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Thermal Desorption of Native Oxides Formed on Si(111) during Chemical Treatments

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The thermal desorption process of native oxides formed on Si(111) surfaces were studied using TDS (thermal desorption spectroscopy) under UHV. The reaction product of the process was identified to be SiO. The desorption temperature of SiO was found to strongly depend on the oxide formation method. This dependence suggests that the interface structure between an oxide layer and a Si substrate significantly affects the desorption temperature of native oxides.

1. INTRODUCTION

Preparation of clean surfaces at low temperature is a fundamental technique in MBE (molecular beam epitaxy) and surface science studies. Several studies have reported low temperature cleaning techniques for Si surfaces. In particular, Ishizaka and Shiraki¹) proposed a cleaning method, which combines formation of native oxides by chemical treatments and thermal removal of the oxides at low temperatures under UHV. This method is most commonly used in Si-MBE because it results in lower cleaning temperature (below 750 °C) and less surface damage. However, the chemical reaction mechanism during the cleaning process and the relation between the cleaning temperature and the chemical treatments have not yet been fully confirmed.

In the present work, we investigate thermal desorption of native oxides formed on Si surfaces by various chemical treatments using the TDS (thermal desorption spectroscopy) technique under UHV. We identify the desorption product during the thermal cleaning and find that the desorption temperatures of native oxides are strongly dependent on the oxide formation methods.

2. EXPERIMENTAL

Si(111) substrates (p-type, 100 $\Omega{\cdot}cm$) were oxidized in boiling HNO₃ for 5 minutes and the formed oxide layer was removed in a dilute HF solution. This procedure was repeated several times for pre-cleaning purposes. Native oxide films were formed by oxidizing pre-cleaned Si surfaces using the 5 different kinds of chemical treatments shown in Table 1. Within 2 minutes after the final chemical treatment and rinse in a flow of deionized water. the sample was loaded into the entry lock chamber of our MBE instrument. The sample was then transferred into an analysis and growth chamber with a liquid nitrogen shroud, where a base pressure of $2x10^{-10}$ Torr was regularly achieved. This chamber was equipped with a RHEED (reflection high energy electron diffraction) system, a 0-400 amu QMS (quadrupole mass spectrometer) used for TDS measurements, and a double pass

Table I. Chemical treatments used for navitive oxide preparation

Treatment	Composition	Temperature	Time
H_2SO_4	$4H_2SO_4 + 1H_2O_2$	RT	4 min
HNO ₃ RT	HNO ₃	RT	5 sec
HCl	3HC1+1H202+1H20	80 °C	10 min
NH ₄ OH	$3NH_4OH + 1H_2O_2 + 1H_2O_3$	80 °C	10 min
HNO_3 BOIL	HNO ₃	BOILING	5 min

CMA for AES (Auger electron spectroscopy) measurements. The QMS was controlled by a personal computer, which can store 6 different mass signals per 1 second. The sample was characterized in situ using AES, RHEED and TDS. The pressure during TDS measurement, in which maximum temperature was 950 °C, was kept below 1×10^{-8} Torr. The surface temperature of Si substrates was measured using a thermocouple calibrated by a pyrometer. The pyrometer operated over a spectral range between 0.7 and 0.96 μ m and the emissivity of the Si surface was assumed to be 0.7.

3. RESULTS AND DISCUSSION

After thermal treatments under UHV, all of the samples exhibited the sharp 7x7 RHEED patterns. No traces of either C or O were observed in in-situ Auger spectra or in the RHEED patterns of the Si surfaces (Fig.1). Therefore, after removing the native oxide layers prepared by any of the chemical treatments studied here, atomically clean surfaces were obtained and the cleanness of the cleaned surfaces did not depend on the treatment used for oxide formation.

Auger spectra obtained from the native oxides prepared by the treatments in Table I reflected the overall composition of the films and showed features quite similar to each other. Typical Auger spectra of native oxides prepared by HCl treatment and HNO_3 boil treatment are represented in Fig. 2. These Auger spectra reflected the overall composition of the films and were insensitive to the interface structure between oxide layers and Si substrates because they were obtained from relatively thick oxide films.

Both oxides in Fig. 2 gave rise to main Auger signals at 92 eV and 76 eV. Auger signals at 92 eV, ascribable to LMM transition of elemental Si^{2} , originated from substrate Si. Distinct signals at 76 eV, which have been reported to be characteristic of SiO_2 or fully oxidized Si^{2} , means that the oxide film mainly exists in the form of SiO_2 . The difference in the relative intensity of these signals between the oxides formed by HCl treatment and those formed by HNO₃ treatment shows that oxide film thickness depends on the oxide preparation method.



Fig. 1. RHEED pattern (a) and in-situ Auger spectrum (b) obtained from a Si(111) sample after thermal removal of the native oxide formed by H_2SO_4 treatment. Neither diffraction spot from SiC nor Auger signals from C, O are observed.



Fig. 2. Auger spectra from native oxides formed by HCl and HNO_3 treatments. The spectra show that the overall composition of the oxide films are quite similar to each other.

Fine structures observed between the signals of elemental Si and fully oxidized Si suggest the existence of Si atoms in intermediate oxidation states, or so-called 'suboxides', in the oxide films. These fine structures in Auger spectra did not exhibit any chemical-treatment dependence. Consequently, the chemical treatments listed in Table I did not significantly affect the overall composition of the native oxides.

TDS signals of 44 amu species were observed at temperatures in the range of 790-950 °C, which corresponded to the thermal cleaning temperature reported previously¹). There are two candidates for the 44 amu species, namely SiO and CO_2 .

In order to determine which it is, 44-46 amu species, which corresponded to 28 SiO, 29 SiO and 30 SiO, respectively, were detected during a single TDS experiment. The observed TD (thermal desorption) spectra are shown in Fig. 3. The good agreement of the relative intensities of the 44-46 amu signals and the relative abundance of Si isotopes (28 Si: 29 Si: 30 Si=92.2:4.7:3.1) proved that SiO is the main desorbing product during thermal cleaning reactions on Si surfaces. This fact, together with the AES result showing that the main component of native oxides is SiO₂, suggest that an interfacial reaction between the native oxide layer and the Si substrate

$$Si+SiO_2 \rightarrow 2SiO$$

should occur, resulting in desorption of SiO species.

It was also observed that 31 amu species showed desorption rate maxima in the TD spectra at the same temperature as SiO species. The 31 amu speies seemed to be SiH^{3+} .

Fig. 4 shows the SiO-TD spectra from the native oxides prepared by various chemical treatments. The peak temperatures of TD spectra was reproduced within 15°C.

The temperature was in the range of 790 to 950 °C, apparently depending on the kind of chemical treatments and roughly in the order

 H_2SO_4 , $HNO_3 RT \leq HCl < NH_4OH < HNO_3$ boil.

In contrast with the peak temperature, all the TD spectra showed almost the same signal shape. This fact means that the lowest temperature at which desorption reaction occurs, or the activation energy of desorption reactions, also depends on the treatment. In this study, the lowest desorption temperature was defined as the temperature at which the desorption rate becomes 5% of the desorption rate at the peak temperature. This is shown by the arrows in Fig. 4.



Fig. 3. Comparison between TD spectra of 44, 45 and 46 amu species. These species correspond to 28 SiO, 29 SiO and 30 SiO, respectively. The relative areas of the TD spectra are nearly equal with isotopic abundances of Si (28 Si: 29 Si: 30 Si=92.2:4.7:3.1).



Fig. 4. TD spectra of SiO from the native oxides formed by the treatments in Table I. The arrows show the lowest temperature of SiO desorption.

There are three possible mechanisms to explain the dependence: overall oxide composition, film thickness and interface structure.

From the above-mentioned results of AES, the behavior of TD spectra could not be explained by the differences in native oxide composition.

Ishizaka and Shiraki¹⁾ reported that the lowest temperature that produced a clean surface from a surface covered with an oxide depended on the preparation method of native oxides. They proposed that this dependence is caused by the differences in oxide film thickness. Their lowest cleaning temperature corresponds to the lowest desorption temperature in our experiment. The peak temperature of TD spectra might increase as the oxide layer becomes thicker in the case where the desorption order is lower than first order. The peak temperature difference of 150°C between the H₂SO₄ treatment, the HNO3 RT treatment and the HNO3 boil treatment, however, cannot be explained only by the film thickness since the difference in oxide layer thickness estimated from the AES intensity ratio $I_O(515eV)/I_{Si}(92eV)$ ranges from 4 to 10 Å.

Moreover, the same minimum desorption temperature should be expected for all native oxides of any thickness if the rate-determining step of the desorption reaction was the interface reaction between an oxide and a Si substrate and if the interface structure did not depend on the oxide preparation method. This expectation did not coincide with the TDS results observed in this study.

These facts indicate that the interface structure and composition between native oxides and Si substrates should be taken into account, as well as oxide thickness when considering the desorption temperature dependence on oxide preparation methods. The interface structure should affect the distribution of suboxides in an oxide film. Hattori et al., using angle-resolved analysis of XPS, observed that the interface structure is dependent on the chemical treatment used for oxide formation³⁾.

In summary, the reaction product of the thermal cleaning process of the Si surface was identified to be SiO. The desorption temperature of SiO strongly depended on the chemical treatments used for oxide preparation. This suggests that the Si-oxide interface structure depended on the treatments. From the viewpoints of cleaning temperature and cleanness after the thermal cleaning, the oxides formed by simple H_2SO_4 or HNO_3 RT treatments were similar to the oxide formed by the method reported by Ishizaka and Shiraki¹), which needs many steps to form oxides.

References

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