Nano-scale morphology and hydrogenation of Si surfaces in the early phase of hydrogen annealing

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Abstract. In this study we experimen tally observed the atomic-level morphology of Si surface in the early phase of hydrogen annealing, in order to investigate the progress of the flattening of trench sidewall surface. We performed both AFM on trench sidewall (011) surface and UHV-STM on Si (001) substrate surface. The AFM image of the trench sidewall surface within 0.5 min of H2 annealing clearly shows the evanescence of chemical Si dioxide formed by RCA cleaning process, and in the void area without chemical oxide the appearance of atomic steps is observed. The observed Si substrate surface morphology by means of UHV-STM shows that the exposed Si surfaces reconstruct to the 2×1 dimer structure, being mono-hydrogen terminated and stabilized. From these experimental results, we can make an early phase model of hydrogen annealing, in which the evanescence of chemical Si dioxide is followed by formation and growth of voids without chemical oxide, where the exposed Si surfaces reconstruct to the 2×1 mono-hydrogen dimer structure, growing to atomic steps and terraces characteristic to the surface orientation.

1. Introduction

In manufacturing process of three-dimensional Si devices, such as micro electro-mechanical systems (MEMS) [1], trench-gate MOSFET [2] and FinFET [3], both sidewall surface flattening and corner rounding of the three-dimensional structures have been important issues in order to increase the performance and secure the reliability of the devices. Recently, in the context of development of trench MOSFETs, the effect of high temperature hydrogen annealing on the nano-scale surface morphology of micron-sized trench sidewalls has been investigated on Si (001) substrates by atomic force microscopy (AFM). Through a series of our investigations [4-9], the sidewall flattening phenomenon by high temperature hydrogen annealing has been found to progress to an atomic dimension very effectively. So, hydrogen annealing technology is expected to be applied to fabrication of various nano-scale devices. However, the surface morphology has not yet been sufficiently observed in the early phase of time evolution so far, notwithstanding the importance for improvement of the controllability of the hydrogen annealing process.

In this study we experimentally observed the nano-scale morphology of Si surface in the early phase of hydrogen annealing after RCA cleaning, in order to investigate the progress of the flattening.
of trench sidewall surface. We performed AFM on trench sidewall (011) surface, and also studied atomic-level surface morphology on Si (001) substrate annealed in hydrogen ambient, using ultra-high vacuum scanning tunneling microscope (UHV-STM).

2. Experimental procedure

In the AFM experiment, we used n-type Si (100) (2 Ω cm) wafers, on which micron-sized trenches along the [1-10] direction were fabricated by anisotropic reactive ion etching (RIE). The width, depth, and length of the trenches are 0.7 μm, 3.0 μm, and 3.0 mm, respectively. The trenches formed by RIE slightly taper from the top to the bottom, and the sidewall surface deviates by about 1° from the {110} plane. After trench etching, the surface was cleaned by the standard RCA cleaning procedure. The samples were annealed in hydrogen pressures of 1.01×10⁵ Pa at 1000 ºC for 0.5 to 3 min by a sheet-fed lamp furnace. We evaluated the trench profiles by scanning electron microscopy (SEM), cleaving samples normal to the trench direction, and also observed the sidewall morphologies of the trenches by AFM, after cleaving the substrate at the center of a trench along its longitudinal direction.

For STM experiment, a H₂ annealing chamber was equipped to an UHV-STM system in order to observe the H₂ annealed surface without exposing the surface to the air ambient. In the experiment n-type Si (100) (2 Ω cm) wafer of 0.6 mm thickness was cut down to a strip of 1×7 mm², and was cleaned chemically using the standard RCA method before being loaded into the STM system. The base pressure of the STM chamber was 2×10⁻⁸ Pa and that of the H₂ annealing chamber was 7×10⁻⁸ Pa. The sample was thoroughly degassed at 600 ºC by direct current heating. Without flashing in UHV, the sample was annealed at 1000 ºC, in H₂ gas ambient of 2.5×10⁴ Pa, by direct current heating in H₂ annealing chamber. The temperature of samples was measured by a pyrometer and the H₂ pressure was measured by a crystal-gage. After the sample was annealed and cooled down to room temperature (RT) in the H₂ ambient, the H₂ annealing chamber was quickly evacuated to high vacuum. Then the sample was transferred to the STM chamber. STM images presented in this paper were taken at RT in UHV. In most cases, the tunneling current was held at 0.1 nA.

3. Results and discussion

3.1. Trench sidewall surface observed by AFM

Figure 1 is a typical cross-sectional profile and AFM image of the sidewall morphology of as-etched trenches. The ion-etched surfaces are rough with ditches introduced by anisotropic RIE. The root-mean-square (RMS) roughness and peak-to-valley height measured from the AFM image are 1.7 nm and 10 nm, respectively. Figure 2 shows the trench structure after hydrogen annealing for 0.5 min at 1000 ºC under 1.01×10⁵ Pa. In the SEM image, we find no distinguishable cross-sectional profile change of the trench by hydrogen annealing. But the AFM image of the sidewall surface shows the clear evanescence of chemical Si dioxide formed by RCA cleaning process. It is expected that Si dioxide reacts with an active Si in the reductive H₂ atmosphere such as SiO₂+Si→SiO ↑ by thermal energy at the interface between Si and dioxide [10]. In the void area without Si dioxide, we can observe the atomic steps and terraces. With the annealing time, the voids become larger, and the Si dioxide film can be completely removed by annealing for 1 min.

After 3 min annealing, a structure composed of fairly straight steps and terraces is seen in the AFM image in figure 3. The steps ascend from the top towards bottom of the trench. Most steps are single layer high, and the average separation between steps is estimated to be about 20 nm. Since this step separation corresponds to about 1° deviation from (110), the observed step configuration is consistent with the slightly tapering profile of the RIE etched trench. RMS roughness and peak-to-valley height are estimated to be 0.3 and 1.0 nm, respectively, which are much smaller than those of the as-etched trench. Thus, we can successfully flatten the sidewall surface at nano-scale by 3 min annealing at 1000 ºC in 1.01×10⁵ Pa H₂ without significant deformation of the fabricated trench structure.

3.2. Si substrate surface observed by UHV-STM
Figure 4 shows the STM image of the Si (100) H₂ annealed surface. Area is 30×30 nm² and sample bias is –2 V. We obtained atomically flat Si (100) surface composed of alternating Sₐ and Sₐ steps only by H₂ annealing at 1000 ºC for 10 min, without flashing the sample at above 1200 ºC in UHV as usual. The majority of the surface was covered by dimers like Si (100) clean surface. It can be seen from figure 4 that the STM image of the H₂ annealed Si (100) surface is similar to the atomic H irradiated surface reported by Hashizume et al. [11]. So, we consider that the surface after H₂ annealing is covered with mono-hydride and the surface structure can be identified as the Si (100) : 2×1-H. Several protrusions, which cannot be seen on clean Si (100) surfaces obtained by UHV annealing, were observed on the H₂ annealed surface. At present, the substance of the protrusions is not determined from the STM images.

Figures 5 (a), (b) and (c) show the annealing time dependence of the STM images of the Si (100) H₂ annealed surfaces. Area is 100×100 nm² and sample bias is –2 V. As shown in figure 5 (a), the Si (100) surface annealed for 5 min was still rough due to existence of many narrow islands and vacancies with atomic defects. We consider that by H₂ annealing, chemically formed silicon oxide was
Figure 5. STM images of Si (100) surface annealed at 1000 °C and quenched to RT in H₂ whose pressure was 2.5×10⁴ Pa for (a) 5 min, (b) 10 min and (c) 15 min. These images were taken with sample bias of –2 V (area 100×100 nm²).

gradually removed by forming volatile SiO, and the rough Si dioxide/Si interface [10] was exposed as in the case of trench sidewall surface. Such a rough surface morphology is smoothened by surface self-diffusion of Si atoms. The surface self-diffusion of Si atoms, however, is extremely slower in H₂ ambient than in UHV [6]. Thus surfaces with wider terraces and smoother steps were only formed after annealing for 10 and 15 min (figures 5 (b) and (c)). It is not certain that those surface exhibit the surface morphology in thermal equilibrium for Si (100) in H₂ gas ambient of 2.5×10⁴ Pa at 1000 °C. We can say, however, that surface is not roughened as a result of the interaction of H₂ with Si (100). We could prepare atomically smooth surface with wider terraces with few atomic defects and smooth steps by annealing chemically treated Si (100) at 1000 °C in 2.5×10⁴ Pa H₂ gas ambient.

4. Conclusion
From these experimental results, we can make an early phase model of hydrogen annealing. In the most early stage, the evanescence of chemical Si dioxide occurs through the reaction of Si dioxide with an active Si in the reductive atmosphere of H₂ like as SiO₂+Si→SiO↑ by thermal energy at the interface between the surface of Si substrate and chemical Si dioxide. In the case of Si (100) surfaces, the exposed surface has 2×1 mono-hydrogen structure. With prolonging annealing time, the roughness of the exposed Si surface is smoothened to form the surface composed of terraces and steps by the surface self-diffusion of Si atoms.

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