Silicon (001) surface after annealing in hydrogen ambient*

Takayuki Aoyama, a) Ken-ichi Goto, Tatsuya Yamazaki, and Takashi Ito
Fujitsu Laboratories Ltd., Morinosato-Wakamiya 10-1, Atsugi 243-01, Japan

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We investigated Si surfaces after annealing in a H2 ambient using attenuated total reflection in the infrared region, reflectively high energy electron diffraction, Auger electron spectroscopy, and atomic force microscopy. We found that at all H2 pressures the surface dangling bonds formed dimers that were related to two-domain (2×1) or c(4×2) reconstructed surfaces. H2 was adsorbed on the reconstructed surface and terminated a pair of dangling bonds that did not form dimers. H2 adsorption was limited by the reaction between H2 and the dangling bonds on the surface. The activation energy of H2 desorption was 0.4–0.6 eV higher than that of H2 desorption. The surface on which H atoms were adsorbed and dimers were formed was inert, which kept the surface clean. We also found that the H2 annealed surfaces were influenced by surface roughness and contaminants including oxygen and carbon. © 1996 American Vacuum Society.

I. INTRODUCTION

Si surface cleaning treatment is an important aspect of wafer processing for ultralarge-scale integration (ULSI). Cleaning removes oxide, carbon, or metallic impurities, reduces surface damage or roughness, and forms surfaces for protection from contaminants between processing stages. The surface conditions after the initial stages influence the processes that follow. For example, in dry etching the surface morphology after the etching and the etching rates is influenced by initial surface conditions. Therefore, it is not an overstatement to say that the initial silicon surface treatment is critical for the success of the processes that follow it.

Si epitaxy is expected to be a process that can fabricate high-performance devices such as metal–oxide–semiconductor (MOS) devices with a stacked source drain structure and an epitaxial base transistor. It is difficult to clean a Si surface on which single crystal films can be grown without introducing defects such as dislocations and stacking faults. The surface treatment for Si epitaxy needs a nearly perfectly clean and flat surface. If there is a small amount of contamination on the surface, such as carbon or oxygen, defects are grown in the epitaxial films. Therefore, the surface condition after the surface treatment is a key factor for Si epitaxy. Many researchers have proposed surface cleaning for Si epitaxy. Among the many Si surface treatments, annealing in H2 is most frequently applied to Si epitaxy. H2 annealing cleans the surface and H2 gas can easily be used because it is a carrier gas for Si epitaxial growth. Most dangling bonds on the Si surface are terminated with H atoms by dipping the wafer in a dilute HF solution. This surface is stable against oxidants, and the H atoms are easily desorbed from the surface at the epitaxial growth temperature. Therefore, a combination of dipping a dilute HF solution, followed by H2 annealing is important for low temperature Si epitaxy. This is because Si oxides, including native oxides, are stable and cannot be removed below 700 °C. Meyerson, Himpel, and Uram reported the annealing temperature dependence of deposited films’ crystallinity when using this surface treatment. They reported that the deposited films had many defects at annealing temperatures of 650–750 °C. Their report predicted that the surface conditions were drastically changed by annealing temperature, which affects the deposited film crystal structure. In addition, Hirose, Suemitsu, and Miyamoto and Liehr et al. reported that the desorption of H2 limits the growth rate in gas-source Si molecular beam epitaxy (Si-MBE). Thus, it is necessary to investigate H-adsorbed surfaces. Other researchers have investigated the surface on which the H was adsorbed using atomic H. We reported H2 adsorption during H2 annealing. However, there are only a few reports that investigate the surface condition after H2 annealing. In this article, we investigate the Si surface condition, mainly the surface structure and H2 adsorption, after annealing in a H2 ambient. We used reflective high energy electron diffraction (RHEED), attenuated total reflection in the infrared region (ATR-IR), Auger electron spectroscopy (AES), and atomic force microscopy (AFM) to analyze the surfaces.

II. EXPERIMENT

Figure 1 is a schematic drawing of the system used in our experiment. This system has five chambers: a load-lock chamber, a transfer chamber, a RHEED analysis chamber, an AES analysis chamber, and a Si epitaxial growth chamber for wafer annealing in H2. Each chamber is connected by a vacuum transfer chamber (7×10⁻⁷ Pa). The epitaxial chamber consists of a gas supply unit, a wafer heating section that uses specially designed long Xe arc lamps, and an evacuation system that uses dry pumping units. The epitaxial chamber is an ultrahigh vacuum chemical vapor deposition (UHV/CVD) system, with a base pressure of 3×10⁻⁶ Pa. The low base pressure is produced by a turbomolecular pump with a pumping speed of 1000 l/s. The main component of the residual gases was H2 because of the low compression ratio we used for the H2 pump. Measurement by quadruple mass spectroscopy (QMS) showed an O2 partial pressure of below.

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a)Electronic mail: aoyama@flab.fujitsu.co

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Fig. 1. Process components of the system used for the experiment.

Even when the wafer was heated to 860 °C in a vacuum, the pressure in the epitaxial chamber was below $1 \times 10^{-7}$ Pa. Wafer temperature was measured using an optical pyrometer with a detection wavelength of 2 μm. The temperature was within 20 °C of the value measured using a thermocouple attached to the wafer. Below 500 °C, the wafer temperature was determined by extrapolating the lamp power dependence of the wafer temperature. Note that the accuracy is within 100 °C, because the wafer temperature below 500 °C varies abruptly with a small input power change.

The wafers were annealed in a H₂ ambient for 20 min. The ramping rate was 3 °C/s, and the cooling speed was over 30 °C/s. After cooling down the wafers, the H₂ gas was evacuated. The H₂ pressure was varied from $1 \times 10^{-6}$ to $4 \times 10^{-5}$ Pa. The pressure was varied by changing the H₂ flow rate and pumping speed. Below 10 Pa, the H₂ was pumped with the turbomolecular pump. The H₂ gas impurity content was under 10 ppb.

The wafers analyzed with RHEED, AFM, and AES were Czochralski (CZ) grown p-type (001) Si (10 Ω cm). The wafers analyzed for ATR-IR, and part of AES and AFM were nondoped (001) Si (1–2 kΩ cm) floating zone (FZ) type. For the ATR-IR analysis, the wafers were cut to 0.5 ×15×50 mm², where each of the shorter sides was beveled to 45° from the surface plane by chemical mechanical polishing (CMP). Before loading the wafers into the experimental system (the annealing chamber), we cleaned them in the following manner. We boiled them in NH₄OH:H₂O₂:H₂O (1:4:4) at 80 °C for 10 min and then in HNO₃ at 100 °C for another 10 min. To terminate the surface dangling bonds with H atoms, we dipped them in a 1.5% diluted HF solution for 30 s. Between each chemical treatment, we rinsed the wafers in de-ionized water (18 MΩ cm) for 5 min, except for the final rinse that was 10 min. Finally, we dried the wafers in a hot N₂ ambient.

After annealing the wafers in H₂, we analyzed the wafer surface using RHEED, ATR-IR, AES, and AFM. The ATR-IR and AFM analyses were performed in air so that annealing wafers were exposed to the air. We analyzed the surface structures using RHEED. The electron acceleration energy was 25 keV, and the electron incident angle was below 2°. We analyzed H₂ adsorption on the surface using the ATR-IR method. The analysis equipment was a Fourier transform infrared (FTIR) spectrometer system (Nicolet, 740). In our ATR-IR analysis geometry, infrared was internally reflected 100 times in the sample. The resolution was 2 cm⁻¹. The background reference spectrum was obtained from the chemically oxidized H terminated surface using a boiling 50% HNO₃ solution at 100 °C. To determine the adsorbed H atom sites, we used partly polarized infrared. We also used AES and AFM (Nanoscope II, Digital Instruments) to measure surface contamination and surface roughness, respectively.

III. RESULTS

A. RHEED analysis

Figure 2 shows typical RHEED patterns before and after H₂ annealing. The direction of incident electrons was almost parallel to the [100]. Figure 2(a) is a RHEED pattern before H₂ annealing, i.e., after the surface is dipped in the diluted HF solution. The diffraction pattern shows a (1×1) periodicity, i.e., an unreconstructed surface. Figures 2(b) and 2(c) are RHEED patterns after hydrogen annealing at 700 °C in 3.2 kPa, and 0.13 Pa, respectively. The surface annealed in the 3.2 kPa H₂ ambient had a well-known two-domain (2×1) structure since half-order Laue zones were observed. In the case of the surface annealed in the 0.13 Pa H₂ ambient, four-fold surface structures weakly appeared; three quarter-order spots between fundamental spots on the zeroth Laue zone.

Figure 2. RHEED patterns of the (001) silicon surface (a) before H₂ annealing (after HF), (b) after annealing in 3.2 kPa H₂ at 700 °C, and (c) after annealing in 0.27 kPa H₂ at 700 °C.
and half-order Laue zones were observed in Fig. 2. The RHEED pattern from [110] azimuth had three quarter-order Laue zones and half-order spots between fundamental spots on each Laue zone (not shown). This reconstructed surface is \(c(4\times4)\) if there is a single domain on the surface. Considering that the surface has two types of terrace domains, analogous to the \(c(2\times1)\) structure, the surface structure may be two-domain \(c(4\times2)\). In addition, since the reciprocal lattices of \(c(2\times1)\) and \(c(2\times2)\) structures partly overlap those of \(c(4\times4)\) or \(c(4\times2)\), the surface may partly have \(c(2\times1)\) or \(c(2\times2)\) structures. Hamers, Tromp, and Demuth observed \(c(4\times2)\) and \(c(2\times2)\) structures using a scanning tunneling microscope (STM). It is, therefore, reasonable that the surface annealed in 0.13 Pa H\(_2\) has \(c(4\times2)\), \(c(2\times2)\), and \(c(2\times1)\) structures. Later, we call this surface “\(c(4\times2)\)” as a general term. They also reported that \(c(4\times2)\) and \(c(2\times2)\) structures resulted from buckled dimers. As a result, we found that the dangling bonds on the Si\((001)\) surface annealed in H\(_2\) formed dimers that were similar to the surface annealed in vacuum.

The surface structures for various annealing temperatures and H\(_2\) pressures are shown in Fig. 3. It is apparent that the \(c(4\times2)\) structures appeared at annealing temperatures between 630 and 790 °C and H\(_2\) pressures below 20 Pa. The temperature range in which \(c(4\times2)\) structures appeared is almost equal to the temperature at which \(c(4\times2)\) structures were observed in the gas-source Si-MBE. The surfaces annealed below 400 °C were \(c(2\times1)\) structures (not shown in Fig. 3). The \(c(2\times1)\) structures were observed in the other annealing condition. It is worth noting that the surfaces annealed at high H\(_2\) pressure were two-domain \(c(2\times1)\) structures.

B. ATR-IR analysis

Figure 4 shows the ATR-IR spectra for various annealing temperatures. The H\(_2\) pressures were all 3.2 kPa. The wave numbers in Fig. 4 corresponded to H–Si stretching absorption energy. Just after the HF dip, the dangling bonds on the surface were terminated by H atoms. The absorption peaks consisted of monohydride (SiH), dihydride (SiH\(_2\)), and trihydride (SiH\(_3\)). As the annealing temperature was raised, the adsorbed H atoms were desorbed. When the temperature went above 500 °C, two new peaks appeared at 2099 and 2088 cm\(^{-1}\). The two peaks grew as the annealing temperature rose. The peak height was independent of annealing time after about 20 min, indicating a steady state. In order to confirm the origin of the H atoms adsorbed at high temperature, we used a surface that had its dangling bonds terminated with deuterium (D). The dangling bonds on the Si surface were partly terminated with D atoms after dipping the wafer in a HF solution diluted with D\(_2\)O. D–Si stretching was detected between 1500 and 1560 cm\(^{-1}\) by ATR-IR analysis (Fig. 5). Small peaks, with about 13 cm\(^{-1}\) spacing, were absorption peaks of H\(_2\)O in the optical path. After annealing in the H\(_2\) ambient at 550 and 700 °C, no D atoms were detected. Therefore, the H atoms on the Si surface annealed above 550 °C were adsorbed from the H\(_2\) gas. The origin of the two peaks was determined to be H–Si stretching where H atoms terminate a pair of dangling bonds that did not form a dimer (Fig. 6). The 2099 cm\(^{-1}\) peak corresponded to the symmetric stretching mode, and the 2088
Fig. 5. ATR-IR spectra before and after annealing the DF-dipped surface in H₂.

The 2099 cm⁻¹ peak to the asymmetric mode. Figure 7 shows polarized ATR-IR spectra, annealed in a 3.2 kPa H₂ ambient at 700 °C. In the ATR-IR analysis geometry, p and s polarization can probe stretchings perpendicular and parallel to the surface, respectively. Thus, the 2099 cm⁻¹ peak was detected with only p polarization, and the 2088 cm⁻¹ with both p and s polarization. These spectra support the model that H was adsorbed at the pair of dangling bonds. We also found that peaks of the other modes were very small compared to the two peaks above 600 °C. This result indicated that the adsorbed H atoms were always paired on the surface. It is surprising that most of the H atoms were adsorbed on the pair of dangling bonds, even with low H coverage.

Figure 8 shows the H₂ pressure dependence of adsorbed H atoms. Obviously, the lower the pressure was, the less the H atoms were adsorbed. The two peaks were not observed at 0.13 Pa. We knew that the c(4×2) structure that was observed in RHEED analysis appeared at this low H adsorption. Hamers, Tromp, and Demuth reported that there are many defects on the c(4×2) structure surface. As will be shown later, we found that O atoms were adsorbed in this pressure range. It is possible that the O atoms make these defects.

Even if the annealing pressure and temperature were the same, the peak heights were different (see the 700 °C spectra in Figs. 4 and 7). The peak height of 2099 cm⁻¹ is smaller than that of 2088 cm⁻¹ in Fig. 4, while peak height of 2099 cm⁻¹ is larger than the 2088 cm⁻¹ in Fig. 7. We do not know...
the exact cause. It may be differences between the two-type terrace width (area). However, there is no relation between the peak height and the polarized spectra. From the AES and AFM analyses, one cause that influenced the phenomena was contamination on the surface and surface roughness. The 2099 cm\(^{-1}\) peak tended to be smaller when contaminants such as oxygen or carbon were adsorbed on the surface or when the surface was roughened. We used a wafer that was intentionally roughened before H\(_2\) annealing by boiling it in a H\(_2\)SO\(_4\) solution for a long time (30 min). The surface roughness after boiling in the H\(_2\)SO\(_4\) solution for 30 min is 2.5–3.0 nm in root mean square (rms), and for 5 min is 2.0 nm. Figure 9 shows the relation between surface roughness and H adsorption. The H–Si stretching peaks became smaller and broader with a rough surface. We found that the H adsorption condition was influenced by surface roughness.

IV. DISCUSSIONS

A. Role of adsorbed H and dimer formation for Si epitaxy

The adsorption of H atoms and dimer formation make the silicon surface inert, and result in keeping it clean. This inert surface is good for Si epitaxy. Figure 10 shows H and O coverage as a function of H\(_2\) pressure. The O coverage was measured by AES, using relative elemental sensitivity factors. The H coverage was estimated from the area of the ATR-IR spectra. The H and O coverage seem to have a complementary relationship. In order to verify this effect, we compared the H\(_2\) ambient to the Ar ambient. The purity of the Ar gas we used was better than that of the H\(_2\) gas. Figure 11 shows the AES spectra of the surfaces annealed in a H\(_2\) and in an Ar ambient. The surface annealed in H\(_2\) was kept clean, while C and O were detected on the surface annealed in Ar. We also noted that H coverage was lower at the temperature range at which Meyerson, Himpsel, and Uram have reported that the epitaxial films have defects. Their results may have been due to the inert surface made by H adsorption.

B. Hydrogen adsorption reaction

We thought that H\(_2\) adsorption was limited by the reaction between H\(_2\) and the dangling bonds on the surface because the H coverage (\(\theta\)) increased as the annealing temperature is raised (Fig. 4). Generally, the adsorption rate did not increased with the substrate temperature. We also found that H\(_2\) desorption and adsorption were not a simple Langmuir isotherms model, since a plot of \(\theta(1-\theta)\), \(\theta(1-\theta)^2\), or \(\theta^2/(1-\theta)^2\) as functions of H\(_2\) pressure (\(P_{H_2}\)) was not linear. From Fig. 10, the relation predicts the Freundlich isotherm as \(\theta \propto P_{H_2}^{1/m}\). We calculated the \(m\) value to be 10 by fitting the data in Fig. 10. This Freundlich isotherm is often observed when adsorption is not simple reaction, for example, H atoms interacting with each other.
If H$_2$ adsorption were limited by the reaction between H$_2$ and the dangling bonds, the temperature dependence of $\theta$ would be related to the adsorption reaction and desorption rates. We estimated $\theta$ for various H$_2$ annealing temperatures from the data shown in Fig. 4. In order to estimate the coverage, we assumed that H coverage on the HF dipped surface was two monolayers. We also assumed the sensitivity of these wave numbers to be the same. We did not correct the coverage to account for some variables, which include dipole screening. The Arrhenius plot is shown in Fig. 12. Using the data from Fig. 12, we then estimate the activation energy of the desorption at 3.2 kPa H$_2$ pressure. In order to simplify this, we assumed that the adsorption occurred according to the two following reactions:

$$H_2 + \text{Si-Si-} \rightarrow \text{H-Si-Si-} + H$$  \hspace{1cm} (1)

$$H_2 + \text{Si-Si-} \rightarrow \text{H-Si-Si-H}.$$  \hspace{1cm} (2)

We do not know which reaction occurred in this case. In these reactions, the H$_2$ concentration is constant because the H$_2$ concentration is proportional to the H$_2$ pressure (3.2 kPa). The concentration of the dangling bonds on the surface is proportional to $(1 - \theta)$. The reaction rate is proportional to $(1 - \theta)^2$ for the dissociative reaction (2). Thus, the adsorption rate is

$$R_{ad} \propto \exp(-E_{ad}/kT)(1 - \theta)$$  \hspace{1cm} or  \hspace{1cm} $$\exp(-E_{ad}/kT)(1 - \theta)^2,$$

where $E_{ad}$ is the activation energy of the adsorption reaction, $k$ is Boltzmann’s constant, and $T$ is the substrate temperature in kelvin. It has been reported that the desorption reaction was first order. Then the desorption rate would be

$$R_{de} \propto \exp(-E_{de}/kT)\theta,$$

where $E_{de}$ is the activation energy for the desorption reaction. Because the reactions are steady state, $R_{ad} = R_{de}$ and $\theta$ is expressed as follows:

$$\theta(1 - \theta) = C_1 \exp[-(E_{ad} - E_{de}/kT)]$$  \hspace{1cm} (5)

or

$$\theta(1 - \theta)^2 = C_2 \exp[-(E_{ad} - E_{de}/kT)],$$  \hspace{1cm} (6)

where $C_1$ and $C_2$ are constants. The slope in the Arrenhius plot of $\theta/(1 - \theta)$ or $\theta/(1 - \theta)^2$ indicates the difference between the activation energy of adsorption and desorption ($E_{ad} - E_{de}$). In Fig. 12, we also show the Arrenhius plot of $\theta/(1 - \theta)$ or $\theta/(1 - \theta)^2$. From the slopes, $E_{ad}$ is 0.4 eV higher than $E_{de}$ in the case of reaction (1), and 0.6 eV for the dissociative reaction (2). The $E_{de}$ reported by Sinniah et al. was 1.96 eV. The $E_{de}$ reported by Höfer, Li, and Heinz was 2.48 eV. Therefore, $E_{ad}$ is estimated to be between 2.4 and 3.1 eV.

Bratu and Höfer have reported H$_2$ dissociative adsorption on the (111)-(7×7) surface. The activation energy for H$_2$ adsorption is lower than that for desorption on the (111) surface. It is in contrast to the (001) surface because the activation energy on the (001) surface is higher than that for desorption. Also, the values were fairly different between the surfaces, that is, 0.89 eV for the (111) surface and 2.4–3.1 eV for the (001) surface. They suggested that H$_2$ dissociative adsorption was a phonon-assisted sticking. The H$_2$ adsorption on the (001) surface may follow a different mechanism from that on the (111) surface.

**V. CONCLUSION**

We investigated Si surfaces after annealing in a H$_2$ ambient using ATR-IR, RHEED, AES, and AFM. We found that at all H$_2$ pressures the surface dangling bonds formed dimers that were related to two domains of (2×1) or c(4×2) recon-
structured surfaces. The H$_2$ was adsorbed on the reconstructed surface and terminated other dangling bonds that did not form dimers. The H$_2$ adsorption rate was limited by the reaction between H$_2$ and dangling bonds on the surface. The $E_{ad}$ of the H$_2$ adsorption reaction was 0.4–0.6 eV higher than that of H$_2$ desorption. Therefore, we estimate that $E_{ad}$ is 2.4–3.1 eV using reported $E_{ad}$ values. The surface on which the H$_2$ was adsorbed and dimers were formed was inert, which keeps the surface clean. We also found that the H$_2$ annealed surfaces were influenced by surface roughness and by contaminants including oxygen and carbon.

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