Initial Stage of Oxidation of Si(001)-2x1 Surface Studied by X-Ray Photoelectron Spectroscopy

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1. Introduction

Recently, MOSFETs with 1.5nm-thick gate oxide was shown to operate at room temperature[1]. Understanding of the oxidation mechanism on Si(001)-2x1 surfaces is requisite issue for the future ULSIs in order to realize a well-controlled SiO_2/Si interface in atomic scale. The initial oxidation has been intensively studied[2,3]. This is explained by a preferential oxygen insertion into a dimer back-bond by scanning tunneling spectroscopy and high-resolution electron energy loss spectroscopy[4] and layer by layer oxidation has been studied by scanning reflection electron microscopy[5] .The initial oxidation kinetics based on first-principles calculations have also been discussed[6].

In this paper we report on the surface composition of a Si(001)-2x1 reconstructed surface after various O_2 exposures and propose an oxidation process in atomic scale based on experimental core-level spectra obtained by X-ray photoelectron spectroscopy (XPS).

2. Experimental

The XPS measurements were performed with a monochromatic Al K α radiation and an acceptance angle of $7°$, a take-off angle of $7° \sim 15°$ to enhance surface sensitivity(ULVAC-PHI Model 1600). Back ground pressure of the analysis chamber was 7×10^{-11} torr. The reconstructed surface were obtained by heating a P type Si(001) substrate to temperatures at around 1100℃ by an infrared lamp in a preparation chamber. The Si surfaces were exposed to pure $O_2(0.5\sim256L)$ at room temperature.

3. Results and Discussion

Fig.1 shows the oxidation-induced changes in Si_{2p} spectra for Si(001)-2x1 surfaces exposed to molecular oxygen at room temperature. After a Shirley background subtraction, the Si_{2p} spectra were normalized to their maximum intensity. Deconvolution of the Si_{2p} spectra for Si(001)-2x1 surfaces was carried out into three components, the bulk, the dimer up atoms and the dimer low atoms[7]. Each peak of suboxide assigned by Si^{1+},Si^{2+} and Si^{3+} had almost the same binding energy as that reported by Himpsel et al.[8]. Fraction of total intensity for the deconvoluted components obtained from an iterative least-squares error fitting procedure were plotted in Fig.2 as a function of the oxygen exposure. The dimer components decreased with increasing the oxygen exposure and instead the suboxide components increased. On the other hand, the observed each O_{1s} spectrum was deconvoluted into two Gaussian curves , low binding energy component at 532.00
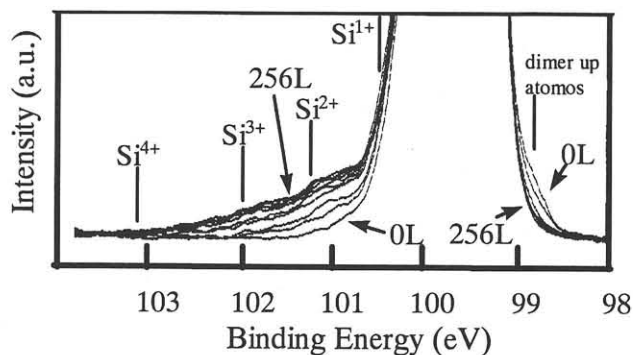

Fig.1 The oxidation-induced changes in Si_{2p} spectra for Si(001)-2x1 surfaces exposed to molecular oxygen at room temperature.
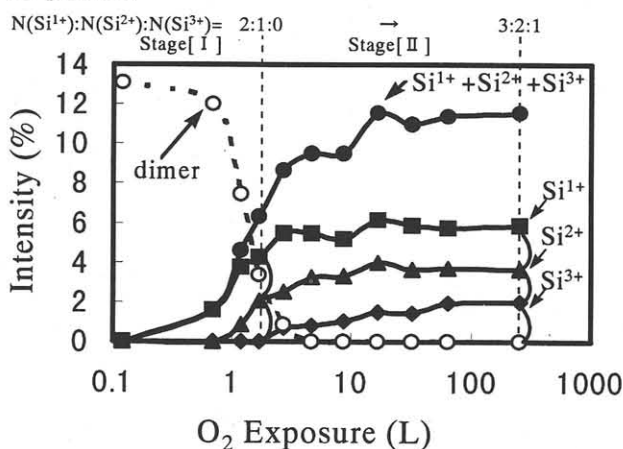

Fig.2 Fractions of total intensity for the deconvoluted suboxide components as a function of the Oxygen exposure.

± 0.25 eV attributed to oxygen at the "bridge sites" and high binding energy component at 532.90 ± 0.25 eV attributed to oxygen at the "on-top sites"[9] as shown in Fig.3.

The observed early oxidation process is considered to be divided into two stages [I] and [II] as illustrated in Figs.2 and 3. The quantities of the oxygen exposure at the stage [I] and [II] were $0\sim2L$ and $2\sim256L$, respectively. At the beginning of the oxygen uptake at the stage[I], Si^{1+} and oxygen at the bridge sites are formed predominantly. This implies that for small oxygen uptake, a top-most Si has a chance to react with only one oxygen at the bridge site. However, for further oxygen supply, Si^{1+} has a chance to accept another oxygen to combine and some of Si^{1+} change to Si^{2+}. Thus during the stage[I], ratio of the suboxide species (Si^{1+}:Si^{2+}:Si^{3+}) is changing gradually from 1:0:0 to 2:1:0. At the beginning of the stage [II], an evolution of the Si^{3+} begins to start. The intensity of the Si^{3+} increases

and saturates till the end of this stage. At the end of this stage, the ratio $(Si^{1+}:Si^{2+}:Si^{3+})$ changes to 3:2:1(Fig.2) and the ratio for bridging oxygen atoms to surface on-top oxygen atoms was about 4:1~5:1(Fig.3).

Furthermore, to explain the Si-O-Si network formation, we evaluated the evolution of the intermediate suboxide species by the random bonding layer by layer mechanism[9]. We calculated the intensity of the Si^{n+}, I_n, according to the following equation

$$I_n = {_4}C_n (x/1.75)^n (1-x/1.75)^{4-n}$$
$$+ \exp(- d / \lambda \sin \theta)\, {_2}C_n (x/1.75)^n (1-x/1.75)^{2-n}, \quad (1)$$

where n , x , d , λ, and θ are the number of oxygen ligands in Si^{n+}, the stoichiometry index in SiOx , the distance between the first and the second layers , the photoelectron mean-free path in the SiO_2 and the photoelectron take-off angle , respectively. The suboxide yields are plotted as a function of x as shown in Fig.4. The inset shows the final configuration at x=1.75. Our results are found to be in good agreement with the calculated curves. From these considerations, we propose a model for this initial stage of oxidation as illustrated in Fig.5. From Fig.3 we assumed that in the low coverage range, the oxygen attacks the surface Si bonds at the bridge sites(dimer bridge sites or back-bond sites). Also from ref.[10] , the additional oxygen is assumed to be preferentially incorporated to the neighboring sites of these bridge sites and spread widely towards surrounding sites step by step.

4. Conclusion

We have proposed a new model for the initial oxidation stages of the Si(001)-2x1 surfaces where the ratios of the suboxide species $(Si^{1+}:Si^{2+}:Si^{3+})$ change gradually from 1:0:0 , 2:1:0 to 3:2:1. The ratio for the bridging oxygen atoms to the on-top oxygen atoms is about 4:1~5:1. The early stage of this oxidation on Si(001)-2x1 is almost consistent with the calculation by the random bonding layer by layer mechanism[9].

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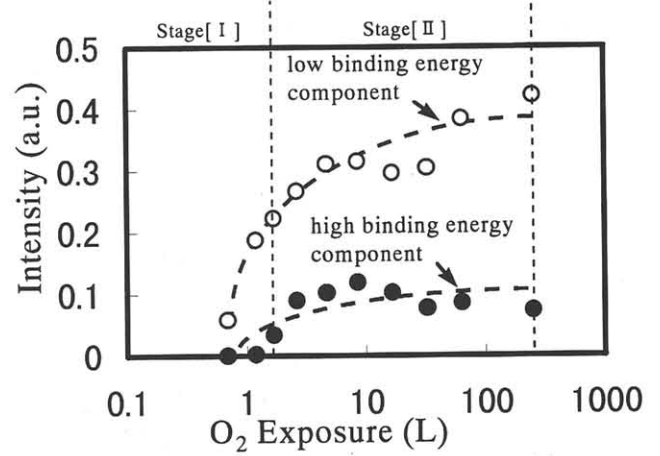[10] J.A.Schaefer, et al.,Surface Sci.**155**(1985)535.

Fig.3 The intensity of O_{1s} spectrums deconvoluted into two Gaussian curves , low binding energy component at 532.00 ± 0.25eV attributed to oxygen at the "bridge sites" and high binding energy component at 532.90 ± 0.25eV attributed to oxygen at the "on-top sites".
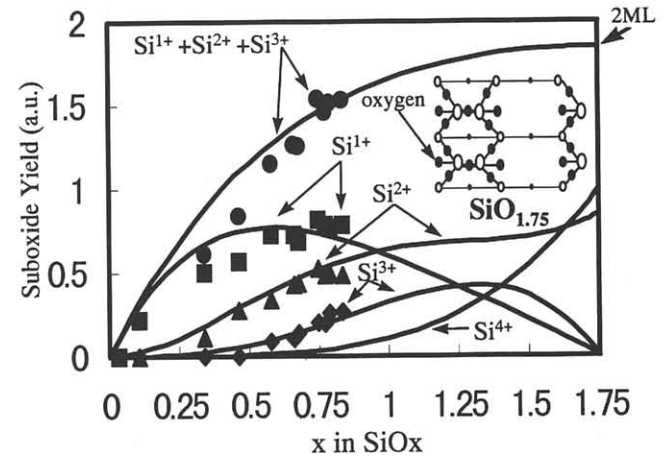

Fig.4 Experimental results from XPS spectra and calculated results for the evolution of the intermediate suboxide species , $Si^{1+}, Si^{2+}, Si^{3+}$ and Si^{4+} by the random bonding layer by layer mechanism.($\bullet$:oxygen ,$\circ$: silicon in the inset)
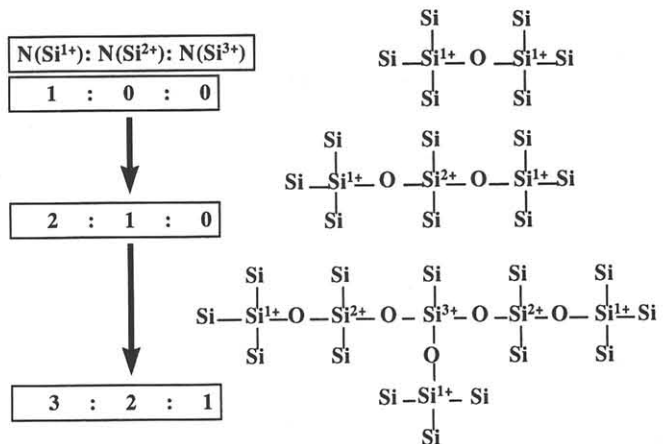
Fig.5 Model of the initial stage of oxidation on Si(001)-2x1 surface. The ratios of suboxide species $(Si^{1+}:Si^{2+}:Si^{3+})$ are changing gradually from 1:0:0, 2:1:0 to 3:2:1.