Development of Ultra High Vacuum Transmission Electron Microscope for *In Situ* Observation of Silicides And Island Formation on Silicon Surface at High Temperatures by Reflection And Transmission Electron Microscope

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An ultra high vacuum transmission electron microscope (UHV-TEM) has been successfully developed for *in situ* observation of the islands and silicides formation on silicon surface at high temperatures by reflection electron microscope (REM) and TEM. The cleaning process of the contaminated Si(100) surface by heating to 1150°C was successfully observed by REM. The thinning process of the Si(100) specimen by heating to 900°C with the oxygen exposure is dynamically observed by TEM. The observation of the surface steps on Si(100) with TEM is also carried out with considerable success. The present results lead us to the confirmation that the developed UHV-TEM can be applied to the study of the islands and silicides formation by *in situ* REM and TEM observation.

I. Introduction

Recently, the formation of islands and silicides on the silicon surface has been attracting much attention because of its potentiality to be applied to the silicon semiconductor devices. For accommodating it for the practical use, it is very important to control the structure, composition, shape, size and interface morphology at atomic scale. For this, understanding of the fundamental phenomena which occur during the fabrication at atomic scale is required. In this regard, the reflection electron microscope (REM) and transmission electron microscope (TEM) are most powerful tools to obtain the dynamic information on the phenomena. In the most studies, in which the TEM and REM have been employed, the observation were performed *ex situ* by preparing specimens for the observation after the fabrication. However, it is essential to perform the *in situ* observation of the nucleation and growth of the islands and silicides for comprehensive understanding of the phenomena.

With respect to the *in situ* REM and TEM observation, most of studies are performed for the metal specimen [1,2]. These studies can be carried out by using the conventional TEM apparatus since the metal surface are not so sensitive to the vacuum condition. Contrast to the metal specimen, the study of the semiconductor surface requires an ultra high vacuum (UHV) condition, in which the column, pumping system, lens system and specimen stage are specially designed [3], to clean the surface and to maintain it during the fabrication. In addition, the TEM should be designed to perform heating the specimen, the

exposure to gases, the deposition of materials in the electron beam column under the UHV condition. These requirements leads the study of the islands and silicides formation on the silicon surface by the *in situ* REM and TEM observation to be difficult because of its construction. Recently, the effectiveness of the UHV-TEM for the *in situ* observation of the islands and silicides formation have been reported by several groups of work [4-9].

In the present paper, therefore, we aim at the development of the UHV-TEM apparatus to study the islands and silicides formation on the silicon surface by the *in situ* observation. For confirmation of the applicability of the developed UHV-TEM to these study, the *in situ* observation of the silicon surface at high temperature by TEM and REM are performed.

II. Experiment

An apparatus used in the present study is 200-kV transmission electron microscope (HF-2000, HITACHI) equipped with the cold field emitter. An evacuation system of the apparatus is modified for the UHV (ultra high vacuum) condition. The schematic diagram of the vacuum system of the apparatus is depicted in Fig. 1. In order to improve the base pressure of the specimen chamber in the column, the specimen chamber is evacuated by tandem two turbo molecular pumps (TMP) (400 ℓ/s). Each part of the electron beam column is evacuated

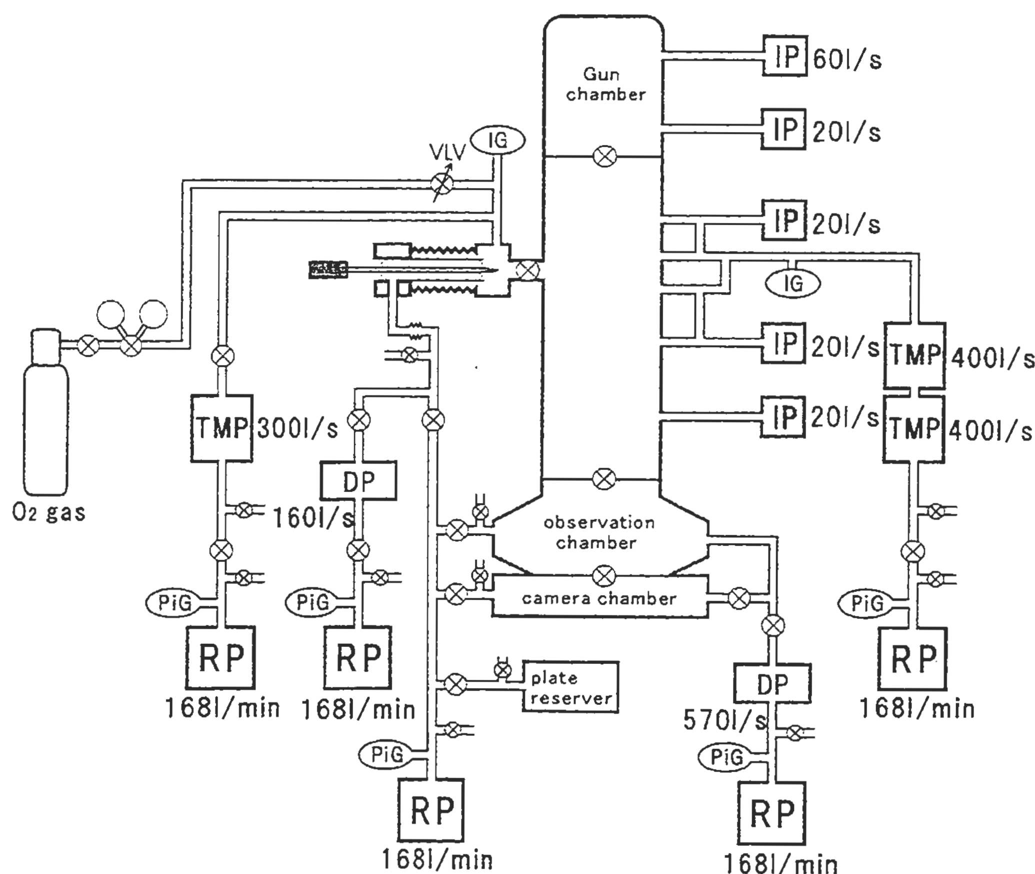

FIG. 1 The schematic of the evacuation system of the experimental apparatus, transmission electron microscope (HF-2000, HITACHI). The evacuation system is modified for the UHV condition.

by three ion pumps (IP) (20 ℓ/s). This vacuum system leads the base pressure of the specimen chamber in the column to be better than 5×10^{-7} Pa. In addition, the pressure during the observation at 1100°C can be kept in the order of 10^{-7} Pa by the help of the liquid nitrogen cooled trap. The evaporator can be equipped through the ICF70 port attached to the column and materials can be deposited on the specimen during the observation.

The apparatus is equipped with two pre-evacuation specimen chambers. First one is evacuated by the diffusion pump (DP) (160ℓ/s). The second one is evacuated by the TMP (300ℓ/s). The base pressure of $\sim1\times10^{-7}$ Pa is achieved in the second pre-evacuation specimen chamber. The second one is used for the treatment of the specimen, e.g., the outgas. An oxygen gas is introduced into the specimen chamber in the column through a variable leak valve attached to the second pre-evacuation specimen chamber. All observations at high temperatures were carried out after the outgas of the specimen and specimen holder was finished. The outgas was performed in the second pre-evacuation specimen chamber by increasing the temperature from 600 to 900°C by 100°C. The outgas at each temperature was continued until the pressure becomes less than 5×10^{-7} Pa. The REM and TEM images at high temperature were recorded by a camera.

Figure 2 shows the photograph of the two-axis-tilting specimen holder for heating. Figures 2(a) and (b) are the photographs taken before and after setting the specimen, respectively. Figure 3 depicts the schematic illustration of the specimen holder. All the parts around the specimen are made of Ta or Mo except for the ceramic for the electric insulation. The specimen is hold on the Mo block by two Ta sheets. The one edge of the specimen is electrically isolated from the Mo block. The specimen is tilted along the axis of the specimen holder with the Mo block. The Mo block is hold by two screws for the insulation. The Mo block is tilted around the screws by the linear motion of the rod for tilting. Another tilting is done by the rotation of the specimen holder around the axis of the specimen holder. The specimen is heated by resistive heating. The electric current for heating goes through the rod for tilting, Mo block, specimen, Ta sheet and specimen holder.

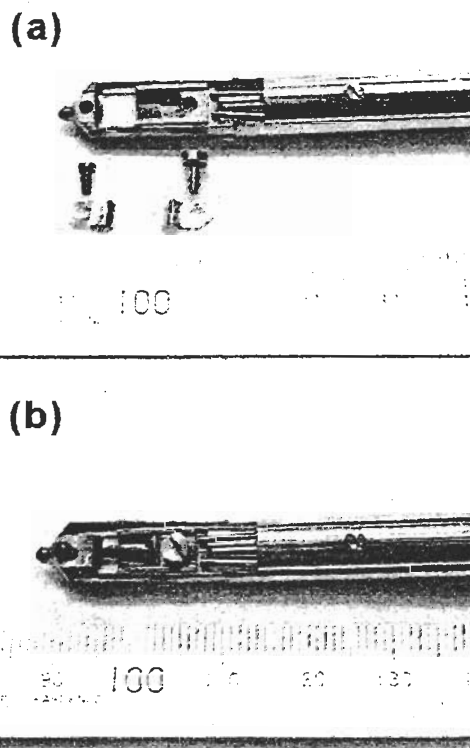

FIG. 2 The photograph of the two-axis-tilting heating specimen holder. (a) and (b) shows the photographs taken before and after setting the specimen, respectively.

The specimen used in the present study is p-type Si(100) wafer. The specimen for the REM observation is prepared by cleaving into the size of 8.0×1.5×0.5 mm^3. Any other pretreatment was performed before being inserted into the apparatus except for the ultrasonic cleaning with the ethanol and acetone. The specimen surface was cleaned by flashing at ~1200°C after the outgas under the UHV condition.

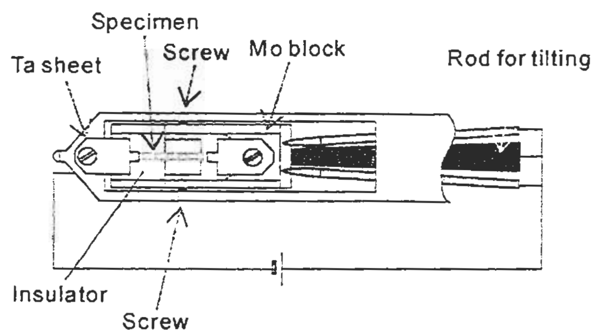

FIG. 3 The schematic illustration of the two-axis-tilting heating specimen holder.

The specimen for the TEM observation is prepared by cleaving, the mechanical etching, the chemical etching and thinning by heating in the apparatus [7,8,10]. The schematic illustration of the preparation of the TEM specimen is depicted in Fig. 4. First, the specimen was cut into the size of 8.0×2.5×0.5 mm^3. After this, only the center part of the un-mirror finished surface of the specimen was mechanically etched. The mechanical etching was performed by the linear dimpling until the thickness of the thinnest part of the specimen become ~100 μm. After the mechanical etching, the specimen was chemically etched using the solution of HF and HNO_3 (HF:HNO_3 = 3:5 and 1:10) until the specimen become thinner than 10 μm. Finally, the specimen is inserted into the apparatus and thinned by heating at ~1200°C in the oxygen atmosphere of 1×10^{-3} Pa after the outgas.

Figure 5 shows a typical result of the measurement of temperature of the specimen surface as a function of an electric power used for heating. The measurement was performed in the second pre-evacuation specimen chamber. Temperature was measured by an optical pyrometer (IR-AP, CHINO). The squares and circles correspond to temperature during the power increases and decrease, respectively. The specimen can be heated to ~1200°C corresponding to temperature required for flashing of silicon. Temperature can be controlled within ±20°C by controlling the electric power for heating.

III. Results and Discussions

A. REM observation during outgas

Figures 6 to 8 show a series of the REM images and corresponding reflection high energy electron diffraction (RHEED) patterns observed during the outgas. All images were observed at room temperature by inserting the specimen into the column after the outgas in the second pre-evacuation specimen chamber

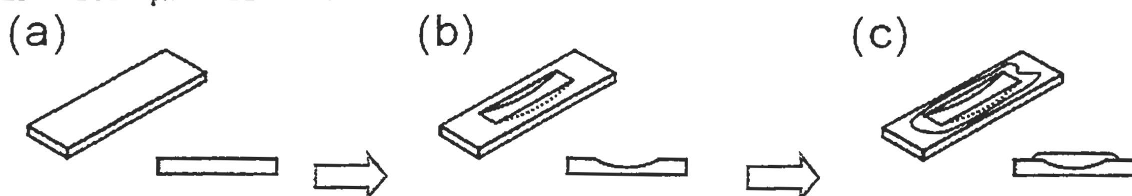

FIG. 4 Preparation of the TEM specimen. (a) cleaving, (b) mechanical etching and (c) chemical etching.

at each temperature was finished. Figures 6(a) and (b) are the REM image and RHEED pattern of the Si(100) surface before the outgas. The REM image was observed using (600) reflection spot. The RHEED pattern is diffuse and spots are not clear because of the existence of the native oxide on the surface. In the REM image, the surface structures like steps are hardly visible.

The REM image and RHEED pattern observed after the outgas at 600°C are depicted in Figs. 7(a) and (b), respectively. The (12 00) reflection spot was used for the REM observation. The RHEED pattern became more clear than that in Fig. 6(b). The higher order spots and Kikuchi lines are also visible. This is attributed to the sublimation of a part of the native oxide on the surface by heating at 600°C under the UHV condition. In the corresponding REM image, the surface structures are not clearly seen yet.

Figures 8(a) and (b) show the REM image and RHEED pattern after the outgas at 900°C. The REM image was observed using (800) reflection spot. The REM image shows the contaminated surface. In the corresponding RHEED pattern, the weak ring pattern shown by the arrow is observed. This ring pattern agrees with the β-SiC of the lattice constant of 0.436 nm. The β-SiC observed in Fig. 7 is considered to be formed on the silicon surface because of the deterioration of the vacuum by heating at 900°C during the outgas since β-SiC can be easily formed around 900°C [11].

The REM image and RHEED pattern observed at room temperature after flashing of the specimen are depicted in Figs. 9(a) and (b), respectively. The image was observed using (800) reflection spot. Flashing was performed by heating to 1200°C. In the REM image, the contamination on the surface observed in Fig. 8 disappear and the steps are observed. From the RHEED pattern, it is found that 2×1

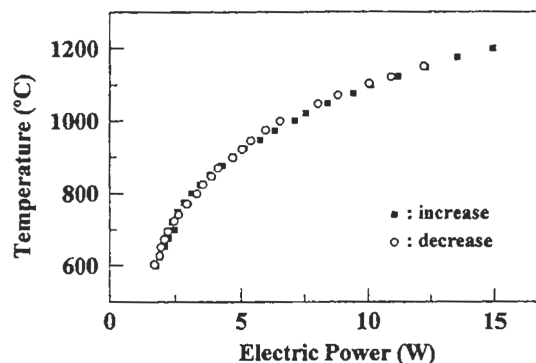

FIG. 5 The typical result of the measurement of the temperature of the specimen surface as a function of the electric power used for the resistive heating of the specimen. The squares and circles correspond to the temperature during the power increases and decrease, respectively.

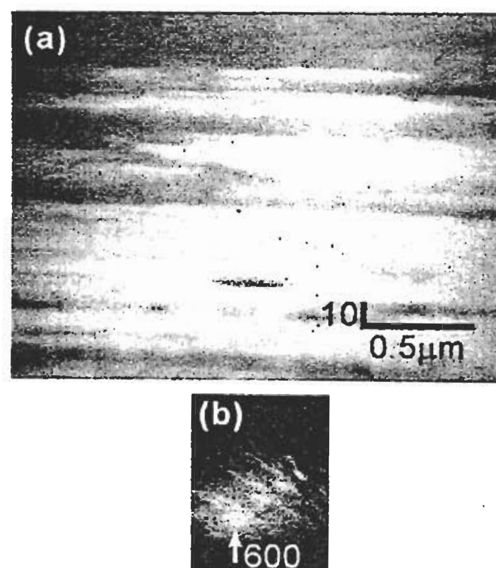

FIG. 6 The REM image (a) and RHEED pattern (b) of the as-received Si(100) surface before the outgas. The REM image was observed using the (600) reflection spot.

reconstructed surface is formed, leading to the confirmation that the clean Si(100) surface is obtained by flashing using the present apparatus.

B. *in situ* REM observation at high temperatures

The *in situ* REM observation was performed at 600~1150°C after the RHEED pattern of the 2×1 reconstructed surface was obtained by flashing. A series of the REM images are shown in Fig. 10. Figures 10(a), (b) and (c) are the results observed at 600, 700 and 800°C after flashing, respectively. Figure 10(d) is the REM image observed at 900°C following to Fig. 10(c) after the surface contamination was induced by focusing the incident electron on the surface for 15 min at 800°C. The REM image shown in Fig. 10(e)

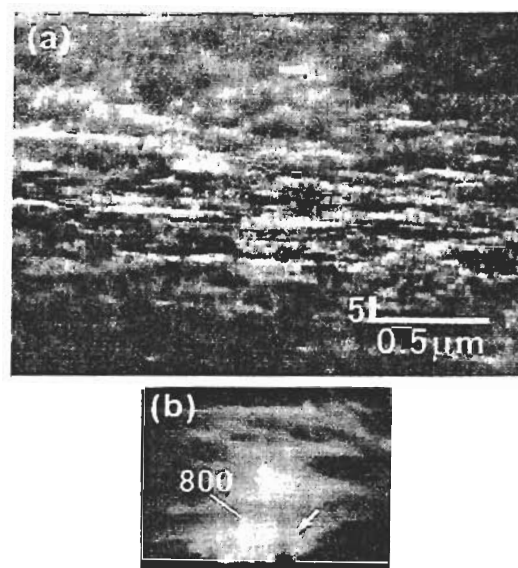

FIG. 8 The REM image (a) and RHEED pattern (b) of the Si(100) surface after the outgas at 900 °C. The (800) reflection spot was used for the REM observation.

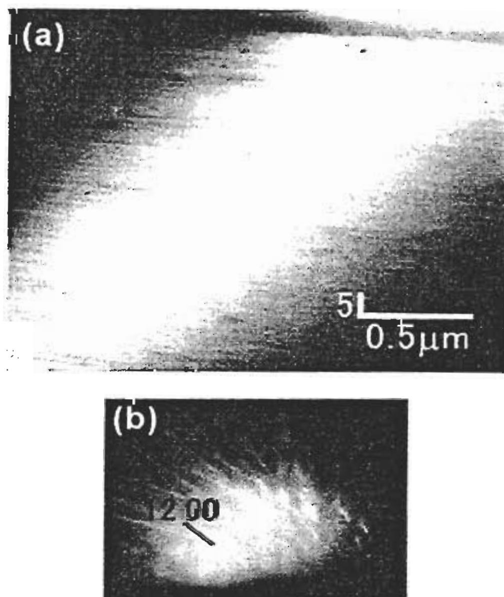

FIG. 7 The REM image (a) and RHEED pattern (b) of the Si(100) surface after the outgas at 600 °C. The (12 00) reflection spot was used for the REM observation.

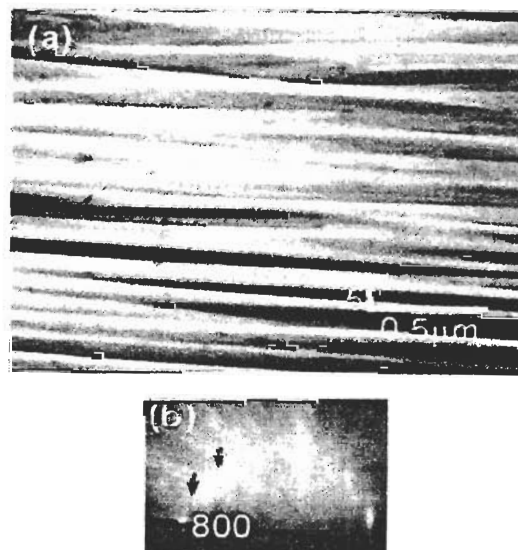

FIG. 9 The REM image (a) and RHEED pattern (b) of the Si(100) surface observed at room temperature after the flashing of the specimen. The image was observed using (800) reflection spot.

was observed at 1000°C after the further surface contamination was induced by focusing the incident electron on the surface for 20 min at 1000°C. Figures 10(f) and (g) are the REM image observed at 1100 and 1150 °C by increasing specimen temperature following to the observation of Fig. 10(e). Figure 10(h) shows the REM image observed at room temperature after the observation shown in Fig. 10(g). The contamination induced by the incident electron in Figs. 10(d) and (e) are disappeared in Fig. 10(f), (g) and (h). These results lead us to the confirmation that the *in situ* REM observation of the silicon surface at high temperature can be performed using the present apparatus.

C. *in situ* TEM observation at high temperatures

The TEM specimen of the Si(100) thinned to ~10 μm thick by the mechanical and chemical etchings is introduced into the apparatus. After the outgas was performed in the second pre-evacuation specimen chamber, thinning of the specimen to less than a few ten nm thick by heating at ~1200°C in oxygen atmosphere of ~1×10^{-3} Pa was performed. Figures 11(a) and (b) show the transmission electron diffraction (TED) patterns of the Si(100) before and after thinning the specimen by heating in oxygen atmosphere, respectively. The intensity of the diffraction spots in (b) is higher than that in (a). The higher order of the diffraction spots and the Kikuchi lines are also clearly visible in (b).

Figure 12 shows a series of the TEM image observed at high temperatures. The observation was carried under the (g, 3g) weak beam condition, where **g** is <220>. The weak beam condition enables us to observe the surface steps, the dislocations and the strain field on the silicon surface [4-7]. The TEM images shown in Figs. 12(a) to (f) are observed at 600, 700, 800, 900, 1000 and 1100°C by increasing temperature by 100°C,

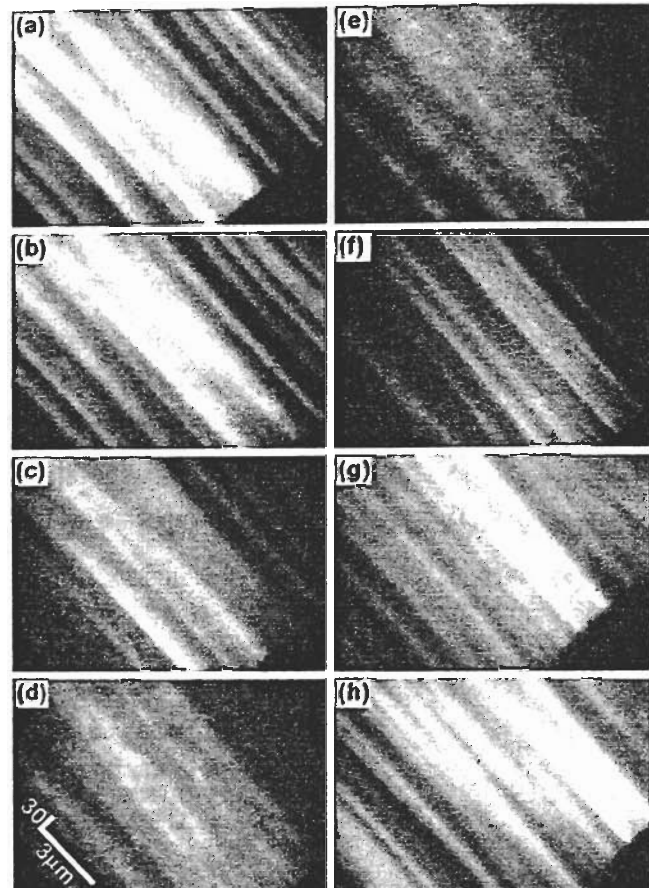

FIG. 10 Series of REM images of the Si(100) surface observed at high temperatures. (a), (b) and (c) are observed at 600, 700 and 800 °C by increasing temperature by 100°C. (d) is observed at 900°C after the surface contamination was induced by focusing the incident electrons on the surface at 800°C for 15 min. (e) is the REM image observed at 1000°C after the further surface contamination was induced by the incident electrons at 1000°C. (f) and (g) are the REM image observed at 1100 and 1150 °C after the observation shown in (e). (h) is the REM image observed at room temperature after (g).

respectively. The thickness fringes are observed at the center of the images. The pressure during the observation was kept below 5.0×10^{-6} Pa, leading to the confirmation that the *in situ* TEM observation of the silicon surface can be performed with the present TEM system.

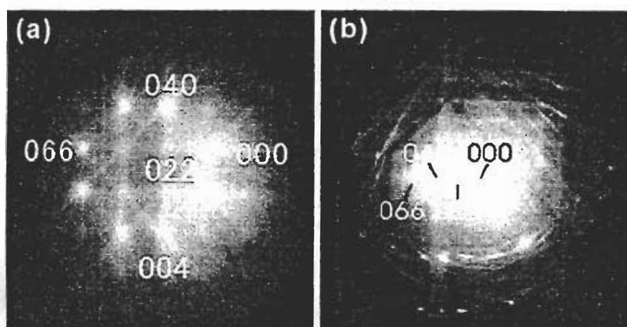

FIG. 11 Transmission electron diffraction (TED) patterns of the Si(100) before (a) and after (b) thinning of the specimen by heating in oxygen atmosphere

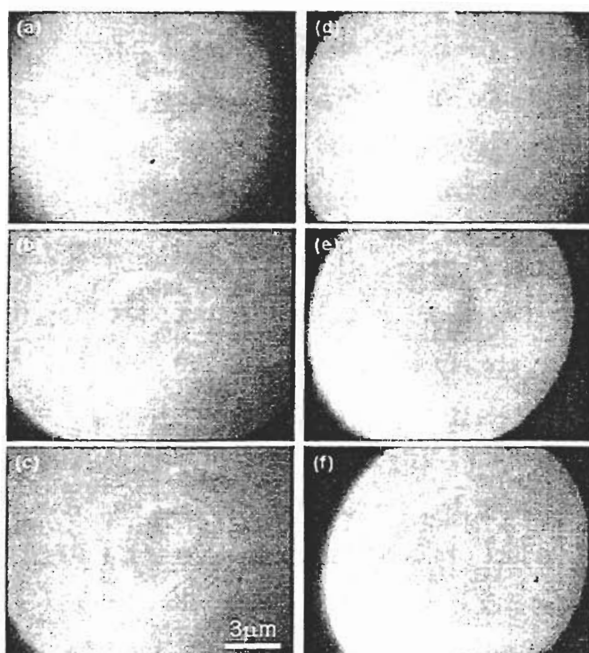

FIG. 12 Series of the TEM images observed at high temperatures. (a) to (f) correspond to the TEM image observed at 600, 700, 800, 900, 1000 and 1100°C, respectively.

The results of the *in situ* TEM observation of the Si(100) at 1100°C under the oxygen exposure of 1×10^{-3} Pa are depicted in Fig. 13. The series of the TEM images were observed after the observation shown in Fig. 12(f). The same position on the specimen was observed as that shown in Fig. 12. The time, at which the TEM images of (b) to (e) were observed, are 10.02, 20.00, 25.13 and 25.17 sec after the observation of (a), respectively. The sublimation of the silicon atoms were induced by heating at 1100°C under the oxygen exposure of 1×10^{-3} Pa [12]. The thickness fringes changes by thinning the specimen. In (d) and (e), the hole was made by the etching due to the sublimation.

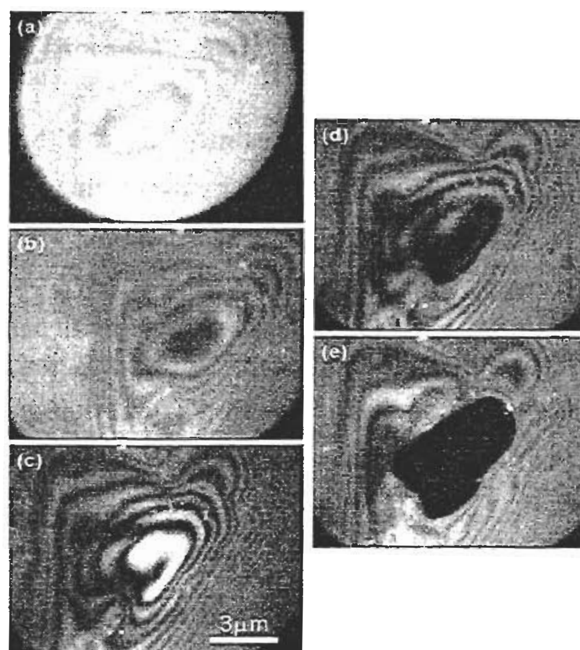

FIG. 13 Results of the *in situ* TEM observation of the Si(100) surface at 1100°C under the oxygen exposure of ~1×10^{-3} Pa. The time, at which the TEM images of (a) to (e) were observed, are 10.02, 20.00, 25.13 and 25.17 sec, respectively.

Figure 14 is the TEM image observed at room temperature after the flashing of the specimen. As shown by the arrows, two fringes, of which the directions are different each other, are observed. In addition, the directions of the lines composing a fringe are almost parallel. These two set of fringes is attributed to the contrast due to the steps existing on the top and bottom surfaces [4,5]. The present observation leads us to the confirmation that the surface steps on the Si(100) surface can be observed with the present UHV-TEM system.

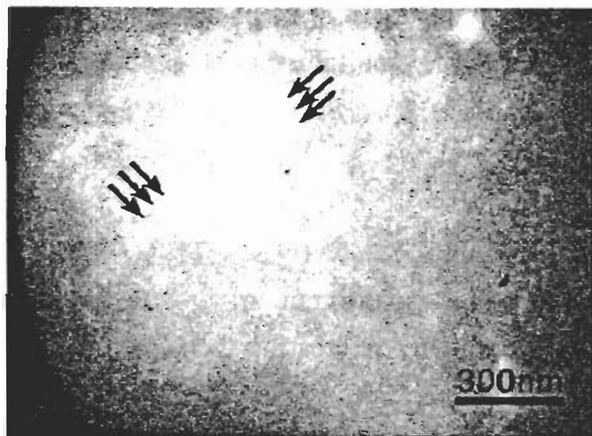

FIG. 14 TEM image of the steps on the surface observed at room temperature after the flashing of the specimen.

IV. Conclusions

The results obtained in the present study are concluded as follows:

(i) The *in situ* REM and TEM observation of the silicon surface can be performed at ~1200°C using the developed UHV-TEM.

(ii) The cleaning process of the contaminated silicon surface is observed *in situ* by REM at high temperature with considerable success.

(iii) The thinning process of the TEM specimen at 1100°C under the oxygen exposure of 1×10^{-3} Pa is successively observed.

(iv) The steps existing on the both sides of silicon surface was observed using the weak beam method.

The present results leads us to the confirmation that the developed UHV-TEM can be applied to the study of the silicides and island formation on silicon surface by the *in situ* REM and TEM observation at high temperature.

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Reviewer's comments

Reviewer: Satoshi Hashimoto (Koukan Keisoku K.K)

In situ observation of surface structure using a newly developed UHV-TEM is explained and its applications to the surface science are described in this article. This article is suitable
for the publication in this journal. However, some minor revisions are required as follows:

1) P9. 2nd paragraph: From FIG. 11, I understood that the thickness became thinner by the heating in the oxygen atmosphere. However, the d spacing in (b) is smaller than that in (a) and the direction is changed. The difference of the diffraction patterns should be commented.

A1) The difference of the direction of the TED pattern is due to the mistake in indexing. The index of the TED pattern in FIG.. 11(a) is revised. The difference of the d spacing is attributed to the camera length. The camera length of FIG. 11(a) is two times longer than that of FIG. 11(b).

2) The contrasts in FIG. 14 are attributed to the surface steps. However, the contrast by weak beam methods is not always caused by the surface step as written in P.9. Could you explain your interpretation on the contrast?

A2) The directions of two fringes are different each other. In addition, the directions of the lines composing a fringe is almost parallel. This is why we consider that the contrast are due to the steps existing on both surfaces. According to the comment, the text describing FIG. 14 was revised.

Reviewer: T. Kitada (NTT-AT)

The experiment of *in-situ* REM and TEM are very interesting theme in this region. High-temperature *in-situ* observation is very difficult and the paper is important. We require a few correct to miss typing. Please check the word to mark a red-pen.

A) The miss types were corrected.