

氏 名 平 野 真 也

学位（専攻分野） 博士(理学)

学 位 記 番 号 総研大甲第373号

学位授与の日付 平成11年3月24日

学位授与の要件 数物科学研究科 構造分子科学専攻

学位規則第4条第1項該当

学 位 論 文 題 目 赤外反射吸収分光法によるSi(100)表面に化学吸着した

水素(重水素)の表面反応に関する研究

論 文 審 査 委 員 主 査 教 授 齋藤 修二

教 授 宇理須 恆雄

助 教 授 青柳 睦

助 教 授 見附 孝一郎

助 教 授 大西 洋 (東京大学)

Synchrotron-radiation (SR) stimulated processes have attracted much attention in semiconductor technology for fabricating submicron- and nano-scale devices, because these are low-temperature and low-damage processes with high selectivity in the excitation of chemical reactions. From this viewpoint, the understanding and the control of the chemical nature of chemisorbed hydrogen on Si(100) surfaces (H(D)-Si(100)) are important research subjects in SR processes as they are commonly occurring processes. The purpose of his thesis is clarifying the annealing and SR irradiation effects on the structure of the H(D)-Si(100) surfaces.

It is well known that the structure of H(D)-Si(100) surfaces is strongly dependent on the condition of the atomic hydrogen exposure. The monohydride surface which is prepared by a saturation exposure of atomic hydrogen at high temperatures of around 600 K yields the ordered 2x1 structure. The saturation exposure of atomic hydrogen on a 2x1 surface at  $380 \pm 20$  K yields an ordered 3x1 structure which consists of alternating coupled monohydride (H-Si-Si-H) and dihydride (H-Si-H) units. It is also reported that saturation exposure below 400 K produces a 1x1 structure which consists mainly of mono- and dihydride and of some trihydride species. Concerning the 1x1 surface obtained by the hydrogen saturation exposure (H(D)-Si(100)1x1), it is reported that the structure is a disordered 3x1 consisting of H-Si-Si-H and H-Si-H when formed at 300 K.

High-resolution infrared (IR) absorption spectroscopy is a powerful tool for the detection of adsorbed hydrogen on silicon surfaces and for the investigation of the associated structures and reaction mechanisms. However, the SR irradiation and annealing effects on the hydrogen terminated systems, have not yet been investigated in detail using this technique.

In this work, the structure of the H(D)-Si(100) 1x1 surface formed at 400 K and its change by annealing and SR irradiation have been investigated by BML-IRRAS method using a CoSi<sub>2</sub> BML Si(100) substrate, and reflective high-energy electron diffraction (RHEED). Here, the initial substrate temperature of 400 K was selected so that the existence of trihydride, which complicates the analysis, can be ignored. The SR irradiation experiments were carried out using the SR beam without monochromatization from the beam line 4B of the 0.75 GeV storage ring (UVSOR) at the Institute for Molecular Science.

From measurements of IRRAS of silicon hydrides on the Si(100) BML substrate surfaces as a function of hydrogen exposure at 400 K. Two peaks, which are assigned to the SiH symmetric stretching and SiH<sub>2</sub> symmetric bending vibration bands, respectively, are observed. At around the saturation exposure (1000 L), the peak height of the SiH symmetric stretching vibration band decreases to about 2/3 of that in 100 L, accompanied by the appearance of a SiH<sub>2</sub> bending vibration band and the change of RHEED pattern from 2x1 to 1x1.

Therefore, it shows that only monohydrides and dihydrides exist as dominant species at the saturation exposure region. Furthermore, since the integrated absorbance (IA) of the Si-D stretching vibration band increases about 1.5 times, as described later, upon 650 K annealing, which decomposes dideuteride to monodeuteride, it is considered that the distribution of Si atoms between dihydride and monohydride is 1:2 on the H-Si(100)1x1 surface. Since, 3x1 unit cell consisting of iterating H-Si-H and coupled monohydride (H-Si-Si-H) is a stable structure at 400 K, and H-Si(100)1x1 surface formed at 300 K is made up of disordered 3x1 units, it is quite possible from the above result that the structure of the H-Si(100) 1x1 surface at 400 K is also a disordered 3x1 structure consisting of H-Si-H and H-Si-Si-H units.

Next, the effects of the annealing and SR irradiation on the D-Si(100)1x1 surface were investigated. From the annealing study, the observed IRRAS spectral change due to annealing is explained from the results of the temperature programmed desorption (TPD) experiments for the hydrogen (deuterium) adsorbed Si(100) surface. It is known that the  $\beta_1$  peak of TPD, which starts to rise at about 670 K and peaks at around 760 K ( $dT/ds=1.7$  K), indicates the hydrogen desorption from monohydride phase, and the  $\beta_2$  peak which starts to rise at around 550 K and peaks at 630 K, indicates the hydrogen desorption from dihydride phase. Therefore, the rapid decrease of the IA at around 700 K is ascribed to the  $\beta_1$  desorption and the corresponding peak shift to the lower frequency side is explained mainly by the decrease of the dipole-dipole coupling interaction. Concerning the  $\beta_1$  desorption, the preparing mechanism is supported by the scanning tunneling microscopy (STM) experiments, i.e., monohydride (monodeuteride) desorbs through the precursor form of H-Si-Si-H (D-Si-Si-D). Therefore, it is concluded that the surface after the annealing at 670 K or higher is covered only by D-Si-Si-D, if there exist no defects on the surface, and the sharp SiD stretching vibration band observed at around  $1525\text{ cm}^{-1}$  in the case of annealing study is assigned to the D-Si-Si-D symmetric stretching vibration.

On the other hand, concerning this  $\beta_2$  decomposition, the IA of the SiD stretching vibration band increases by about 1.5 times with annealing temperature increase from 400 to 650 K. This supports the fact that the distribution of Si atoms between dideuteride and monodeuteride is about 1:2 on the D-Si(100)1x1 surface and  $\beta_2$  desorption is explained by the thermal decomposition of  $2\text{SiD}_2$  to D-Si-Si-D +  $\text{D}_2(\text{gas})$ .

Next, the change of the SiD stretching vibration band due to the annealing plus SR irradiation is observed. Here, the SR was irradiated on the surface during 15 min annealing at each annealing temperature. It is reported that the SR irradiation decomposes di- and trihydrides but not the monohydride. In the present case, a slight increase of the IA of the SiD stretching vibration band is observed upon 570 K annealing plus SR irradiation. This increase is explained by the decomposition of dideuteride to monodeuteride by the SR irradiation, since no increase is observed only upon 570 K annealing. The decomposition of dideuteride to monodeuteride by the SR

irradiation is more clearly shown by taking the difference spectrum between the spectra before and after the SR irradiation. It has also been found that the RHEED pattern did not change from  $1 \times 1$  by the SR irradiation on the D-Si(100) $1 \times 1$  at 400 K. It is assumed that the decomposition of dideuteride by SR at low temperature does not mainly result in the formation of D-Si-Si-D. The main process is probably the decomposition of single D-Si-D. Concerning this dideuteride decomposition by SR irradiation, not only the desorption of deuterium atom by breaking the Si-D bond, but also the possibility of the etching (desorption of SiD or SiD<sub>2</sub>) must be considered.

By comparing both cases, they discussed this etching effects from a different viewpoint. By annealing at 650 K or higher, if there is no defect on the Si(100) surface, the existing surface deuteride species should become to be only D-Si-Si-D, and therefore, the SiD stretching vibration band shape should become sharp and symmetric as observed in annealing study. However, the observed results are quite different in the case of SR irradiation plus annealing. The SR irradiation effects clearly appear in the shape of the IRRAS SiD stretching vibration band i.e., at the annealing temperature higher than 650 K, where only monodeuteride exists, the band shape becomes broad and asymmetric. In the case of annealing (670 K) + SR irradiation. This asymmetric shape can be explained by the etching of the Si(100) surface by the SR irradiation. If there are no defects on the Si(100) surface, the surface hydride species should be, as already mentioned, only D-Si-Si-D, which are thermodynamically stable in the high temperature region where the surface migration of deuterium atoms frequently occurs. But, the observed SiD stretching vibration band shape shows that the surface species are not only D-Si-Si-D. Therefore, it is concluded that some defects are generated by SR irradiation on D-Si(100) $1 \times 1$  surface which consists of D-Si-Si-D and D-Si-D, and it is concluded that the defects are generated by SR stimulated desorption (etching) of D-Si-D, because monodeuteride is not decomposed by SR irradiation. Since only monodeuteride exists on the surface after 650 K annealing, the component of the low frequency side tail of the SiD stretching vibration band in the high temperature region above 650 K is assigned to the stretching vibration of Si-D at the defect site generated by the etching. This means that the SR irradiation induces not only the desorption of D by breaking the Si-D bond, but also the desorption of SiD and/or SiD<sub>2</sub> by breaking the backbonds of D-Si-D.

## 論文の審査結果の要旨

本申請論文は、半導体表面反応のその場観察に有効な手法である、埋め込み金属層赤外反射吸収分光法(BML-IRRAS)を用いて、反応前の Si(100)表面における水素の吸着構造とその吸着水素の熱分解、熱脱離の特性を明らかにした上で、放射光照射により吸着構造がどのように変わるかを明らかにしたものである。

本論文は5章からなり、第一章ではシンクロトロン放射光の特色と半導体プロセスへの応用、その際の H-Si(100)表面反応の重要性を概説した上で、これまでの研究例を紹介し、本研究の位置付けを行っている。第二章では、H(D)-Si(100)表面の構造が、高速電子線回折法 (RHEED)で得られる回折パターンにより分類されること、この構造の解明のために、表面水素の昇温脱離法と組み合わせた走査型トンネル顕微鏡観察を適用すると、 $2 \times 1$  構造が2量体 Si 原子それぞれに水素原子が結合した2倍周期構造に対応すること、 $3 \times 1$  構造が、両端に水素が結合した2量体 Si と  $\text{SiH}_2$  とが並んで存在する構造の繰り返しに対応していること、これら二つの構造が安定である一方、 $1 \times 1$  構造は不安定であり、水素と Si の結合状態について議論が多いことを、これまでの研究に基づいて紹介している。第三章では、実験装置の紹介、特に、その場観察の手法としての埋め込み金属層赤外反射吸収分光法の詳細、減衰全反射法との比較、および双方の得失を議論している。第四章では、先ず、400 K で準備した基板に原子状水素を十分に吸着させた表面状態を準備し、その H(D)-Si(100)の構造が  $1 \times 1$  構造であることを RHEED の方法により明らかにし、しかも BML-IRRAS の方法により SiH と  $\text{SiH}_2$  の形で結合している Si 原子の分配比が 2:1 となっていることを示した。これらの結果から、この  $1 \times 1$  構造は  $3 \times 1$  が不均一で分布していることに対応していると結論した。この基板に放射光を照射すると IRRAS の SiH 振動スペクトルの低波数側に新しいサイドローブが現われることから、放射光照射により  $\text{SiH}_2$  の SiH 結合あるいは  $\text{SiH}_2$  のバックボンドが切断されるとの結論に到達した。第五章では、本研究の総括と今後の課題の議論を展開している。

本研究は、H(D)-Si(100)の表面構造、特に  $1 \times 1$  構造を、埋め込み金属層赤外反射吸収分光法と言う新しい方法を用いることにより、 $3 \times 1$  ユニットが不均一に分布したものであることを初めて明らかにし、また、放射光の照射により、その中の  $\text{SiH}_2$  基が選択的、かつ不均一に攻撃を受けていることを明らかにした。これらの結果は固体表面での化学反応、光反応の基礎としてのみならず放射光励起プロセスなどの半導体デバイス製造過程への応用の基礎として学問的に価値の高い水準にあり、また、十分に価値のあるものである。以上に基づき審査委員会は、本申請論文が学位授与に値すると全員一致で判断した。

また、博士論文の審査終了後、関連する専門分野およびその基礎となる分野、光反応、固体表面物性、半導体材料物性、表面化学反応、赤外線分光学、化学反応論などについて口述による試験を行った。これらに対して出願者は十分な対応を示した。なお、出願者はこれまでに5報の論文を英文で発表しているので、出願者の英語能力は十分であると判断できた。また、出願者は公開の論文発表会において博士論文の主要点を分かりやすく、意欲的に報告するとともに、発表後の質疑応答においても十分な対応を示した。以上の結果、出願者は学位取得に十分な学識を有すると判断した。