidation. Based on the STM image they also proposed possible models of oxidized PP sites. However, to date, abstraction of surface D by H on the Si(110) surfaces is not yet reported. To

give a picture of Si(110)surfaces, an STM image[100] of 16-stricture and a 3D model of 1 monolayer (ML) H/ Si(110) surface are shown in fig.1.6.

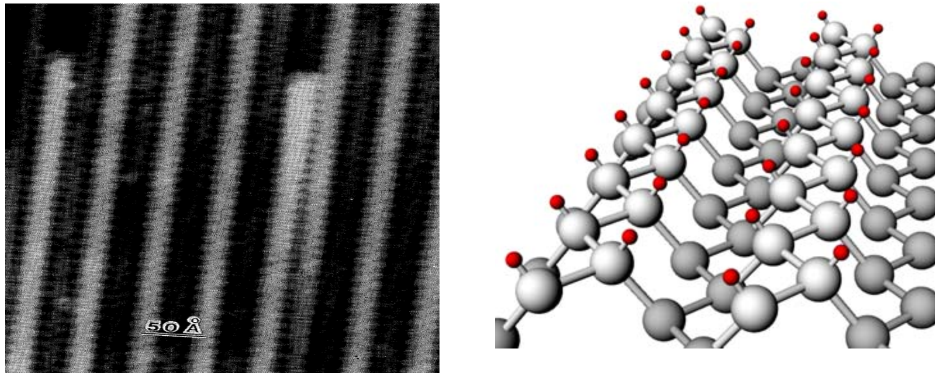

Fig. 1.6 STM image (left) of Si(110)-16-structure taken under sample bias of 2.0 V and tunneling current of 0.3 nA. A 3D model of H/Si(110) surface is shown. (Right).

On the other hand, the fundamental unit of the Si(100)-2x1 reconstruction is a surface Si dimer. Schlier et al.[101] first observed the Si(100)-2x1 reconstruction and proposed that the (2x1) structure arises from the formation of surface Si dimers. In this picture, Si dimer formation eliminates half of the dangling bonds after making Si-Si bonds (bond length ~2.35 Å and bond energy ~2.3 eV[102]) but leaves one dangling bond per Si atom. Early calculations by Appelbaum et al.[103] reported that these dangling bonds participate in π-bonding interaction (0.22-0.52 eV[104]). When this surface is exposed to hydrogen atoms, weaker π-bonds are broken followed by monohydride formation (Si-H) passivating the surface dangling bonds. Saturation of monohydride phase, that is, adsorption of two H atoms per Si dimer, appears to stabilize the symmetric dimer and relives some of the subsurface strain associated with the reconstruction.[105,106] According to the accepted ideal model, the adsorption process can be seen as a sequence of following stages: initially, adsorption of H atoms take place at the Si

dangling bonds leading to the formation of the monohydride Si(100)-2x1 surface. In this arrangement, each surface Si atom is bonded by one H atom and accepted as 1ML (monolayer) H covered Si surface (θ_H = 1ML). Fig.1.7[107] is an ideal example.

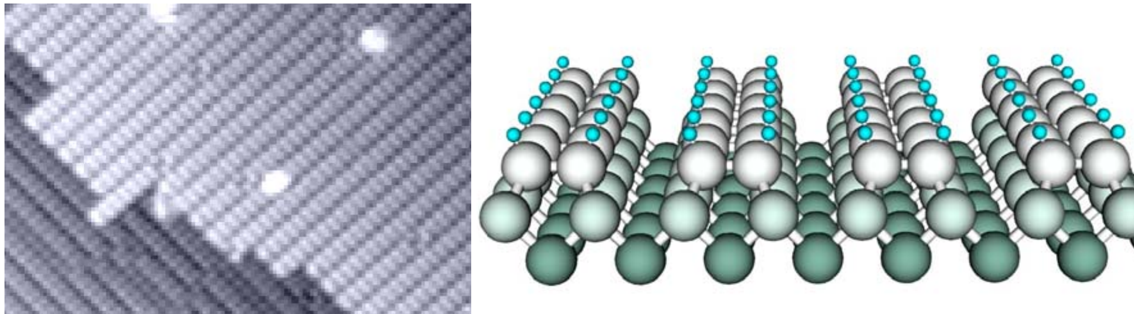

Fig. 1.7 STM image (left) of H/Si(100)-2x1 surface taken at -2.5 V bias voltage and 20 pA tunneling current. Corresponding 3D model is shown (right).

At the second stage, incident H atoms break a fraction of surface dimers to form a mixed phase of monohydrides and dihydrides known as Si(100)-3x1 with a maximum coverage of θ_H = 1.33 ML. In the well-reconstructed (3x1) phase, a row of dihydride is added in between two rows of Si dimer, that means, dihydride and dimer rows are alternately arranged. One example is shown in the Fig.1.8.[108]

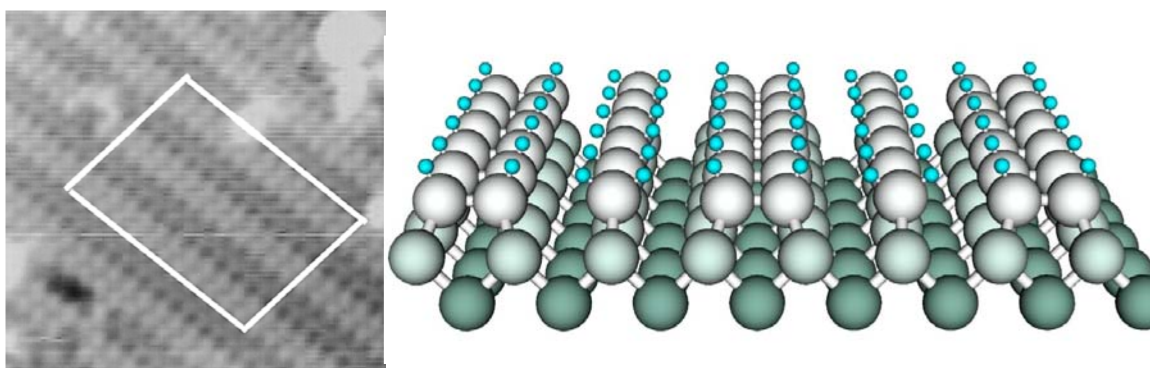

Fig. 1.8 STM image (left) of H/Si(100)-3x1 surface taken at 3.5 V bias voltage. Corresponding 3D model is shown in the right side.

After the long time H exposure, all the surface Si dimers are broken followed by the formation of Si(100)-1x1 surface (Fig. 1.9). In this phase, two H atoms are on every Si atom (H-Si-H) and hence, $\theta_H = 2$ ML. Generally speaking, such a dihydride surface is roughened due to etching of the surface Si atoms.[109,110,111,112] According to the experiments of the low energy electron diffraction[113,114] and the scanning tunneling microscopy (STM)[108,115,116,117] the 3x1 phase is stable only at the narrow temperature region around 400 K. As the surface temperature is raised to, say 450 K, the 3x1 phase tends to be unstable, generating molecular desorption along β_2 TD. Hence the saturation coverage becomes smaller than 1.33 ML. For 1.0 ML < θ_H <1.33 ML the surface contains both 3x1 and 2x1 phases characterized with an antiphase boundary with respect to Si dimer rows.[116,117]

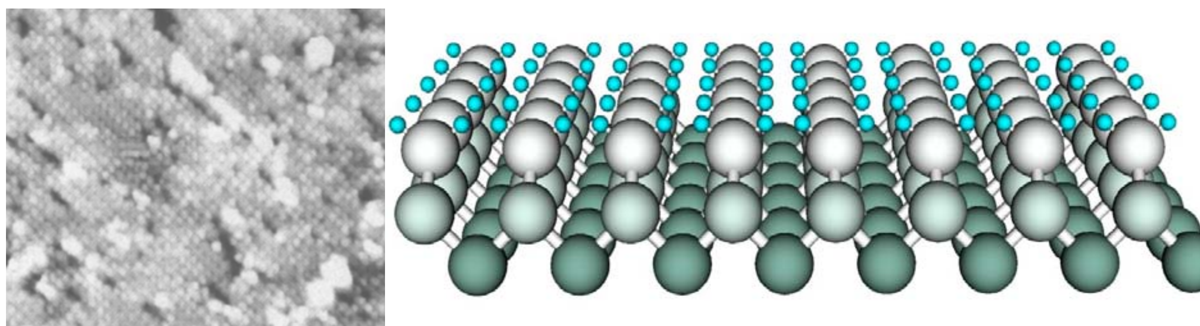

Fig. 1.9 STM image (left) of H/Si(100)-3x1 surface after long time H exposure at RT. An ideal 3D model of H/Si(100)-1x1 is shown in the right side.

As *T*s is further raised above 600 K, all the dihydride species get extinguished and the surface turns to fully monohydride with the saturation coverage $\theta_H = 1.0$ ML. Further increase of *T*s, generates H_2 desorption through β_1 TD leaving behind the bare Si atoms over the surfaces.

1.5 Aim and outline of this thesis

Despite of a great deal of reports on H-induced adatom abstraction on D/Si surfaces, mechanisms to form HD and D_2 desorptions are still of theoretical and experimental controversy. Recently the hot complex (HC) mechanism has been proposed to explain the H induced HD and D_2 desorption on D/Si(100) and D/Si(111) surfaces, ruling out the Eley-Redeal (ER) and hot atom (HA) mechanisms.

As was mentioned in the previous subsection, various surface structures of Si(110) have been proposed. However, there was no report of adatom abstraction by H on these surfaces. The reaction kinetics of H-induced HD (ABS) and D_2 (AID) desorption on the D/Si(110) surfaces may be important to reveal the role of different surface entities formed during the H atom exposure and to check the validity of the HC model proposed on Si(100) and Si(111) surfaces. Keeping this in mind, I have performed the above mentioned abstraction reactions on D/Si(110) surfaces at various surface temperatures (Ts) and D coverages. These experimental results have been published in Surface Science.[118] Details of the experiments and results are explained in Chapters 2 and 3.

Since the Si(110) surface structure is not well understood, this surface may not be a appropriate substrate to study the reaction details for both ABS and AID pathways. On the contrary, various reconstructions (2x1, 3x1, 1x1) on H/Si(100) surface are well defined and widely accepted. This is why, Si(100) surfaces have been chosen to study the reaction lifetimes of H induced HD (ABS) and D_2 (AID) desorptions. To reconfirm the reaction lifetimes of HD and D_2 desorptions, a sharper chopper has been employed and four D_2 components are discriminated based on their reaction lifetimes. The changes of Si(100) surface morphology under the H irradiation and its role on the reaction lifetimes of D_2 desorption are discussed with possible atomistic mechanisms in Chapter 4, based on the results published in Surface Science.[119]

So far, O induced D_2 and D_2O desorptions were reported for D/Si(100) and D/Si(111) surfaces. However, the role of dideuterides was not clearly elucidated. Together with this, activation energies and reaction mechanisms were not revealed. In Chapter 5, I will discuss the details of O induced D adatom abstraction reactions followed by the reaction mechanisms considering the role of various surface species on D_2 and D_2O desorptions, which has been published in Surface Science.[120]

Finally, in Chapter 6, I will summarize the H- and O-induced reactions on the Si surfaces and its potential applications in silicon based industries. I will also mention future plan related to these experiments.

This thesis is based on the papers published in Surface Science.

Chapter 3

Adsorption and abstraction of atomic hydrogen on the Si(110) surfaces.
R. Khan, Y. Narita, A. Namiki, A. Kato and M. Suemitsu.
Surface Science 602 (2008) PP. 1979-1986

Chapter 4

Transient desorption of HD and D_2 molecules from the D/Si(100) surfaces exposed to a modulated H-beam.
A.R. Khan, A. Takeo, S. Ueno, S. Inanaga, T. Yamauchi, Y. Narita, H. Tsurumaki and A. Namiki.
Surface Science 601 (2007) PP. 1635-1641

Chapter 5

Reaction of atomic oxygen with the D-covered Si(100) surfaces.
F. Khanom, A. R. Khan, F. Rahman, A. Takeo, H. Goto and A. Namiki.
Surface Science 601 (2007) PP. 2924-2930

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