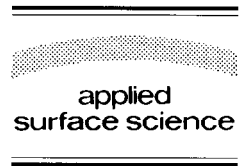




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# Time-of-flight positron-annihilation induced Auger electron spectroscopy studies of adsorption of oxygen on Si(100)

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## Abstract

The initial stage of adsorption of oxygen on Si(100) was studied by the time-of-flight positron-annihilation induced Auger electron spectroscopy (TOF-PAES). The adsorption of oxygen on top of Si(100) was investigated by the real-time measurements of oxygen and Si PAES intensities during and after O<sub>2</sub> exposure. It was found that the initial stage of the top-site adsorption depends strongly on surface temperature, and that the top-site adsorption state is not stable. © 1999 Elsevier Science B.V. All rights reserved.

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*Keywords:* Auger electron spectroscopy; Positron spectroscopy; Silicon; Oxygen; Oxidation

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## 1. Introduction

The oxidation of Si surface is one of the most important processes for the fabrication of Si devices. So far a number of surface analytical techniques have been used to study the oxidation processes [1]. However, the initial stages of adsorption of oxygen on Si surfaces are still not yet fully understood. Positron-annihilation induced Auger electron spectroscopy (PAES) [2–4] can be a useful technique for the study of the initial stage of adsorptions, because this technique has an extremely high sensitivity to the atoms on the surface top-layer. In PAES, core

holes are created by the annihilation of the core electrons with positrons. The top-layer selectivity of PAES is based on the fact that most of the positrons implanted into a solid at low energies (a few 10 eV) diffuse back to the surface and are trapped in the image potential outside the surface before annihilation. Therefore, the core annihilations take place exclusively for the atoms on the surface top layer. In addition, the beam irradiation effects (desorption, decomposition, etc.) can be significantly reduced by the elimination of the background of secondary electrons. Recently, Kim et al. [5] utilized PAES to study the adsorption of oxygen on Si(100), and found that the attenuation of the Auger signal from Si substrate by the oxygen adsorption was much larger for PAES than for the conventional electron-induced Auger electron spectroscopy (AES). Their result demonstrates the high sensitivity of PAES to the adsor-

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bates. However, they did not measure the oxygen Auger signal (presumably due to low count rates).

In the present study, the initial stage of adsorption of oxygen on Si(100) was studied with a time-of-flight (TOF) PAES apparatus which was recently developed by our group [6]. This apparatus enables PAES measurements with higher count-rates and higher energy-resolution than the previous apparatus. With this apparatus, we carried out real-time measurements of oxygen and Si Auger signals during and after exposure to  $O_2$  to investigate the reaction dynamics of oxygen with Si(100).

## 2. Experiments

Details of the slow positron beam-line and the TOF-PAES apparatus were described previously [6,7]. Briefly, a slow positron beam with an intensity of  $10^8$   $e^+$ /s was produced with an electron linear accelerator at the Electrotechnical Laboratory. The positron beam was guided to the sample in the TOF-PAES apparatus with an axial magnetic field. In the TOF-PAES apparatus, a pulsed beam (pulse width 7 ns, pulse period 450 ns, energy 45 eV) was incident into the sample. The electrons emitted from the sample surface were detected with a micro-channel-plate detector which was placed 1 m away from the sample. The energy distribution of the electrons was determined by measuring the time-of-flight of the electrons travelling from the sample to the detector. To improve the energy resolution, the electrons were retarded in a negatively-biased flight tube (0.6 m long) installed in the flight path.

In the present study, a Cz-Si(100) wafer (n type, P doped,  $0.01 \Omega \cdot \text{cm}$ ) was used as sample. Before loading into the PAES chamber, the sample was etched in 5% Hf to remove native oxide layers. In the PAES chamber, the sample was outgassed at  $500^\circ\text{C}$  for 24 h. Before PAES experiments, a clean surface was obtained by the repetition of flash annealing up to  $1100^\circ\text{C}$  followed by slow cooling at a rate of  $2^\circ\text{C}/\text{s}$ . During the annealing, the pressure was below  $1 \times 10^{-9}$  Torr. The exposure to  $O_2$  was done by backfilling the PAES chamber with  $O_2$  gas. During the exposure, ion-gauge and ion-pump were turned off. The PAES measurements were done at a pressure below  $2 \times 10^{-10}$  Torr.

## 3. Results and discussions

Fig. 1 shows the typical TOF-PAES spectra for clean and oxygen-adsorbed Si(100). The time spectrum of the annihilation  $\gamma$  rays measured with a photomultiplier behind the sample was also plotted. The PAES spectrum taken after the annealing at  $1100^\circ\text{C}$  showed a strong Auger peak from Si ( $L_{2,3}VV$ ) at 90 eV and no Auger peaks from contaminants. The count rate of the Si-LVV Auger peak from the clean Si(100) was about 20/s. After exposure to 10 L ( $1 \text{ L} = 10^{-6}$  Torr s)  $O_2$  at a surface temperature of  $-80^\circ\text{C}$ , the Si-LVV peak was reduced significantly, and an Auger peak from oxygen (KLL) appeared at  $\sim 500$  eV.

To study the initial stage of oxygen adsorption, we measured the time dependence of the Si-LVV and O-KLL Auger intensities in situ during the  $O_2$  exposure. The exposure was done at an  $O_2$  pressure of  $1 \times 10^{-8}$  Torr. Fig. 2 shows the time evolutions of the Si-LVV and O-KLL Auger intensities for surface temperatures of  $-80$ ,  $30$ , and  $300^\circ\text{C}$ . All data points are normalized to the same beam dose. As can be seen, the results strongly depend on

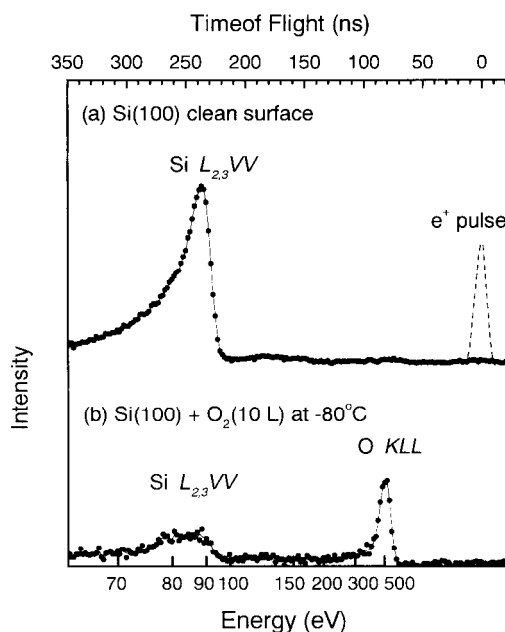


Fig. 1. TOF-PAES spectra from (a) clean Si(100) and (b) 10 L  $O_2$  exposed Si(100). The exposure was done at a surface temperature of  $-80^\circ\text{C}$ . The dotted line is the time spectrum of the annihilation  $\gamma$  rays emitted from the sample.

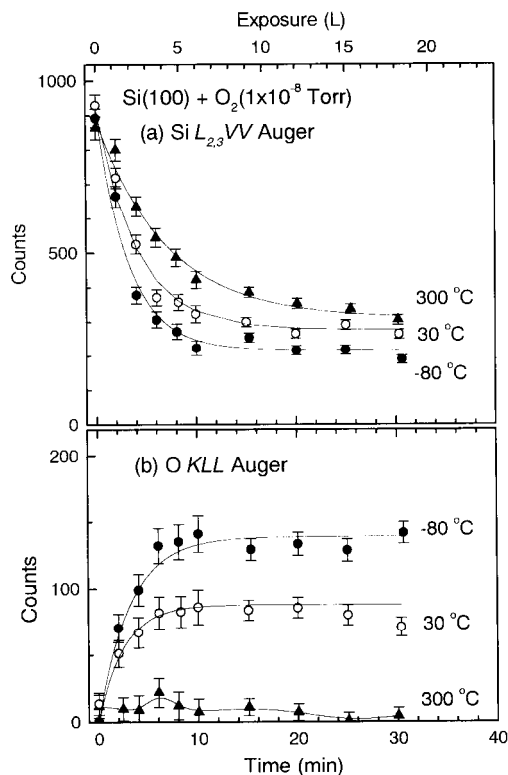


Fig. 2. (a) Si-LVV and (b) O-KLL Auger intensities during  $O_2$  exposure at surface temperatures of  $-80$ ,  $30$ , and  $300^\circ\text{C}$ . The exposure was done at an  $O_2$  pressure of  $1 \times 10^{-8}$  Torr.

surface temperature. On the whole, the O-KLL Auger intensity decreased with increasing temperature. In the present measurements, the O-KLL Auger peak was not observed at temperatures above  $300^\circ\text{C}$ . The result indicates that the top-site adsorption is unstable at higher temperatures.

At temperatures below  $\sim 300^\circ\text{C}$ , the O-KLL intensity increased with  $O_2$  exposure below  $\sim 5$  L ( $\sim 10$  min), and leveled off above  $\sim 5$  L. The result differs from that obtained by the conventional AES [8,9] and X-ray photoelectron spectroscopy (XPS) [10,11]. In the AES and XPS works, the oxygen signal increased at  $O_2$  exposures up to  $\sim 100$  L. The difference can be attributed to the different surface sensitivities. Since the observation depth of AES and XPS is 1–10 nm, these techniques detect the oxygen in several layers beneath the surface. In contrast, PAES is sensitive exclusively to the topmost layer. Therefore, the O-KLL PAES intensity would reflect

the amount of oxygen adsorbed on top of the Si surface. Recent scanning tunneling microscopy studies [12,13] revealed that the initial oxidation on Si(100) $2 \times 1$  surface occurred preferentially at C-type defects [14]. Thus, the O-KLL PAES intensity would reflect the adsorption at the defect sites.

We found that the oxygen adsorbed on top of Si(100) is unstable. We observed the decrease in the O-KLL Auger intensity after the  $O_2$  exposure, as shown in Fig. 3. The decay lifetime was shorter for higher surface temperatures. The result suggests that the insertion into the sub-surface site or the desorption from the surface occurred by the thermal activation. It is noted that we observed a similar result for the molecular oxygen adsorbed on Si(111) [15].

At temperature above  $\sim 300^\circ\text{C}$ , the O-KLL Auger peak disappeared. This indicates that the top-site adsorption does not occur or the decay of the top-site adsorption state is too fast. In this temperature regime, although the O-KLL peak was not detected, the Si-LVV peak intensity was significantly reduced by the  $O_2$  exposure (as shown in Fig. 2). We believe that the decrease in the Si-LVV Auger intensity was

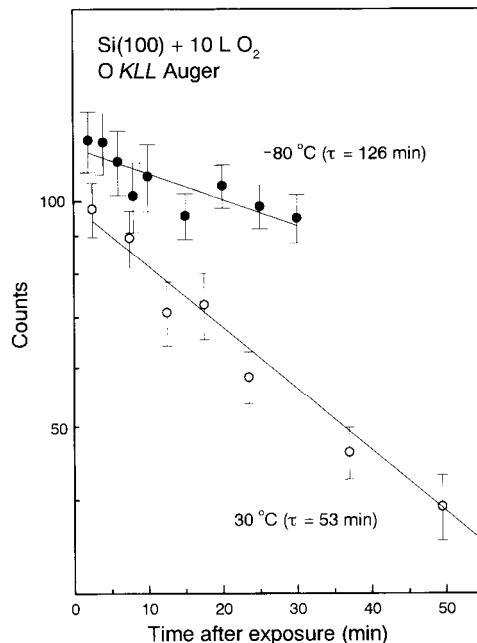


Fig. 3. Decay of the O-KLL Auger intensities for 10 L  $O_2$  exposed Si(100) at  $-80$  and  $30^\circ\text{C}$ . The solid lines were fits to an exponential decay function  $I(t) = I_0 \exp(-t/\tau)$ .

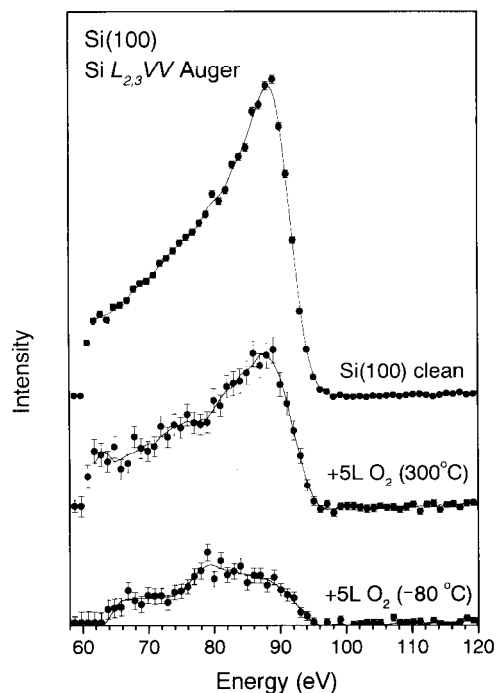


Fig. 4. Si LVV Auger lineshapes obtained by PAES for clean Si(100) at room temperature and 5 L O<sub>2</sub> exposed Si(100) surfaces at  $-80$  and  $300^{\circ}\text{C}$ .

caused by the oxidation in sub-surface sites. The AES works [8,9] showed that the oxygen uptake occurs significantly even at temperatures up to  $\sim 600^{\circ}\text{C}$ . To obtain further information on the O<sub>2</sub>-exposed surface, we measured the Si-LVV Auger lineshape. The Si-LVV Auger lineshape is sensitive to chemical environment of the Auger emitting Si atoms, because the lineshape is determined by the density of states of the valence electrons. Fig. 4 shows the Si-LVV Auger line-shape from the Si(100) exposed to 5 L O<sub>2</sub> at  $300^{\circ}\text{C}$ . Auger line shape from clean Si(100) and Si(100) exposed to 5 L O<sub>2</sub> at  $-80^{\circ}\text{C}$  are also shown for comparison. The energy resolution was better than 3 eV. For the surface exposed to O<sub>2</sub> at  $-80^{\circ}\text{C}$ , a large chemical shift was observed. A peak at  $\sim 80$  eV is associated with Si–O bond formation [16]. At  $300^{\circ}\text{C}$ , on the contrary, the Auger lineshape was almost the same as that obtained for the clean surface. The result indicates that most of the top-layer Si atoms are not bonded with oxygen. Therefore, the oxygen would be adsorbed directly into the sub-surface sites at this

temperature. Possible explanations of the decrease in the Si Auger signal at high temperatures are that the positrons were trapped at structural defects below the surface produced by the insertion of the oxygen atoms, or that the positron surface-state was changed by the sub-surface oxidation. The measurements of the positron lifetime or the positron (positronium) re-emission yield would give useful information.

#### 4. Conclusion

The initial stage of adsorption of oxygen on Si(100) was studied by TOF-PAES. It was found that the top-site adsorption depends strongly on surface temperature. The time-resolved PAES measurements revealed that the top-site adsorption state is not stable even at room temperature. Above  $300^{\circ}\text{C}$ , the top-site adsorption does not occur. The reduction of Si-LVV Auger intensity suggests that the oxygen is adsorbed directly into sub-surface sites above  $300^{\circ}\text{C}$ .

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