

B-5-4

Low temperature oxidation of Si(100) with ozone radicals: Chemical Reaction Mechanism and Surface Stress

T. Narushima,^{1,2*} A.N. Itakura,² M. Kitajima² and K. Miki^{1,3}

¹Nanotechnology Research Institute (NRI), National Institute of Advanced Industrial Science and Technology (AIST)
AIST Tsukuba Central 4, Higashi 1-1-1, Tsukuba 305-8562, Japan

*Phone: +81-298-61-5080 ext. 55009 Fax: +81-298-61-2777 E-mail: narushima.tetsuya@aist.go.jp

²Materials Engineering Laboratory and ³Nanomaterials Laboratory, National Institute for Materials Science (NIMS)
1-2-1 Sengen, Tsukuba 305-0047, Japan

1. Introduction

The oxidation of the Si(001) surface is one of the most intensively studied fields, because of its importance in the technological application to MOS devices. The trend towards oxide films of 1-2 nm thickness in such devices requires reduction of the oxidation temperature to prevent dopant diffusion from the substrate through the oxide. Oxidation by a radical species is one candidate to realize this. We have succeeded for the first time in an *in-situ* observation with scanning tunneling microscopy (STM) of the initial stages of ozone oxidation of Si(100)-2×1. We evaluated its surface strain by an optical cantilever technique under the same conditions. In this paper, we report differences both in the oxidation mechanism and in its related strain between ozone and conventional thermal oxidation methods.

2. Experimental

Scanning Tunneling Microscopy can observe the oxidation process directly, however to achieve this, there is an important point to keep in mind about surface contamination. As already confirmed by STM, oxidation begins preferentially from C-type defects [1] that may be related to contamination. We will report [2] that the origin of the C-type defect is residual water even under UHV condition, therefore we have carefully baked the STM chamber, the Si sample and gas line.

The Si(001) sample was cleaned by an H₂SO₄:H₂O₂ after removal of sacrificial oxidation surface and then it was prebaked in UHV at around 600°C overnight. A clean surface was obtained by flashing the sample around 1050°C. The cleanliness of the initial surface was checked, and the absence of C-type defects was confirmed. The sample was oxidized by introducing either high purity oxygen gas or highly concentrated ozone gas in a split second into a UHV chamber. The substrate temperature during the experiments was between RT and 600°C. To avoid dissociation of the molecular oxygen or ozone, both oxidation procedures were carried out without use of an ion gauge in the STM chamber. STM observation of thermal (O₂) oxidation was also performed in *real time* at elevated temperatures

during the oxidation process.

To investigate the difference of surface strains between ozone oxidation and thermal oxidation, we evaluated the surface stress at room temperature during ozone and oxygen gas exposure using the optical micro-cantilever method. We used as samples Si(100) micro-cantilevers with dimensions of 450×50×2.0 μm whose long side is parallel to the <011> axis. A laser light beam incident on the back side of the micro-cantilever sample at the free end was reflected through a UHV window and detected by a position sensitive detector (PSD). The deflection of the free end of the lever, δ , was determined by monitoring the position of the reflected laser light on the PSD. This method allows *in-situ*, real-time detection of the deflection [3]. The surface stress change σ was obtained from the δ using Stoney's formula [4].

3. Results and discussion

We first report differences in the oxidation mechanism between ozone and thermal oxidation. Over 400°C, ozone oxidation produces a single feature on the surface forming a line of oxide (Fig. 1ab). Such one dimensional (1D) structure appear in the case of thermal oxidation, too indicating that both final oxidation states are identical. But ozone oxidation does not exhibit other features due to the dissociation of the molecular oxygen, as indicated in case of thermal oxidation (Fig. 2) [5]. At low temperature up to 300°C, ozone oxidation again produces a single feature on the surface dimers suggesting a stable oxide has formed (Fig. 3), even at RT, although thermal oxidation does not form an energetically stable structure in the same temperature regime. We assigned the common 1D feature to oxidation of the back bonds of (2×1) dimer since we have general agreement that the final energetically stable thermal oxide is the back bond state [6].

We can conclude from our STM results that ozone selectively oxidizes the back bonds of (2×1), moreover a stable oxide can be realized with ozone radicals at a much lower temperature. The same chemical reaction selectivity

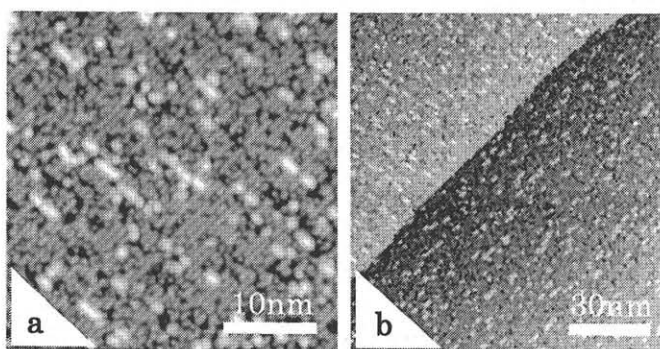


Fig.1 STM images of Si(100) surface in the initial stage of ozone oxidation at $T=400^{\circ}\text{C}$. One dimensional extension of back bond oxidation, normal to dimer row is seen as like in case of conventional thermal oxidation.

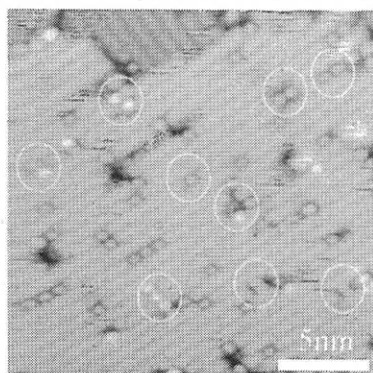


Fig.2 STM images of Si(100) surface in the initial stage of thermal oxidation at $T=548^{\circ}\text{C}$. Circles show many patterns of footprints of dissociation of oxygen molecules. Those features could not be recognized in the case of ozone oxidation.

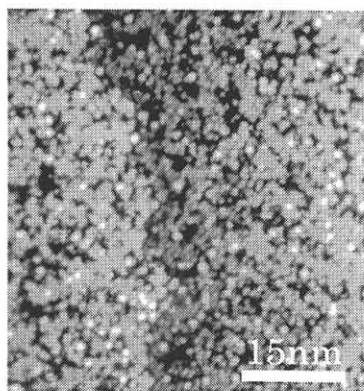


Fig.3 STM images of Si(100) surface in the initial stage of ozone oxidation at room temperature. Bright spot is an energetically stable backbond state, while there is no stable structure in the case of thermal oxidation.

was seen in another case, where we exposed ozone gas onto the Si(111): (7×7) surface [7].

Second, we report differences in the resulting surface stress between ozone and conventional thermal oxidation methods. We found that the surface develops compressive stress during the initial stage of ozone oxidation at room temperature as shown in Fig.4.

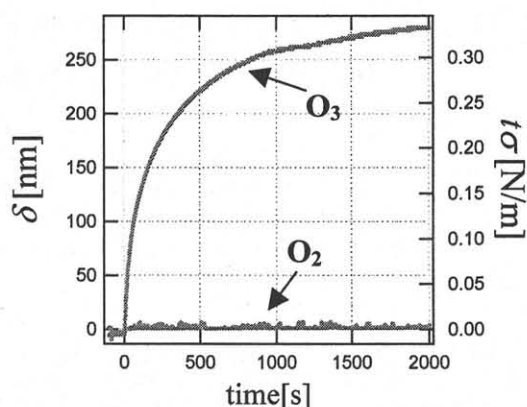


Fig.4 Surface stress evolution during ozone and oxygen gas exposure as a function of exposure time under similar condition at room temperature[8]. Positive stress corresponds to compression.

The stress increased rapidly at the beginning of the oxidation and then leveled off. The maximum stress was about 0.3 Nm^{-1} . It is unlike thermal oxidation under the same conditions, i.e., oxygen gas exposure at room temperature does not induce a significant surface stress change in our experimental error. This result supports the conclusion from our STM data, that ozone is able to react to form a stable oxide at room temperature, while molecular oxygen does not.

4. Summary

We investigated the difference between conventional thermal oxidation and the oxidation using the ozone radical species. We found that ozone is an actual candidate to realize oxidation at lower temperatures.

Our conclusion is that the high reactivity of ozone enables oxidation at lower temperatures by site-selective (back bond) oxidation and this oxidation causes compressive surface strain. So far, the evaluation of the surface strain was done only at room temperature. We will extend this research to include temperature effects to explain completely the differences in surface stress due to oxidation method.

References

- [1] M. Udagawa et al., *Jpn. J. Appl. Phys.* **32**, 282 (1993).
- [2] M. Nishizawa, T. Yasuda, S. Yamasaki, K. Miki, M. Shinohara, N. Kamakura, Y. Kimura, and M. Niwano, *Phys. Rev.* **B65**, 161302(R) (2002).
- [3] T. Narushima, A.N. Itakura, T. Kawabe and M. Kitajima, *Appl. Phys. Lett.* **79**, 605 (2001).
- [4] G. G. Stoney, *Proc. R. Soc. London, Ser. A* **82**, 172 (1909).
- [5] K. Miki, Y. Kudo, N. Tokuda, J.H.G. Owen, T. Narushima, M. Murata and K. Yamabe, submitted to *PRL*.
- [6] T. Uchiyama and M. Tsukada, *Phys. Rev.* **B53**, 7917 (1996).
- [7] K. Miki, T. Narushima and M. Kitajima, submitted to *Nature*.
- [8] A. Kurokawa, S. Ichimura, T. Narushima, A. N. Itakura, M. Kitajima, *Proceeding of ISTC2001 (The Electrochemical Society)*, pp. 212-217.