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学位論文題目 Studies of Chemical Reactions with Atomic Hydrogen  
on Si(100) Surfaces by Infrared Reflection  
Absorption Spectroscopy

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## 論文内容の要旨

Chemical reactions on silicon surfaces are very important and interesting from the viewpoint of both semiconductor technology and surface science. In this thesis they shall focus on (I) the hydrogen diffusion into silicon bulk causing infrared peak width broadening, (II) the reaction of water with ideally hydrogen terminated Si(100)-(2×1) surfaces and (III) the reaction of atomic hydrogen with water covered Si(100)-(2×1) surfaces.

Hydrogen reaction with Si(100) surface is an important model system in surface science studies. This system has been used extensively in semiconductor fabrication technology preventing the Si(100) surfaces from contamination and also employed as a precursor in several chemical vapor deposition reactions. Interaction of hydrogen with silicon surfaces has been extensively studied by several surface techniques such as temperature programmed desorption (TPD), scanning tunneling microscopy (STM), electron energy loss spectroscopy (EELS) as well as Fourier-transform infrared spectroscopy (FTIR). These investigations have thrown light on several aspects of hydrogen reaction with Si(100) surfaces. When silicon surface is exposed to atomic hydrogen, it generally forms (3×1), (2×1) and (1×1) surface structures depending on the adsorption conditions. However, very few reports have appeared on hydrogen diffusion into silicon bulk on nearly ideally hydrogen terminated silicon surfaces. Most of them have focused on theoretical and TPD studies.

They have investigated the dependence of the line width of the coupled monohydride symmetric stretching vibration on the H-terminated Si(100)-(2×1) surface as a function of temperature and hydrogen exposure by infrared reflection absorption spectroscopy (IRRAS) using CoSi<sub>2</sub> buried metal layer substrate (BML-IRRAS) (Fig. 1). They find that even for nearly ideally H-terminated Si(100) surface, the line width changes significantly depending on the hydrogen exposure and exposure temperatures. The minimum line width observed on the nearly ideally H-terminated surface at around 670 K and 500 L hydrogen exposure agrees or even better than the reported homogeneous line width determined by the dephasing effects. The dependence of line width broadening on hydrogen exposure and temperature on nearly ideal H-terminated regions can not be explained by either dephasing effects or inhomogeneities due to the coexistence of higher hydrides, or contamination by the residual water. The line width broadening is also not due to the surface roughness induced by the hydrogen etching. They suggest that the line width broadening is essentially caused by subsurface hydrogen..

They have carried out a number of experiments to investigate the presence of subsurface hydrogen and its effect on the infrared line width broadening. The Si(100) surface was initially cleaned by flashing it to high temperature (~1150 K) and exposed to 5000 L atomic deuterium at about 670 K. Then the surface silicon deuterides were completely replaced by exposing 500 L atomic hydrogen at 620 K. The sample was then annealed for one minute at fixed higher temperatures in order to check the reappearance of surface deuterium from silicon bulk by IR at 1525 cm<sup>-1</sup>. They find that with increasing annealing temperatures, the decomposition rate of coupled monohydride ( $\nu$  Si-H<sub>CM</sub>) characterized by 2098 cm<sup>-1</sup> becomes faster. This is

simultaneously followed by the appearance of coupled monodeuteride peak at  $1525\text{ cm}^{-1}$  which can only be explained by the diffusion of deuterium atoms from silicon bulk to the surface at higher annealing temperatures.

They have also measured the amount of deuterium incorporated into the Si bulk by conventional TPD experiment for the samples made by the similar process of deuterium exposure and replacement by hydrogen as described above. The  $\nu\text{ Si-H}_{\text{CM}}$  IR line width, separately measured for 500 L hydrogen exposure, is found to increase from  $2.1\text{ cm}^{-1}$  at 673 K to  $3.2\text{ cm}^{-1}$  at

598 K which is roughly in proportion to the amount of deuterium atoms incorporated in the Si bulk as determined by TPD measurements. Similarly, by keeping the exposure temperature constant, for example at 673 K, the IR peak width broadening occurs from  $2.1\text{ cm}^{-1}$  at 500 L to  $2.5\text{ cm}^{-1}$  at 1000 L of hydrogen exposure. They have carried out several measurements to confirm these trends.

The IR and TPD experiments clearly demonstrate that the diffusion of hydrogen atoms does occur into the Si(100) bulk and causes inhomogeneous broadening of the IR line width.

The interaction of water with Hydrogen-terminated Si(100) surface is another important topic for investigation by BML-IRRAS technique. For this purpose, nearly ideally H-terminated Si(100) surfaces were prepared by exposing the clean Si(100) surface to 500 L hydrogen at 650 K. These surfaces were exposed to controlled amount of water and the changes occurring on the surfaces were monitored by BML-IRRAS as a function of the water exposure. The surface oxidation of Si has been observed due to water adsorption and it is concluded that the nearly ideally H-terminated Si(100) surface is still quite reactive with water. However, it has also been noted that the reactivity of H-terminated surface has diminished due to the passivation effect of the surface hydride layer on Si against the background water in the ultrahigh vacuum.

The water-adsorbed Si(100) systems have received considerable attention due to its apparent simplicity and the widespread use of  $\text{H}_2\text{O}$  in industrial oxidation processes. In spite of many excellent scientific and technological studies, much remains to be understood about this system at microscopic level. Vibrational spectroscopy and *ab initio* quantum chemical cluster calculations have established that there is no barrier to dissociative chemisorption of  $\text{H}_2\text{O}$  on Si(100)-(2 $\times$ 1) surfaces forming stable Si-H and Si-OH bonds. Annealing of water exposed Si surfaces induces the insertion of oxygen atoms into Si back bonds or the formation of epoxides through dehydrogenation. It has also been reported that the initial Si(100) surface is comprised of an array of isolated and intra-row coupled dimers, which are coupled by a hydrogen bonding between OH groups that reside on the same end of adjacent dimers in a dimer row. It is

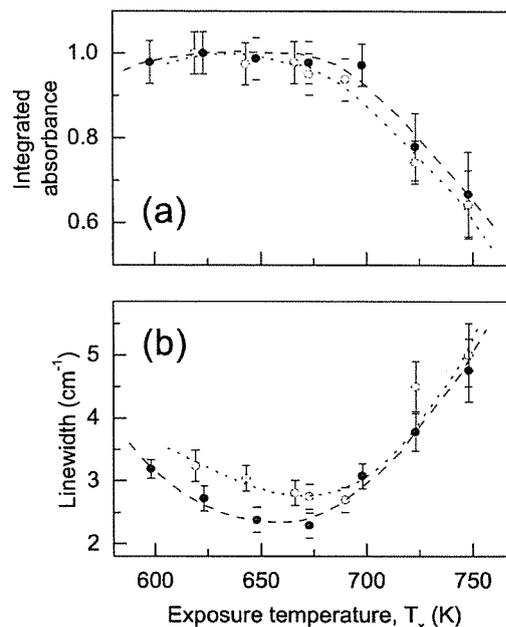


Fig. 1 Dependence of the normalized integrated absorbance (a) and the linewidth (b) on hydrogen exposure temperature for the hydrogen exposure of: (1)  $\bullet$ : 500 L; (2)  $\circ$ : 1000 L

proposed that such inter-dimer coupling facilitates the subsequent transfer of oxygen between dimers forming oxygen agglomeration, so that the initial oxidized surface is comprised of an inhomogeneous array of zero-, one-, and two-oxygen containing dimers.

Recently the water-covered Si(100) surface exposed to atomic hydrogen at 220 K has been studied using external transmission (ET) infrared geometry method (Weldon et al. *J. Chem. Phys.* **113**, 2440, (2000)). These experiments conclusively show that the atomic hydrogen exposure induces oxygen insertion which is usually achieved by annealing the water-covered Si(100) surface. However, in this case, single O incorporation predominates which can be explained by the following mechanism. The first step is the elimination of H<sub>2</sub> into gas phase by the abstraction of hydrogen atom from the surface Si-OH group forming the SiO· radical species. The oxygen radical is preferentially inserted into the Si-Si dimer bond, thereby forming the single oxygen-inserted species. In spite of its scientific and technological importance, the investigation on atomic hydrogen induced-oxidation has only been performed over a limited range of temperature and hydrogen exposures.

In the present work, the BML-IRRAS has been used to investigate the atomic hydrogen-induced oxidation on the water-adsorbed Si(100)-(2×1) surface over a wide range of temperatures (268 ~ 373 K) and exposures of atomic hydrogen (Fig. 2). The BML-IRRAS has high sensitivity for the perpendicular component over a wide frequency range including less than 1000 cm<sup>-1</sup> (the frequency cut off region of a multiple internal reflection (MIR) geometry). Owing to this unique characteristic of BML-IRRAS, a series of bending modes consisting of oxidized and nonoxidized SiH<sub>2</sub>, which are not observed or very weak by the ET geometry because of its low sensitivity to the perpendicular component, are observed clearly for the first time, and the new oxidation mechanism is proposed.

Using the well-documented B3LYP gradient corrected density functional method with the polarized 6-31G\*\* basis set for all atoms, They calculated the IR vibrational frequencies. The calculated harmonic frequencies are obtained by multiplying uniform frequency shift factors for each type of vibration, which were determined by using the assignment-established modes:  $\nu$  SiH<sub>CM</sub> = 2099 cm<sup>-1</sup>,  $\nu$  SiH<sub>CM(M)}</sub> = 993 cm<sup>-1</sup>, and  $\nu$  SiO<sub>CM(O,M)}</sub> = 1042 cm<sup>-1</sup> (Weldon et al. *Phys. Rev. Lett.* **79**, 2851, (1997)),  $\nu$  SiH<sub>ID</sub> = 2090 cm<sup>-1</sup>,  $\nu$  SiH<sub>AD</sub> = 2107 cm<sup>-1</sup>,  $\delta$  SiH<sub>ID</sub> = 902 cm<sup>-1</sup>, and  $\delta$  SiH<sub>AD</sub> = 913 cm<sup>-1</sup> (Noda et al. *Chem. Phys. Lett.* **326**, 163 (2000)). By comparing the

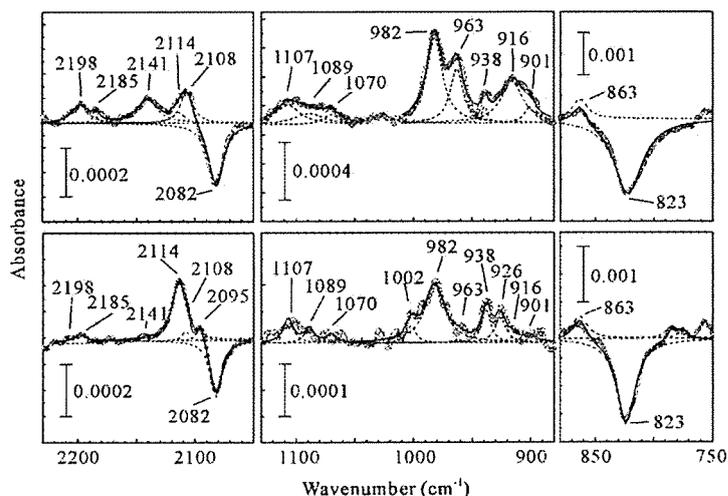


Fig. 2 Observed BML-IRRAS spectra (circles) of atomic H-exposed H<sub>2</sub>O:Si(100)-(2×1) surfaces at T<sub>m</sub> = 373 K for D=1000 L (top) and D=50 L (bottom). The results of curve-resolutions assuming a Lorentzian form are compared (solid and dotted lines).

observed peaks with calculations many important peaks are uniquely assigned. (The definitions of these symbols are given in the captions of Fig. 3 ). The most interesting observations are three pairs of doublet peaks, 901 and 916  $\text{cm}^{-1}$ , 926 and 938  $\text{cm}^{-1}$ , and 963 and 982  $\text{cm}^{-1}$ . These are assigned to  $\delta \text{SiH}_{\text{ID}}$  and  $\delta \text{SiH}_{\text{AD}}$  with zero, one and two inserted oxygen atoms at Si back bonds, respectively. The perpendicular dynamic dipole moments of these modes make these peaks insensitive for the ET geometry (Even at 60 degree incidence, the  $\delta \text{SiH}_{\text{ID}}$  peak intensity observed on the H:Si(100)-(3 $\times$ 1) surface by ET geometry (Weldon et al. *Phys. Rev. Lett.* **79**, 2851, (1997)) is about 1/5 of the BML-IRRAS method (Noda et al. *Chem. Phys. Lett.* **326**, 163 (2000))). The small peaks observed at 990  $\sim$  1050  $\text{cm}^{-1}$  range are assigned to the SiO

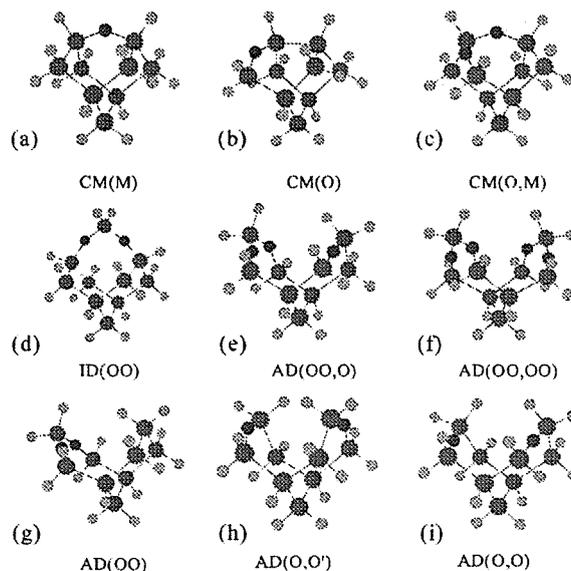


Fig. 3 Models of the different clusters investigated in this work. Atoms are represented as follows: dark blue denotes Si, red denotes O, light blue denotes H, and green denotes tritium. The meaning of the symbols are as follows: CM is coupled monohydride, ID is isolated dihydride, AD is adjacent dihydride, M in a bracket is an oxygen atom inserted into Si-Si dimer bond, and O is an oxygen atom singly inserted to Si back bond, and OO is doubly inserted oxygen atoms. O,O and O,O' are two singly inserted oxygen atoms at the *cis* and *trans* positions of back bonds with coupled or adjacent Si atoms, respectively.

stretching mode of coupled monohydrides with one to three oxygen atoms at the Si back bonds and/or the Si-Si dimer bond. The strong peak at 2114  $\text{cm}^{-1}$  is assigned to the overlapping of the perpendicular components of  $\nu \text{SiH}_{\text{CM}(\text{M})}$  and  $\nu \text{SiH}_{\text{CM}(\text{O},\text{M})}$ . The peak at 2141  $\text{cm}^{-1}$  observed in the high atomic dose region is assigned to the overlapping of the perpendicular components of  $\nu \text{SiH}_{\text{CM}(\text{OO},\text{OO})}$  and  $\nu \text{SiH}_{\text{CM}(\text{OO},\text{O})}$ . The peaks at 2198 and 2185  $\text{cm}^{-1}$  are assigned to the overlapping of the perpendicular components of  $\nu \text{SiH}_{\text{AD}(\text{OO},\text{OO})}^2$  and  $\nu \text{SiH}_{\text{AD}(\text{OO},\text{O})}^3$ , and  $\nu \text{SiH}_{\text{AD}(\text{OO})}^2$ , respectively. The 2108  $\text{cm}^{-1}$  peak may be assigned to the overlapping of  $\nu \text{SiH}_{\text{CM}(\text{O},\text{OO})}$  (calc. = 2108  $\text{cm}^{-1}$ ) and  $\nu \text{SiH}_{\text{CM}(\text{O},\text{O})}$  (calc. = 2106  $\text{cm}^{-1}$ ). The band observed at  $\sim$  1107  $\text{cm}^{-1}$  is assigned to the overlapping of  $\nu \text{SiO}_{\text{ID}}$  and  $\nu \text{SiO}_{\text{AD}}$  with one to four oxygen atoms inserted into Si back bonds and  $\nu \text{SiO}_{\text{CM}}$  with three and four oxygen atoms inserted into Si-Si dimer and/or Si back bonds. From the studies, They have found that the atomic hydrogen-induced oxidation on water covered Si(100)-(2 $\times$ 1) surface has different reaction routes depending on the atomic hydrogen dose. At low atomic hydrogen dose region (< 100 L), the mechanism is well explained by the reaction  $\text{H-Si-Si-OH} + 2\text{H} \rightarrow \text{H-Si-O-Si-H}$  or  $\text{H-Si-Si(O)-H} + \text{H}_2$  proposed by Weldon et al. It is observed that the vibrational band at 982  $\text{cm}^{-1}$  appears in IRRAS spectra only on Si(100) surface exposed to atomic hydrogen but not on the Si surface thermally annealed after water adsorption. The appearance of this peak, even in the lower hydrogen exposure region (< 100 L), suggests the existence of another hydrogen atom-induced oxidation channel,  $\text{H-Si-Si-OH} + 2\text{H} \rightarrow \text{SiH}_2 + \text{Si(O)H}_2$  which is followed by the formation of two oxygen atoms inserted  $\text{SiH}_2$  through the inter-dimer oxygen atom migration. The increase of 982  $\text{cm}^{-1}$  peak intensity with decreasing 2114  $\text{cm}^{-1}$  peak intensity at hydrogen exposures greater than 100 L suggests that the O-inserted

dihydride species are also formed by the hydrogen atom-induced reaction of O-inserted dimer species such as  $\text{H-Si-O-Si-H} + 2\text{H} \rightarrow \text{SiH}_2 + \text{Si(O)H}_2$ . The observed IRRAS spectra show that double oxygen insertion is clearly favored over single oxygen insertion. This is also reasonable from the thermo-dynamical point of view. The calculated energy of AD(OO) is 0.449 eV and 0.438 eV lower than those of AD(O,O) and AD(O,O'), respectively. Also, CM(OO) is 0.561 eV and 0.509 eV more stable than the respective energies of CM(O,O) and CM(O,O').

## 論文の審査結果の要旨

王志宏君の学位論文は、Si(100)表面での水素や水の反応を BML-IRRAS という所属グループが開発した新しい赤外反射吸収分光法で調べたもので全 5 章から構成されている。

BML-IRRAS ではイオン注入法で形成した BML 基板を使用しているため、イオン注入による表面の損傷の影響が無いことを確認する必要がある。基板表面に well-define の Si 単結晶層を形成した後、 $2 \times 1$  の準理想的水素終端表面を形成する条件を見つけ、その条件下で SiH 対称伸縮振動のスペクトル幅が理論的に予想される均一幅と一致することにより確かめた。そして、 $\text{SiH}_2$  や  $\text{SiH}_3$  の混在や水の吸着による不均一広がりがない条件の、準理想的水素終端と考えられる領域においても、水素原子の照射量を増やしたり、照射時の基板温度を下げると、この SiH 伸縮振動の線幅が増大することを発見した。王君は重水素を利用して、IRRAS スペクトルや TPD の基板温度依存性を調べ、最表面 Si 下層の水素原子の存在量と線幅との相関を調べた結果、この線幅の増加は水素原子が Si 下層へ拡散するためである事を証明した(第 3 章)。水素終端表面については Si(111)面は良く調べられているが、Si(100)表面はあまり調べられていない。王君は準理想的水素終端表面形成の条件を見いだしたので、Si(100)表面と水との反応性を BML-IRRAS で調べた。裸の Si(100)表面はほぼ附着確率 1 で解離吸着するのに対し、水素終端することにより二桁ほど安定になること、さらに、準理想的終端面よりも  $\text{SiH}_2$  と  $\text{SiH}_3$  の混在する  $3 \times 1$  や  $1 \times 1$  表面のほうが不活性であることを明らかにした(第 4 章)。

第 4 章での研究の発展として、水で飽和吸着した Si(100)表面に水素原子を照射し、Si 表面の酸化が加速される現象を調べた。この現象自体は Y. Chabar らが透過方式の赤外吸収スペクトルを用いて報告しているが、王君は BML-IRRAS で測定した結果、 $900 \text{ cm}^{-1}$  付近にこれまでに報告のない 3 組の対ピークを見いだした。9 個の Si 原子からなる 29 種類のクラスターモデルについて密度汎関数法による基準振動計算を行い、測定したほぼ全てのバンドの帰属に成功した。これらの新しい 3 組のバンドがバックボンドに 0、1、2 個の酸素を持つ  $\text{SiH}_2$  で、それぞれの対は隣接した  $\text{SiH}_2$  を有するものと、有しないものによるピークの分裂であることを明らかにした。この帰属に基づいて新しい酸化機構の存在を提案した。また、透過方式では基板表面に平行な遷移に、BML-IRRAS では垂直な遷移にのみ感度があるため、両者は相補的であること、そして、Si 表面の指紋領域で垂直成分を高感度、高分解で測定できるのは BML-IRRAS が唯一の手法であることを明らかにした。

これらの成果は 2 報の論文として国際学術誌に発表され、さらに 1 報が投稿中である。第 3 章については 2001 年 MNC 国際会議において最優秀発表賞の表彰を受けている。以上、王君の研究業績はいずれも国際水準からみて非常に高いレベルの研究であると判断し、審査委員会はお願論文が博士(理学)の学位授与に値すると結論した。

口述試験においては、出願者が学位論文の内容を 1 時間説明し、引き続いて 1 時間にわたって質疑応答を行った。研究発表では高度な実験技術に基づく新しい事実の発見、丹念な理論計算、それらを総合した新しい反応モデルの提案を分かりやすく説明した。質問は専門的な観点からのものと表面物理化学や測定法に関する基礎的なものの両面からなされたが、それらの質問に対して的確に答えた。研究発表、発表論文、論文要旨は全て英語で行われており、英語の学力については十分である。

公開発表では学位論文の要点をよく整理して発表した。引き続き行われた質疑応答に対しても、すべての質問に的確に答えたと判断する。

以上を総合的に判断し、審査委員会全員一致で合格と判定した。