

Thermal Desorption Mechanism of Native Oxides on Si Substrates: TDS and STM Observation

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The thermal desorption mechanism of native oxides on Si(111) substrates formed by chemical treatment was investigated using TDS under UHV and STM in air. TDS dependences on oxide thickness and substrate misorientation angle show that the oxide/Si interface structure, which depends on the oxide formation method, affects the interfacial reaction which forms SiO. Void-like structures on the oxide layer were observed on the surfaces during oxide desorption using STM. The good correlation between void area estimates from STM and AES results proves that the oxide layer removal proceeds with the formation of voids rather than layer-by-layer desorption.

1. Introduction

In surface science and MBE studies on Si substrates, ex-situ formation of thin native oxides and subsequent thermal removal of the oxides under UHV is a common method of preparing a clean Si surface,¹⁾ because this allows a lower cleaning temperature and results in less surface damage. We have been studying thermal desorption during the cleaning process of Si surfaces with native oxides formed by various chemical treatments using TDS (thermal desorption spectroscopy) and RHEED (reflection high energy electron diffraction) under UHV. We reported in the previous SSDM that the desorption product in the cleaning process was identified as SiO for the first time, and that the desorption temperature of SiO depends on the oxide formation method.²⁾ This dependence suggested that the interface structure between an oxide layer and a Si substrate³⁾ significantly affected the desorption temperature of the native oxides. Based on TDS and RHEED results, we proposed the following 5-step thermal desorption scheme.⁴⁾

2. SiO diffuses from the interface into the oxide surface.
3. SiO desorbs from the surface, leaving voids in the oxide. This process is observed at the minimum temperature of SiO desorption.
4. Once voids are formed, the interfacial reaction proceeds only at the edges of the voids and the void area grows.
5. Finally, the native oxides are completely removed and clean surfaces are obtained.

The present work investigates the origin of the temperature dependence and confirms the proposed desorption mechanism using TDS, RHEED, AES (Auger electron spectroscopy) and STM (scanning tunneling microscopy) in air. The further measurements of TDS, which were performed on surfaces with various thicknesses of oxide and various substrate misorientation angles, prove that the interface structure is essential to desorption process. The STM observation of the surface, which was radiation-quenched during the oxide desorption process, shows the validity of the mechanism involving void formation and growth.

1. Interfacial reaction between native oxides and Si substrates results in formation of SiO at the interface.

2. Experimental

A native oxide layer was formed on pre-cleaned Si(111) substrates according to the procedure described previously.⁴⁾ Samples with various thicknesses of oxide layer were obtained by varying the treatment time.

The oxide thickness of each sample was determined from the intensity ratio $I_{O_{KLL}}(515\text{eV})/I_{Si_{LVV}}(92\text{eV})$ ⁵⁾ of in-situ AES according to the procedure described by Ishizaka and Shiraki.¹⁾ The absolute value of the thickness was calibrated by comparing the results of in-situ AES and ex-situ AR-XPS (angle-resolved X-ray photoelectron spectroscopy). The samples were examined by TDS under UHV and STM in air.

The experimental setup and procedures for TDS measurements have been described previously.⁴⁾

STM images were acquired in the constant current mode using a commercial instrument (Nano Scope II: Digital Instruments Inc., CA, USA). Images were taken in air at room temperature and ambient pressure. The typical sample bias voltage with respect to the tip was +3 V and the tunneling current was 0.6 nA. Pt-Ir tips were used for the observations. The scan area was fixed at $7 \times 7 \mu\text{m}^2$. Highly Sb doped n-type Si substrates ($\rho=0.02 \Omega\cdot\text{cm}$) were used to obtain sufficient stable tunneling current to observe STM images. A relatively thick (about 12 Å) oxide layer formed by treatment with HNO_3 boiling for 10 minutes was used for STM to make the observation easy.

3. Results and discussion

3-1. TDS dependence on oxide thickness

Figure 1 shows the relationship between TDS peak temperature and oxide thickness estimated from the AES. The TDS peak temperature tends to increase as oxide thickness increases. Therefore, the diffusion of SiO formed at the oxide/Si interface through the oxide film governs the desorption temperature. Moreover, the increasing ratio of the peak temperature to thickness for the oxides formed by HCl treatment is apparently smaller than for the other treatments. In particular, the peak temperature was much

lower for HCl treatment at thicknesses of 8 Å or more than for the other treatments at the same thickness. This result cannot be explained only by SiO diffusion through oxides because the overall composition of the oxide layer is virtually independent of the oxide-forming treatments. Accordingly, the diffusion constants of SiO in oxides can be assumed to be similar. This result shows that the interface structure depends on the kind of the treatment and this dependence affects the activation energy needed to initiate the reaction of SiO formation at the interface.

3-2. TDS dependence on substrate misorientation angle

The vicinal Si substrates are expected to consist of terraces and steps on the surface. Thus the vicinal surface provides the means to modify interface structure. To clarify the effect of the the oxide/Si interface structure on desorption temperature, we examined TD (thermal desorption) spectra from vicinal Si(111) substrates. Figure 2 shows TD spectra from samples with misorientation angles of 0° , 4° and 8° from (111). They have virtually the same thickness of oxide overlayers on the surface.

The interface step formation under the oxide overlayer is confirmed by (00) spot splitting in the RHEED pattern at $[1\bar{1}0]$ azimuth, which is the direction parallel to the step edge. Figure 3 is a typical RHEED

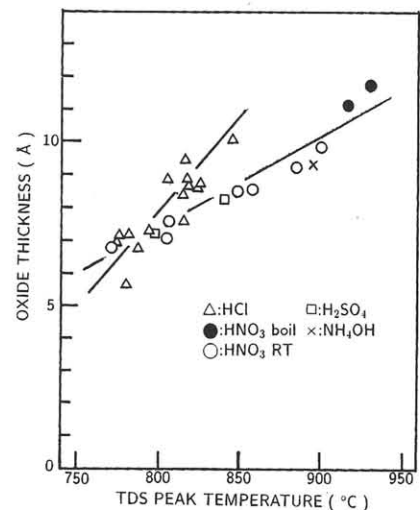


Fig. 1. Comparison of TDS peak temperature and oxide thickness estimated from AES results. Note the difference in dependence for HCl treatment.

pattern observed from oxide (8 \AA)/Si(111) with a misorientation angle 8° . Average terrace width estimated from the spot splitting (21 \AA) is consistent with that expected from the misorientation angle (22 \AA).

All TD spectra from Si(111) exhibit main signals at the peak temperature of about 780°C . In addition, vicinal Si(111) surfaces give rise to minor signals at temperatures higher than that of the main signals. The minor signals were reproducibly observed in all TD spectra from the vicinal surfaces. Therefore, the minor signal was assumed to originate from the reaction products at and near the step edge on vicinal surfaces. The reproducibility of the peak temperature and the shape of the minor signals, however, were relatively low. This was supposed to be caused by low reproducibility of the step structure between oxide layer and Si. The area of the minor signal was not always proportional to the misorientation angle. This suggests that there is an unidentified surface structure other than the step which contributes the formation of the minor signal.

The peak temperatures of the main signals are independent of the misorientation angle. This seems reasonable, since the desorption process on the terraces on the stepped surface is similar to that from a flat surface, that is, not affected by the existence of the steps. As we reported previously⁴⁾ and will discuss in detail below, the oxide desorption is initiated by interfacial reaction to form SiO resulting in void nucleation. Thus the fact obtained here shows that the nucleation of voids is independent of the nature of the surface step.

3-3. STM observation of oxide/Si surfaces during oxide desorption

The RHEED pattern was observed to change during SiO desorption in the following way.⁴⁾

- High background+ 1×1 (before desorption)
- high background+streaky 7×7 (during desorption)
- low background+sharp 7×7 (after desorption)

We presume from this result that the oxide layer removal does not proceed with uniform layer-by-layer

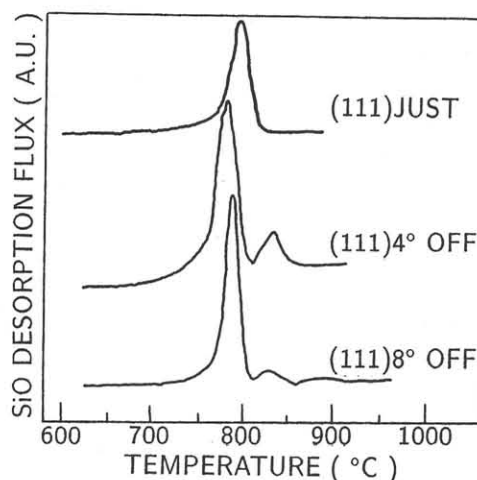


Fig. 2. Dependence of TD spectra on surface orientation. Minor signals shown by arrows were observed on vicinal Si(111) surface at higher temperature side of main signals.

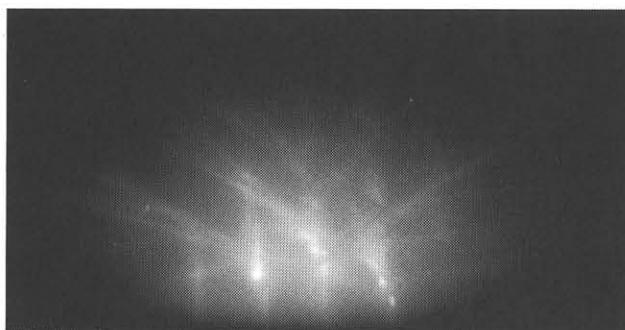


Fig. 3. Typical RHEED pattern obtained from oxide ($\sim 8 \text{ \AA}$)/vicinal Si(111) (8° off). The (00) spot splitting is consistent with the step periodicity expected from the misorientation angle.

desorption, but with the formation of voids.⁴⁾ In this work, the Si(111) surfaces during desorption, where the amount of desorbed SiO is monitored by TDS and controlled by radiation quenching, are studied using in-situ AES and STM in air.

Figure 4 shows the STM image and its cross-section profile taken from such a sample. Good images like this figure were obtained within 1 hour after the sample was taken out of the UHV chamber. Void-like structures with 1000 \AA in diameter and 20 \AA in depth are clearly observed. The diameter is compatible with the domain size of the (7×7) structure estimated from RHEED pattern. The depth of these structures is also consistent with the oxide thickness (12 \AA) estimated by AES before desorption.

Figure 5 shows the correlation between the oxide area ratios determined from AES data and from STM

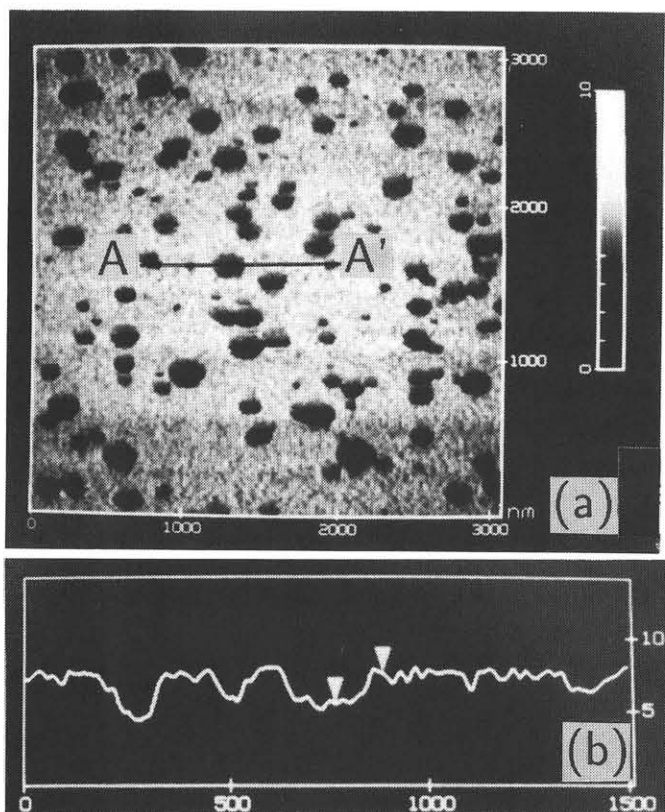


Fig. 4. (a) Typical STM image (zoomed down to $3 \times 3 \mu\text{m}^2$) and (b) its cross-section profile along the direction A-A' of Si(111) surface during oxide desorption taken in air. Unit of scale displayed in the figures is nm. Void-like structures with $\sim 1000 \text{ \AA}$ in diameter and 20 \AA in depth are clearly observed.

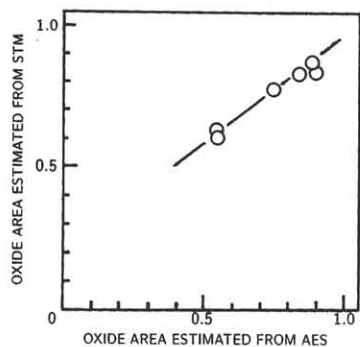


Fig. 5. Correlation of the oxide areas determined from STM and AES.

images. The samples were obtained by stopping the heating at various stages of the desorption. In the calculations of the fraction area of the remaining oxide to the total scan area from AES, it was assumed that the oxide film is uniform and its thickness is constant before and during desorption.

The high correlation in Fig. 5 indicates that the void-like structures observed in STM images reflect the oxide structure during the desorption process.

Possibilities to regard segregated dopant domains or an oxide layer grown in air as the void-like structure could be ruled out by this result. Thus, we conclude that the thermal desorption of oxides proceeds with void formation.

4. Summary

The thermal desorption process of native oxides on Si(111) substrates was studied by TDS and STM in air. All the results were consistent with the desorption mechanism proposed previously.⁴⁾

TDS dependences on oxide thickness show that the interface structure, which depends on the kind of treatment, affects the activation energy required to initiate the reaction of SiO formation at the interface. TDS on the substrate with a misorientation angle confirms the significant role of the interface in the reaction and suggests that the void formation is not dominated by the nature of the step at the interface. The STM observations of surfaces during oxide desorption support our previous RHEED result that the oxide layer removal proceeds not with uniform layer-by-layer desorption, but inhomogeneously through the formation of voids.

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