

Initial Oxidation of Clean and Metal-Deposited Si(100) Surfaces by Super-Pure Oxygen Gas

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Initial oxidation processes of clean Si(100) surfaces oxidized by super-pure and normal grade oxygen gases are analyzed by synchrotron radiation photoemission spectroscopy to investigate the effect of H₂O impurities. A significant difference in initial oxidation features such as oxidation rate and band bending relaxation is found for the two oxygen gases in the sputter-cleaned Si(100)2x1 surface and the Ag-deposited Si(100) surface. The higher oxidation rate and the larger band bending relaxation obtained with the normal grade oxygen can be attributed to molecular H₂O impurities.

1. Introduction

Although the initial oxidation processes of Si(111) and Si(100) surfaces have been studied extensively[1-3], much attention has not been paid to oxygen gas quality. We think this is probably one of the reasons why the data on oxidation features are still considerably scattered.

In this study, the initial stages of oxidation by two oxygen gases of different grades are analyzed with synchrotron radiation photoemission spectroscopy(SRPES) to investigate the effect of H₂O impurities on the oxidation features. For this purpose, a new gas purifying system which can provide the super-pure oxygen with H₂O impurity of less than 20 ppb was designed and attached to the SR analysis chamber. Furthermore, the effect of a metal-overlayer on the oxidation processes is studied by depositing non-reactive Ag and reactive In metals on clean Si(100)2x1 surfaces. Both metals having 4d electrons do not form metal silicides, but are expected to form M-Si(M: metal) bondings of different strength.

Band bending features in the oxidation processes of clean Si and metal-deposited Si surfaces for both gases are also investigated to understand the effect of the H₂O impurity on band bending relaxation. The difference in these oxidation features due to oxygen gas grade is discussed with respect to H₂O molecules.

2. Experimental

Experiments were performed at the Photon Factory BL-1A beamline in the National Laboratory for High Energy Physics. Photoemission spectra of Si2p and the valence band, including O2p, were taken at a photon energy of 127.6 eV. Since a 600 g/mm grating was used in this experiment, the energy resolution was not good enough to resolve the Si2p spin-orbit splitting. However, the main objective of this study was to investigate the H₂O impurity effect on oxidation by means of surface sensitive SRPES.

The samples were n-Si(100) substrates of $1 \times 10^{15} \text{ cm}^{-3}$, n⁺-Si(100) with carrier density of $1 \times 10^{19} \text{ cm}^{-3}$ and p-Si(100) with carrier density

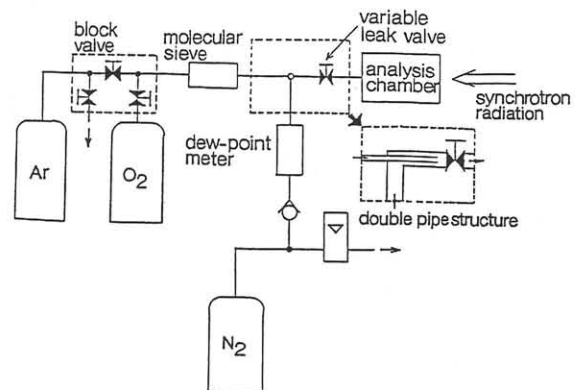


Fig. 1 A super-pure oxygen supply system with dew-point meter.

of $5 \times 10^{17} \text{ cm}^{-3}$. After cleaning with $\text{H}_2\text{O}_2 + \text{H}_2\text{SO}_4$ solution and dilute HF solution several times, the samples were introduced into the analysis chamber and heated in UHV by electron bombardment at about 1 keV accelerating energy and 150 mA emission current from the rear side. Following this treatment, the surfaces exhibited a 2×1 LEED pattern. Initial oxidation was performed by exposing the clean surfaces to oxygen gas of different amounts at room temperature, 350°C and 500°C . Two oxygen gases, namely super-pure oxygen and normal grade oxygen (H_2O impurity of 72 ppm) were used to investigate the H_2O impurity effect on the initial oxidation features. Since the dominant difference between these two gases is the H_2O concentration, we regard the oxidation feature difference as the H_2O impurity effect.

A very pure oxygen gas produced specifically for this experiment was passed through a super-pure oxygen supply system which includes a dew-point meter (Fig. 1). A key point for maintaining such a low H_2O concentration is a double pipe structure which allows a continuous flow of dry Ar gas even when the oxygen gas flow is stopped.

Ag and In metals were deposited in three steps onto the clean Si(100) 2×1 surfaces, and initial oxidation was performed to investigate the effect of the metal overlayer on the initial oxidation. The H_2O impurity effect was also studied using these metal-covered Si surfaces. The thickness of the metal overlayers was measured to be less than 10 \AA by using XPS core level signal intensities and photoionization cross sections.

3. Results and discussion

3.1 H_2O Impurity effect on oxidation rate

A significant difference in initial oxidation features between the super-pure and normal

Table 1 Components of five oxidized states for 10^5 L O_2 -exposed surfaces of differently-treated Si substrates.

		Si^{0+}	Si^{1+}	Si^{2+}	Si^{3+}	Si^{4+}
n-Si Ar sputtered ⇌ heated	Super pure O_2	38%	22%	18%	15%	7%
	Normal O_2	29%	20%	18%	20%	13%
n-Si heated	Super pure O_2	43%	23%	15%	13%	6%
	Normal O_2	40%	26%	14%	13%	7%

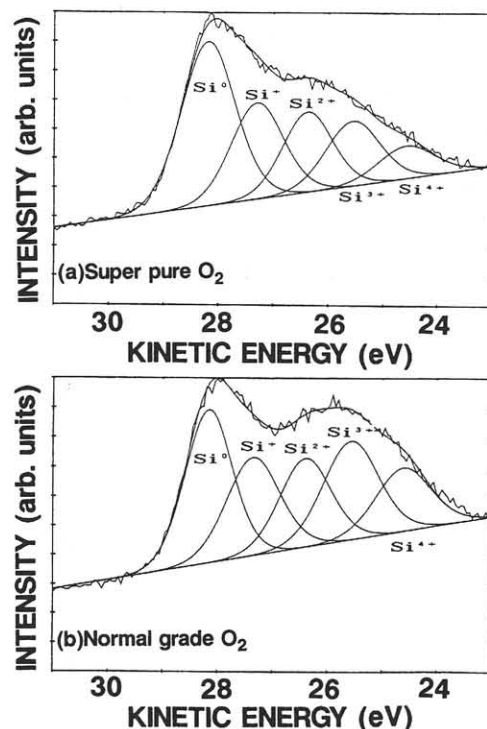


Fig. 2 Si2p spectra deconvoluted into five components using a peak-fitting computer program. Samples are Ar-sputtered and heated n-Si(100) surfaces exposed to (a) the super-pure O_2 and (b) the normal grade O_2 of 10^5 L .

grade O_2 gases was found for the Ar-sputtered and annealed Si(100) surface. While the surface exposed to the super-pure O_2 of 10^3 L showed no Si^{4+} component, a considerable amount of this fully-oxidized state appeared on the part of the surface exposed to the same amount of normal grade O_2 . For 10^5 L exposure to the super-pure O_2 and the normal grade O_2 , the H_2O impurity effect is more remarkable (Fig. 2).

Si2p spectra were deconvoluted into five different components using a peak-fitting computer program. The chemically shifted peak positions of these components reported by Himpsel et al[1] were used in this peak deconvolution procedure. In this procedure, the ratio of Lorentzian to Gaussian contribution was set at 30%. The resulting deconvoluted component ratios are listed in Table 1. The main difference between the two gases lies in the amounts of Si^{3+} and Si^{4+} components. Thus, the enhanced oxidation rate for the normal grade oxygen can be attributed to the H_2O molecules just as in the wet-oxidation process[4]. However, it should be noted that almost no difference was observed on the merely annealed n-Si(100) surface, as can be seen in Table 1, implying that the impurity H_2O effect strongly

depends on the surface condition. The same tendency as the heating-cleaned n-Si was also observed for n⁺-Si and p-Si surfaces. We interpret these results as follows: the Ar-sputtered and annealed surface is heavily damaged, and more steps or dangling bonds which might be easily attacked by H₂O molecules are generated than for the merely annealed surface. Although both surfaces showed a 2x1 LEED pattern, the percentage of flat area for the sputter-cleaned surface might be smaller than the heat-cleaned surface.

Then, metal-deposited Si(100) surfaces were also oxidized with both gases to investigate the H₂O impurity effect on oxidation features. As shown in Fig. 3, a slightly faster oxidation rate was observed for In/Si(100) with the normal grade oxygen. For Ag/Si(100), a more remarkable difference especially in the fully-oxidized state was found, implying that Ag-Si bonds[5] are vulnerable to H₂O molecule attack. Table 2 shows components of five oxidized states for 10³L O₂-exposed Ag/Si and In/Si surfaces. Only the fully-oxidized state, that is Si⁴⁺, increases for Ag/Si, while both Si³⁺ and Si⁴⁺ states increase for In/Si, like for the sputter-cleaned Si(100) surface (Table 1).

We compared the initial oxidation features of various surfaces exposed to super-pure oxygen. It is found that n⁺-Si is more easily oxidized than n-Si, and that p-Si shows the same oxidation feature as n-Si. This is probably because carrier electrons are supplied to the adsorbed oxygen molecules to make atomic oxygen. Although Cros[6] reported the weaker oxygen adsorption on the V3xV3 Ag/Si(111) surface than on the clean Si, the Ag-Si bonds play the role of enhancing surface oxidation in our disordered Ag/Si(100) case. This effect is thought to be due to the breaking of Si sp³ hybrid bonds by

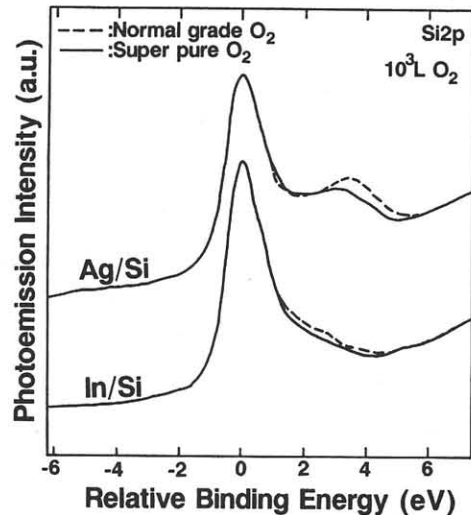


Fig. 3 Si2p spectra of 10³L O₂-exposed Si(100) surfaces covered with about 6 Å of Ag and In. Solid lines are for the normal grade O₂, and dashed lines for the super-pure O₂.

Table 2 Components of five oxidized states for 10³L O₂-exposed Ag/Si and In/Si surfaces.

		Si ⁰⁺	Si ¹⁺	Si ²⁺	Si ³⁺	Si ⁴⁺
Ag/Si(100)	Super pure O ₂	45%	24%	10%	10%	11%
	Normal O ₂	45%	24%	9%	8%	14%
In/Si(100)	Super pure O ₂	51%	30%	11%	7%	1%
	Normal O ₂	50%	27%	11%	9%	3%

the Ag-Si bond formation, and/or the metal-like density of states(DOS) at E_F, which give electrons to oxygen molecules to create atomic oxygen. The similar enhancement effect is reported by Franciosi et al[7] for Cr/Si(111). On the other hand, In has almost no oxidation enhancement effect, probably because of its weak In-Si bonds and small DOS at E_F.

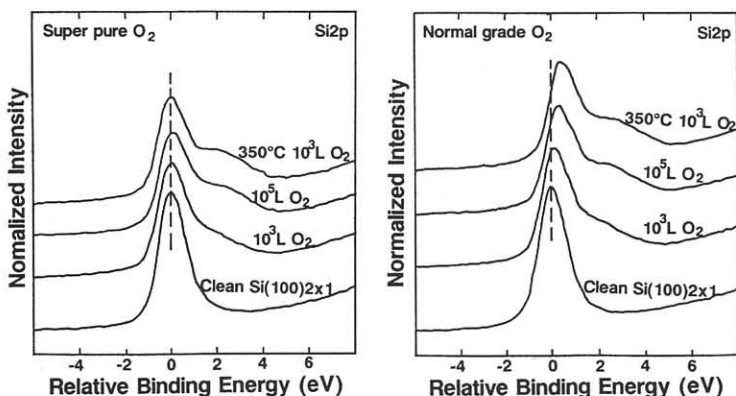


Fig. 4 Si2p photoemission spectra for heating-cleaned n-Si(100) surfaces exposed to (a) the super-pure O₂ and (b) the normal grade O₂.

3.2 H₂O Impurity effect on band bending relaxation

Next, band bending changes during oxidation were analyzed to determine the effect of H₂O molecules on extinguishing surface states. Since the n-Si(111)2x1 reconstructed surface is reported to have the large upward band bending as 0.8 eV[8], our Si(100)2x1 surface is thought to have similar band bending because of surface defects at the beginning. When the heat-cleaned n-Si(100) surface was exposed to the super-pure oxygen, Si2p peak positions remained almost unchanged, as shown in Fig. 4(a). On the other hand, exposure to normal grade oxygen moved the

Si2p peak sharply towards higher binding energy in the course of oxidation, as shown in Fig. 4(b). The similar but not so strong H₂O effect was also observed on the sputtering-cleaned surface. Although the exact mechanism of H₂O molecules to terminate surface defects, these phenomena can be attributed to the relaxation effect of band bending by H and/or OH species decomposed from H₂O molecules.

In order to compare these results on clean Si surfaces with metal-overlayer-caused defects on Si surfaces with respect to terminate by H₂O adsorption, band bending change during oxidation was investigated. When Ag metal was deposited on the n-Si(100)2x1 surface, the Si2p peak moved by about 0.3 eV towards lower binding energy. This peak shift is thought to be mainly due to a chemical effect such as Ag-Si bond formation. However, there may be a small shift due to band bending change. For the In-covered Si(100)2x1 surface, about 0.14 eV shift of the Si2p is observed, indicating that the weaker In-Si bonds are formed at the interface than the Ag-Si bonds.

The band bending features during oxidation with both super-pure and normal grade O₂ gases for the clean Si, Ag/Si and In/Si are summarized in Fig. 5. Although the Ag-covered Si surfaces show the peak shift which is a little smaller than that reported by Rossi et al[9], it should be noted that no H₂O impurity effect was observed for metal-deposited Si surfaces.

At the present stage, we think that the oxidation enhancement effect is due to OH⁻ species decomposed from H₂O molecules, and that the band bending relaxation is due to termination of surface defects or dangling bonds on Si by H and/or OH adsorption. Further study is strongly needed to elucidate the mechanism of the H₂O impurity effect.

4. Conclusion

A significant difference in the features of oxidation by super-pure and normal grade oxygen of clean Si(100) and Ag-deposited Si(100) surfaces is observed by synchrotron radiation photoemission spectroscopy for the first time. Slower oxidation was observed for the super-pure oxygen. It is also found that the surface band bending is relaxed by about 0.4 eV by oxidizing the heat-cleaned Si(100)2x1 surface with normal grade oxygen gas, whereas the super-pure oxygen has no relaxation effect on the band bending. The fast oxidation rate and large band bending

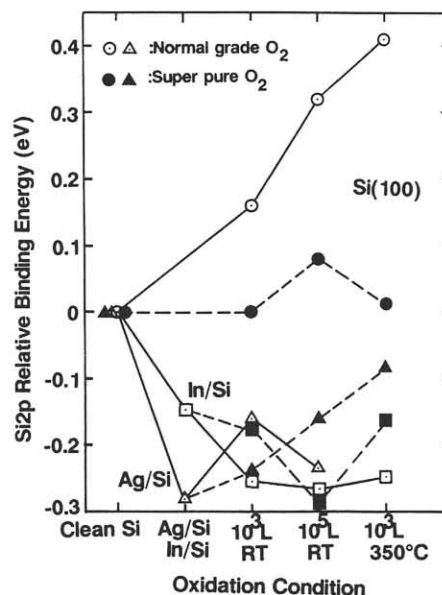


Fig. 5 Si2p core level shifts due to band bending in the course of oxidation with the super-pure oxygen and the normal grade oxygen. Samples are clean Si(circles), Ag/Si(triangles) and In/Si(squares).

relaxation obtained with the normal grade oxygen can be attributed to H and/or OH species decomposed from H₂O impurity molecules.

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【References】

- [1] F.J. Himpsel, F.R. McFeely, A. Taleb Ibrahim, J.A. Yarmoff and G. Hollinger, *Phys. Rev.* B38, 6084 (1988).
- [2] M. Nakazawa, S. Kawase and H. Sekiyama, *J. Appl. Phys.* 65, 4014 (1989).
- [3] C.Y. Su, P.R. Skeath, I. Lindau and W.E. Spicer, *J. Vac. Sci. Technol.* 19, 481 (1981).
- [4] B.E. Deal and A.S. Grove, *J. Appl. Phys.* 36, 3770 (1965).
- [5] J.J. Yeh, D.J. Friedman, R. Cao and I. Lindau, *J. Vac. Sci. Technol.* A4, 1479 (1986).
- [6] A. Cros, *J. Phys. (Paris)* 44, 707 (1983).
- [7] A. Franciosi, S. Chang, P. Philip, C. Caprile and J. Joice, *J. Vac. Sci. Technol.* A3, 933 (1985).
- [8] J.G. Clabes G.W. Rubloff and T.Y. Tan, *Phys. Rev.* B29, 1540 (1984).
- [9] G. Rossi, L. Caliarì, I. Abbati, L. Braicovich, I. Lindau and W.E. Spicer, *Surf. Sci.* 116, L202 (1982).