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Real-time monitoring of oxidation processes on Si(0 0 1) surface using O_2 gas under 1000 K by synchrotron radiation photoemission spectroscopy

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Abstract

The thermal oxidation of Si(0 0 1) surface under 1000 K in the O_2 pressure of 1×10^{-4} Pa has been in situ investigated using real-time photoemission spectroscopy with high energy-resolution synchrotron radiation. Using a reaction kinetics model, we found that the oxidation at 1000 K progressed with a two dimensional island growth mechanism involving desorption of SiO molecules. Si^{2+} species relating to the backbond oxidation at the topmost Si dimers appeared in conjunction with Si^{1+} species at the initial oxidation stage at 1000 K. We clarified that the topmost Si atoms bonding to two oxygen atoms played an important role as an initial adsorbate. Since Si oxidation states with higher oxidation numbers, such as Si^{4+} and Si^{3+}, appeared at the early oxidation stages as well, we concluded that SiO_2 adsorbates constructed with the Si^{4+} species were preferentially formed even in the oxide nucleus as well as the two dimensional islands on the Si(0 0 1) surface at 1000 K.

Keywords: Silicon; Oxygen; Oxidation; Synchrotron radiation photoelectron spectroscopy; Growth; Surface electronic phenomena (work function, surface potential, surface states, etc.)

1. Introduction

The thermal oxidation on Si(0 0 1) surfaces using O_2 gas, generally called as dry oxidation, is an important chemical reaction in the semiconductor processes for fabrication of metal-oxide-semiconductor field effect transistors (MOSFETs). In order to obtain high-quality and ultra-thin oxide films to develop the next-generation ultra-large-scale-integrated (ULSI) devices, the control of the oxidation on Si(0 0 1) surfaces is becoming more and more serious. Furthermore, the oxidation of Si(0 0 1) surfaces by O_2 gas is an interesting chemical reaction in the research field of surface science, because it involves fundamental surface chemical reactions, such as adsorption, rearrangement of chemical bonds and desorption [1].

The Si(0 0 1) oxidation has been investigated by many experimental techniques, such as real-time photoemission spectroscopy [2–5], reflection high energy electron diffraction combined with Auger electron spectroscopy [6,7] and scanning tunneling microscopy [8,9]. The real-time photoemission

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spectroscopy using not only an ultraviolet light source but also soft X-rays is a powerful method to determine the chemical composition of the oxide films. Although time evolution of peak height for O-1s photoemission has been observed [2–4], time evolution of Si photoemission spectra has not been observed yet except our experiments. Thermal oxidation is generally categorized into three types as a function of O_2 pressure and surface temperature. The first is called as *passive* oxidation, in which chemisorbed oxygen atoms were used to form oxide layers. The second is so-called *active* oxidation, which involves Si etching processes (SiO desorption). Another important oxidation is called as the *transition region*, in which the oxide layers are formed in conjunction with the SiO desorption.

We have already reported the real-time O-1s and Si-2p photoemission spectroscopy for the initial oxidation using O_2 gas at 1×10^{-4} Pa on the Si(0 0 1) surface depending on surface temperature [10]. It was found that the oxidation at 860, 895 and 945 K was explained by the Langmuir-type adsorption kinetics, whereas the time evolution of O-1s intensity at 1000 K was explained by the auto-catalytic oxidation model [3]. Thus, the transition region was between 945 and 1000 K at 1×10^{-4} Pa [10]. On the other hand, the changes of Si oxidation states (Si^{n+}, $n: 1$–4) were clearly monitored in the time-resolved Si-2p photoemission spectra using high energy-resolution synchrotron radiation in a temperature range lower than 945 K corresponding to the passive oxidation condition [10]. We have obviously revealed that the development of Si oxidation states depended on surface temperature in the passive oxidation condition at the initial oxidation stages [10]. However, the time evolution of Si oxidation states in the transition region has not been clarified yet. The oxide-layers are probably formed by the two-dimensional (2D) island growth in the transition region. The important point is whether the SiO_2 structure evidenced by the Si^{4+} species in the Si-2p core-level spectra would be formed even at the early oxidation stage or not.

We have studied the initial thermal oxidation on the Si(0 0 1) surface using O_2 gas at 1×10^{-4} Pa in the transition region under 1000 K. The time evolution of Si oxidation states has been clarified by in situ time-resolved Si-2p photoemission measurements.

2. Experimental

All experiments were carried out at the surface chemistry end-station (SUREAC2000) [11,12] constructed at the high energy-resolution and high brilliance soft X-ray beamline, BL23SU, in the SPring-8 [13–15]. The energy resolution of synchrotron radiation used in the present study was better than 100 meV and the photon flux was roughly estimated to be of the order of 10^{10} photons s^{-1}. The surface reaction analysis chamber was mainly pumped out by two turbomolecular pumps in a tandem fashion. The base pressure of the analysis chamber was better than 3×10^{-8} Pa. Photoelectrons were collected using a 125-mm hemispherical electron energy analyzer with five channeltrons (EA125-5MCD Omicron NanoTechnology, GmbH). Detailed photoemission measurements for Si-2p and O-1s core-levels were described elsewhere [10].

An N-type Si(0 0 1) wafer with the resistivity of 0.5–10 Ωcm was used as a sample. The Shiraki method [16] was employed for the wet chemical cleaning of the Si(0 0 1) substrate before installing it into the vacuum chamber. The substrate was annealed up to 1300 K several times keeping the pressure below 5×10^{-7} Pa. The substrate was finally heated up to 1100 K in the surface reaction analysis chamber. Hardly any contamination of oxygen and carbon was detected by the photoemission spectroscopy just after the thermal cleaning. After the thermal cleaning, the sample was in situ oxidized by exposing it to the O_2 ambience. The pure O_2 gas (99.9995%) was fed into the reaction analysis chamber through a variable leak valve. The O_2 pressure (1×10^{-4} Pa) was monitored by an ionization gauge located at a position such that it indirectly faced the sample surface.

3. Results and discussion

Fig. 1(A) and (B) shows the oxygen uptake curves obtained from the O-1s photoemission

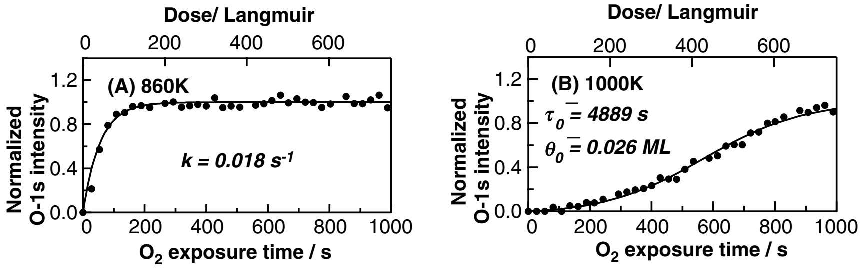

Fig. 1. Oxygen uptake curves for oxidation on Si(0 0 1) surface at (A) 860 K and (B) 1000 K. The pressure of O_2 gas is 1×10^{-4} Pa.

spectra at 860 and 1000 K, respectively. The intensities were normalized by the photocurrent of a final mirror at the beamline. We have analyzed the time evolution of integrated peak area intensities of O-1s photoemission spectra on the basis of adsorption kinetics models [3,4]. The observed time evolution was fitted by the least squares method using Eqs. (1) and (2) corresponding to the Langmuir and the auto-catalytic oxidation model, respectively. The single exponential function shown in Eq. (1), which described the conventional Langmuir-type adsorption, was applied to fit the time evolution of O-1s intensities at 860 K:

$$I_{\mathrm{O\,1s}} = 1 - \exp(-kt). \tag{1}$$

Here $I_{\mathrm{O\,1s}}$ is the O-1s peak area intensity normalized by the intensity at the saturation level. The k (s^{-1}) and t (s) denote the rate coefficient of O_2 adsorption and the O_2 exposure time. The measured data points and the fitted results were indicated by the full circles and the solid curve, respectively. Fitting parameters are also indicated in Fig. 1. The measured uptake curves were well fitted by Eq. (1). The oxygen uptake curves were clearly different depending on surface temperature as shown in Fig. 1. The O-1s intensity increased rapidly with increasing O_2 exposure time and was almost saturated at about 200 s at 860 K. On the other hand, the rate of oxygen uptake at 1000 K was considerably slower, so that it took a longer time to reach the saturation level. The oxidation at the surface temperatures of 860 K progressed by the Langmuir-type adsorption. The rate coefficient (k) is equal to $S \times F$, where S is the sticking coefficient and F is the density of oxygen atoms exposed to the Si(0 0 1) surface for the unit time, i.e. the oxygen flux density. When the pressure of O_2 gas was 1×10^{-4} Pa, the number of oxygen atoms exposed to the Si(0 0 1) surface was estimated to be about 2.7×10^{14} $\mathrm{cm^{-2}\,s^{-1}}$. Since the density of Si atoms on the Si(0 0 1) surface was 6.8×10^{14} $\mathrm{cm^{-2}}$, the oxygen exposed to the Si(0 0 1) surface was about 0.4 $\mathrm{ML\,s^{-1}}$. The sticking coefficient value was deduced to be 0.04, which was close to the initial sticking coefficient (S_0) values of 0.06–0.08 [17].

The oxygen uptake curve was more complex at 1000 K. The O-1s intensities gradually increased for a certain period after introducing O_2 gas and the increasing rate of O-1s intensity slowed down. According to the reaction kinetics model for the 2D island growth involving the SiO desorption, the time evolution of oxygen coverage (θ) was well reproduced by Eq. (2) derived from the auto-catalytic oxidation model [3,4].

$$I_{\mathrm{O\,1s}} = \theta_0 \cdot \frac{1-\exp(-\kappa t/\tau_0)}{\theta_0 + \exp(-\kappa t/\tau_0)}. \tag{2}$$

Here $\kappa = (\theta_0 + 1)/\theta_0$. The τ_0 determines the initial slope of θ. The θ_0 represents the critical θ at which the burst-like increase of θ starts. The resultant parameters obtained by the curve fitting are also shown in the Fig. 1(B). From the analysis of the oxygen uptake curve at 1000 K shown in Fig. 1(B), we obtained that the parameters of τ_0 and θ_0 were 4889 s and 0.026 ML, respectively. The product term of $\tau_0 \cdot \theta_0$ resulted in 127 s. In the auto-catalytic oxidation models [3,4], the physical meaning of the product term ($\tau_0 \cdot \theta_0$) is the incubation time, at which the surface reaction mode is changed from the increase of the number of nucleus to the increase of the size of islands, i.e. 2D island growth. The parameter (θ_0) gives the oxide coverage where the 2D island growth commences [3,4]. We confirmed that the oxidation at 860 K was characterized to be passive oxidation, whereas the oxidation at 1000 K was classified in the transition region.

Fig. 2(A) and (B) shows the typical time-resolved Si-2p photoemission spectra in the O_2 gas pressure of 1.0×10^{-4} Pa at 860 and 1000 K, respectively. It was found that the suboxide components clearly appeared at the higher binding energy side of the Si-2p core-level spectra. With increasing oxidation time, there was a marked and progressive increase of peaks at the higher binding energy side. In order to obtain each component for Si oxidation states, the de-convolution of Si-2p core-level spectra was achieved by the curve fitting procedures. The raw data were plotted by the dotted curves and the line curves exhibited the fitted results in Fig. 2. Detail curve fitting procedures for Si-2p photoemission spectra were indicated elsewhere [10]. It is shown that the high energy-resolution Si-2p photoemission spectrum for the clean Si(0 0 1)-2 × 1 surface, corresponding to the bottom (0 L) in Fig. 2, consists of the bulk and additional components appearing at the core-level shifts of −0.500, 0.280 and 1.00 eV, respectively. We have concluded that the peak at −0.500 eV was due to the up-atoms of buckled Si dimers (D_u) and the peak at 0.28 eV was assigned to the down-atoms (D_d) [18,19]. The small broad component around +1.0 eV was also observed for the initial Si(0 0 1)-2 × 1 surfaces (0 L). Since oxygen was not observed in the O-1s photoemission spectrum, the broad and weak features lying on the high-binding energy tail of Si-2p photoemission spectra were assigned as the bulk and/or surface electron energy loss structure. The curve fitting for the oxidized Si(0 0 1) surface was performed using the core-level shift values of 1.00 eV (Si^{1+}), 1.81 eV (Si^{2+}), 2.63 eV (Si^{3+}) and 3.77 eV (Si^{4+}) with respect to the binding energy of the bulk Si-2p$_{3/2}$ peak position (Si^0). Two components denoted as α (0.25 eV) and β (−0.32 eV) around the bulk component were necessary for obtaining the best fitting results. The component α and β are due to the defects or subsurface (the second and/or third layer) Si atoms [20,21]. Thus, the possible origins of these components are the Si layers or defects in contact with the interface layers. In other words, they are explained in terms of the slight distortion of bonding angles of interface Si atoms. Consequently, the Si-2p photoemission spectra were fitted by seven components, that is, one bulk (Si^0), four oxidation related components (Si^{1+}, Si^{2+}, Si^{3+} and Si^{4+}) and two interface components (α and β).

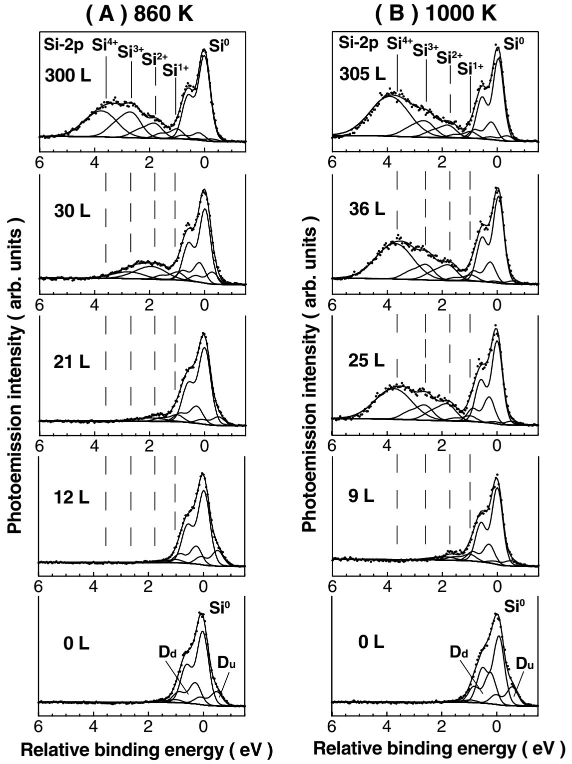

Fig. 2. Real-time Si-2p photoemission spectra using high energy-resolution synchrotron radiation for oxidation on Si(0 0 1) surface at (A) 860 K and (B) 1000 K. The pressure of O_2 gas is 1×10^{-4} Pa.

In the spectrum corresponding to the dose of 21 L at 860 K, the oxidation states Si^{1+} and Si^{2+} were observed. On the other hand, the much higher oxidation states of Si^{3+} and Si^{4+} species were clearly observed in addition to the Si^{1+} and Si^{2+} components at 25 L at 1000 K. It was found that the Si oxidation states with higher oxidation number appeared at 1000 K at the much earlier oxidation stage than that at 860 K. The formation of SiO_2 was enhanced by increasing surface temperature. The thermal migration processes of oxygen atoms after the oxygen chemisorption competes with SiO desorption.

Fig. 3(A) and (B) shows the time evolution of each Si oxidation state derived from the Si-2p photoemission spectra described in Fig. 2. The intensity of each Si oxidation state was normalized by the thickness of oxide layers, evaluated by the equation in the literature [22]. At the surface temperature of 860 K, only the Si^{1+} component appeared at first and then the Si^{1+} species abruptly decreased. After that, higher Si oxidation states appeared. The oxygen atom must adsorb randomly on the surface because the Langmuir-type adsorption takes place at 860 K. Si atoms at the topmost Si dimers must be oxidized consecutively from Si^{1+} to Si^{4+} at 860 K [10]. Thus, we found that the changes of oxidation states proceeded consecutively at 860 K [10].

The time evolution of each Si oxidation state at 1000 K showed the clear difference from the results at 860 K. After 1000 s oxidation, the amount of oxygen obtained from the O-1s uptake curve was almost saturated. Since the thickness of oxide layers in the almost saturated region was estimated to be 0.41 nm from the calculation based on the measured photoemission intensity of suboxide components [22], the Si(0 0 1) surface was oxidized at least up to the backbonds of Si dimers. Although the Si oxidation proceeds consecutively at 860 K, the oxidation at 1000 K is expected to be the 2D island growth. Indeed, the Si^{2+} species was simultaneously observed with Si^{1+} species even at 9 L at 1000 K. This result indicates that oxidized Si atoms bonding to two oxygen atoms are stable even at 1000 K at the initial oxidation stage. The oxidized Si atoms is expected to be the dimer Si atoms on the top of Si(0 0 1) surface, because the oxide layers thickness is less than 0.4 nm. The theoretical investigations showed that the backbond sites of dimer Si atoms on the clean Si(0 0 1)-2×1 surface could be oxidized without energy barriers [23]. The higher Si oxidation states, such as Si^{3+} and Si^{4+}, appeared markedly with the simultaneous decrease of Si^{1+} and Si^{2+} components at the early oxidation stage. Consequently, a part of Si^{1+} and Si^{2+} species changes to Si^{3+} and Si^{4+} species by the further dissociative O_2 adsorption on the Si(0 0 1) surface followed by oxygen migration. We can recognize that the Si^{4+} states related to SiO_2 species, is originated from the topmost Si atoms in the oxidation of Si(0 0 1) surface at 1000 K.

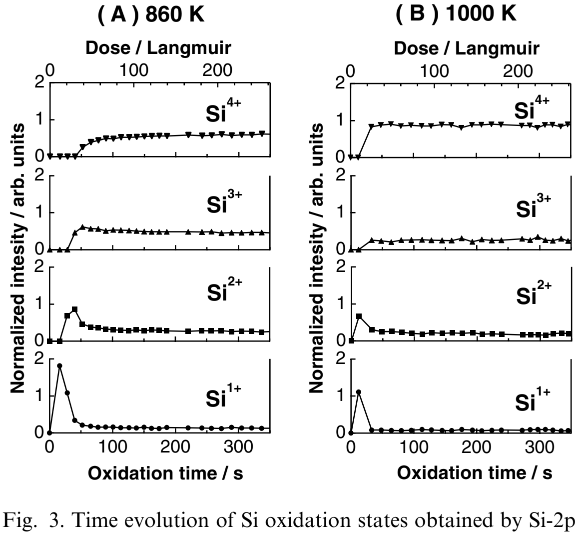

Fig. 3. Time evolution of Si oxidation states obtained by Si-2p photoemission spectra at (A) 860 K and (B) 1000 K. The pressure of O_2 gas is 1×10^{-4} Pa.

The SiO desorption occurred simultaneously with the formation of oxidized films at 1000 K, at which the 2D island growth progresses. We pointed out that the backbond oxidation of dimer Si atoms accelerated the SiO desorption [24]. As predicted by the first-principle calculations, the backbond oxidation occurs easily without an energy barrier when the dangling bond exists at the dimer Si atoms [23]. In fact, we found that the oxidation on the clean Si(0 0 1)-2×1 surface progressed up to Si^{4+} oxidation state at room temperature in a thermal energy condition of O_2 [20,25,26]. We assume that an adsorbed structure of oxygen atoms bonding to backbonds of dimer Si atoms is formed as an initial adsorbate for formation of the nucleus and the precursors of SiO desorption.

The dual-oxide-species (DOS) model was presented to explain the concurrent 2D island growth and SiO desorption [27]. The auto-catalytic oxidation model is also explained using the DOS model [3,4]. In the auto-catalytic oxidation model, an oxide nucleus generation stage is expressed by Langmuir term before an incubation time ($\tau_0 \cdot \theta_0$). After that, a 2D island growth stage is expressed by the logistic term. In other words, the number of nucleus increases before the incubation time, whereas the size of nucleus increases after that [3,4]. We found that in our real-time photoemission measurements the Si oxidation states did not change before and after the incubation time. This fact reveals that the oxide nucleus has the same Si oxidation states with those of the 2D island. We concluded that the oxide nucleus consisted of not only Si^{1+} but also the higher oxidation states, such as Si^{4+}.

4. Summary

We have investigated the oxidation on Si(0 0 1) surface under 1000 K by real-time Si-2p photoemission measurements using high energy-resolution synchrotron radiation photoemission spectroscopy. We found that the Si^{2+} species was simultaneously observed with the Si^{1+} species in the early oxidation stage at 1000 K. Si oxidation states at which the backbonds are oxidized in addition to the bridge sites are formed at the first oxidation stage. The oxide nucleus is formed from the Si^{2+} state by further oxidation. The oxide nucleus has the same Si oxidation states with those of the 2D island because the Si oxidation states do not change before and after the incubation time. We concluded that the oxide nucleus consisted of not only Si^{1+} but also the higher oxidation states, such as Si^{4+}.

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References

[1] T. Engel, Surf. Sci. Rep. 18 (1993) 91.
[2] Y. Takakuwa, T. Yamaguchi, T. Hori, T. Horie, Y. Enta, H. Sakamoto, H. Kato, N. Miyamoato, J. Electron Spectrosc. Relat. Phenom. 88–91 (1998) 747.
[3] M. Suemitsu, Y. Enta, Y. Miyanishi, Phys. Rev. Lett. 82 (1999) 2334.
[4] M. Suemitsu, Y. Enta, Y. Takegawa, N. Miyamoto, Appl. Phys. Lett. 77 (2000) 3179.
[5] Y. Enta, Y. Takegawa, M. Suemitsu, N. Miyamoto, Appl. Surf. Sci. 100–101 (1996) 449.
[6] Y. Takakuwa, F. Ishida, J. Electron Spectrosc. Relat. Phenom. 114–116 (2001) 401.
[7] Y. Takakuwa, F. Ishida, T. Kawawa, Appl. Surf. Sci. 190 (2002) 20.
[8] J.V. Seiple, J.P. Pelz, J. Vac. Sci. Technol. A 13 (1995) 772.
[9] J.V. Seiple, C. Ebner, J.P. Pelz, Phys. Rev. B 53 (1996) 15432.
[10] A. Yoshigoe, K. Moritani, Y. Teraoka, Jpn. J. Appl. Phys. 42 (2002) 3976.
[11] Y. Teraoka, A. Yoshigoe, Jpn. J. Appl. Phys. 38 (1) (1999) 642.
[12] Y. Teraoka, A. Yoshigoe, Appl. Surf. Sci. 169–170 (2001) 738.
[13] A. Yokoya et al., J. Synchrotron Radiat. 5 (1998) 10.
[14] T. Nakatani, Y. Saitoh, Y. Teraoka, T. Okane, A. Yokoya, J. Synchrotron Radiat. 5 (1998) 536.
[15] Y. Saitoh, T. Nakatani, T. Matsushita, A. Agui, A. Yoshigoe, Y. Teraoka, A. Yokoya, Nucl. Instrum. Meth. Phys. Res. A 474 (2001) 253.
[16] A. Ishizaka, Y. Shiraki, J. Electrochem. Soc. 133 (1986) 666.
[17] U. Memmert, M.L. Yu, Surf. Sci. Lett. 245 (1991) L185.
[18] T.-W. Pi, C.-P. Cheng, I.-H. Hong, Surf. Sci. 418 (1998) 113.
[19] T.-W. Pi, I.-H. Hong, C.-P. Cheng, G.K. Wertheim, J. Electron Spectrosc. Relat. Phenom. 107 (2000) 163.
[20] Y. Teraoka, A. Yoshigoe, Surf. Sci. 507–510 (2002) 797.
[21] H.W. Yeom, R. Uhrberg, Jpn. J. Appl. Phys. 39 (2000) 4460.
[22] F.J. Himpsel, F.R. McFeely, A. Taleb-Ibrahimi, J.A. Yarmoff, G. Hollinger, Phys. Rev. B 38 (1988) 6084.
[23] K. Kato, T. Uda, K. Terakura, Phys. Rev. Lett. 80 (1998) 2000;
K. Kato, T. Uda, K. Terakura, Phys. Rev. B 62 (2000) 15978.
[24] Y. Teraoka, K. Moritani, A. Yoshigoe, Appl. Surf. Sci. 216 (2003) 8.
[25] H.W. Yeom, H. Hamamatsu, T. Ohta, R.I.G. Uhrberg, Phys. Rev. B 59 (1998) 413.
[26] J.H. Oh, K. Nakamura, K. Ono, M. Oshima, N. Hirashita, M. Niwa, A. Toriumi, A. Kakizaki, J. Electron Spectrosc. Relat. Phenom. 114–116 (2001) 395.
[27] J.R. Engstrom, D.J. Bonser, M.M. Nelson, T. Engel, Surf. Sci. 256 (1991) 317;
J.R. Engstrom, D.J. Bonser, M.M. Nelson, T. Engel, Surf. Sci. 268 (1992) 238.