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The temperature dependence of monolayer oxidation on Si(001)-(2 × 1) studied with surface differential reflectance spectroscopy

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Abstract
The initial process of dry oxidation on a Si(001)-(2 × 1) surface was investigated using surface differential reflectance (SDR) spectroscopy. The photon energy dependence of the difference spectra and their time courses during oxidation were analysed. It is suggested that oxidation processes at different adsorption sites can be identified from the SDR spectra. The temperature dependence of the time courses was investigated in order to obtain the activation energies. Finite activation energies for monolayer oxidation were found in the temperature range of 623–823 K, corresponding to Langmuir-type adsorption. The photon energy dependence of the activation energies could reflect the involvement of different reaction processes. Chemical reaction processes of both oxygen and silicon during oxidation in a monolayer regime are discussed.

1. Introduction

Research on ultrathin oxide films has drawn particular interest because of its growing importance in semiconductor device fabrication. A practical thickness of SiO_2 as the gate oxide is considered to be about 0.7–1.2 nm (four to five atoms across the film), which would permit leakage current through direct tunnelling [1]. In this thickness range, fabrication of future silicon-based electronic devices would meet various obstacles that would need to be overcome to improve device performance [2]. An understanding of the formation mechanism of SiO_2 films with a thickness below 2 nm will remain important, because such films can be utilized as a buffer layer for the growth of highly dielectric materials, including ZrO_2 and HfO_2 [3].

The initial oxidation process of Si(001) is one of the most intensively studied topics in surface science, yet remains controversial. A rate equation for the growth of SiO_2 layers over a

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wide range of oxidation conditions was proposed by Deal and Grove [4], but the thickness regime close to 1 nm still presents difficulty [5]. It has been pointed out that the growth process of monolayer oxide substantially affects the progress of further oxidation [6]. Thus, a detailed understanding of the monolayer oxidation mechanism is indispensable for control of the compositional homogeneity and flatness of ∼1 nm oxide layers on Si(001).

Real-time observation is increasingly recognized as a powerful means for clarifying oxidation kinetics. Different growth modes of monolayer oxide film, namely, Langmuir-type adsorption and two-dimensional island growth, were distinguished by means of ultraviolet photoemission spectroscopy (UPS) [7] and a combination of reflection high energy electron diffraction (RHEED) and Auger electron spectroscopy (AES) [8]. However, the probe beams might have significant effects on surface reactions. In the case of oxidation on silicon surfaces, even a low energy electron beam below 100 eV can enhance the oxidation rate [9] and change the chemical composition [10]. Optical spectroscopy is generally a useful means for non-destructive measurement of surface phenomena.

In the present study, surface differential reflectance (SDR) spectroscopy is employed to investigate various surface reactions in real time. This method has a wide range of applicability to both semiconductor and metal surfaces, and can be used equally in an atmosphere and under ultrahigh vacuum [11]. In the same context, reflectance difference spectroscopy (RDS) is also considered to be a powerful tool for investigating surface anisotropy. SDR and RDS are both linear optical techniques, like spectroscopic ellipsometry (SE) [12]. All of these methods are closely related to the conventional modulation spectroscopies, such as differential reflectance spectroscopy (DRS; also known as differential reflectometry, DR) [13]. SE measures the ratio of reflection coefficients for different polarizations, while the SDR signal is obtained from the relative difference in reflectance of the clean and adsorbate-covered surface, and RDS probes the difference between the reflection coefficients for two mutually perpendicular polarizations. A common theoretical framework for SDR, RDS and SE has been developed [14]. Compared with SE, both SDR and RDS are more sensitive as precise probes of real-time coverage of adsorbate in the submonolayer regime during adsorption processes. The SDR and RDS spectral features of an oxidized Si(001) surface at room temperature (RT) have been reported [15, 16].

In the early study, the time courses of SDR spectra were investigated during oxidation of Si(001) at below RT [17]. Recent theoretical investigation enables us to analyse site-dependent coverage of adsorbates as demonstrated in the case of hydrogen adsorption on Si(001) [18] or halogen adsorption/etching processes on Si(111) [19]. On the other hand, RDS is more sensitive to change of surface anisotropy. An examination of layer-by-layer oxidation on Si(001) by Yasuda *et al* demonstrated that activation energies could be estimated for the growth of two or more oxide layers [6]. Theoretical considerations led to the proposal of barrierless dissociation of oxygen molecules on the Si(001) surface at low coverage [20]. Scanning reflection electron microscopy (SREM) study combined with AES supported this picture at temperatures below 473 K for monolayer oxidation [21]. However, the process is not necessarily barrierless, especially at high temperatures above 473 K.

To clarify this issue, we should consider several points. Firstly, does the absence of activation energy persist throughout the growth of the monolayer oxide? Secondly, if finite activation energies exist, how different are the energies for oxidation at different adsorption sites? What is the cause of these activation energies, accumulated stress or kinetic effects? Thirdly, is there any essential difference in activation energies at different temperatures? Here, we show that SDR can be used to access the reaction rates at different adsorption sites, and we describe its possible application for evaluating activation energies in a monolayer regime.

2. Experimental details

Experiments were performed in an ultrahigh vacuum chamber, whose base pressure was under 2.0×10^{-8} Pa. The samples used were p-type Si(001) single crystals with resistivities of 12.0–14.0 Ω cm and 0.02 Ω cm, cut to the size of $3 \times 20 \times 0.63$ mm^3. We observed no effect of the doping concentration on the SDR spectra, and we present here the data for the 12.0–14.0 Ω cm crystal. Heating was performed by applying direct current to the sample. The sample was well degassed for over 12 h at 873 K and cleaned by flashing at 1470 K. Formation of Si(001)-(2 × 1) structure was confirmed by means of low energy electron diffraction (LEED). A 4° miscut sample was prepared to obtain single-domain Si(001)-(2 × 1) structure. In the present study, we did not observe any significant difference between double-domain and single-domain surfaces. Here, we present data for the single-domain Si(001)-(2 × 1) surface. The sample was subjected to oxidation with molecular O_2 at room temperature and at 623–923 K. The substrate temperature was calibrated using the same heating set-up with a K-type (alumel–chromel) thermocouple attached directly to the sample. An infrared pyrometer was also used to measure sample temperatures above 823 K for temperature calibration. The relation between the temperature, T, observed with a thermocouple and the direct heating current, I, approximately obeys the equation $I = A(T - T_{\mathrm{RT}})^B$ over the temperature range of 623–823 K. The parameters A and B are pre-determined. In the experimental set-up, we did not attach a thermocouple to the sample, to avoid Ni contamination. The oxygen exposure was performed at a constant pressure of 1.0×10^{-5} Pa.

The optical set-up has been described elsewhere [22]. A halogen lamp was used as the light source around the visible region. The p-polarized light was applied to the surface with an incident angle close to the Brewster angle, at which reflectance from the substrate is considered to be minimized, and the SDR intensity mainly reflects the changes of the electronic states compared with the clean surface [23]. The light reflected from the sample was passed to a photodiode array through a monochromator. Fluctuation of the intensity of a halogen lamp was cancelled out by using reference spectra obtained through a beam splitter. To eliminate second-order light, the light reflected through a grating in the monochromator was filtered above 2.6 eV.

3. Results

Figure 1 shows the time courses of the SDR intensity observed for oxidation at 823 and 923 K at the fixed oxygen pressure of 1.0×10^{-5} Pa. The intensity of the difference spectra ($\Delta R/R$) is defined as

$$\frac{\Delta R}{R} = \frac{R_{\mathrm{a}} - R_{\mathrm{c}}}{R_{\mathrm{c}}}, \tag{1}$$

where R_{c} and R_{a} represent the reflectance of the clean surface and that of the oxygen-adsorbed surface, respectively. We chose two representative photon energies, 1.4 and 2.5 eV, which were interpreted as representing adsorption at different bond types in our previous work [24]. This assignment for the adsorption sites will be re-examined in this paper. The SDR intensities are normalized as denoted by $(\Delta R/R)_N$ so that the saturation value is equal to one. These curves can be well fitted with the known functions that describe the time evolution of total oxygen coverage at high temperatures [7, 8]. The results show that the SDR intensity is almost proportional to the total coverage of oxygen above 823 K. In figure 1, the exponential curve at 823 K represents Langmuir-type adsorption, while the sigmoid curve at 923 K corresponds to two-dimensional island growth [7]. The normalized time courses show no photon energy dependence within the range of 1.3–2.6 eV at these temperatures.

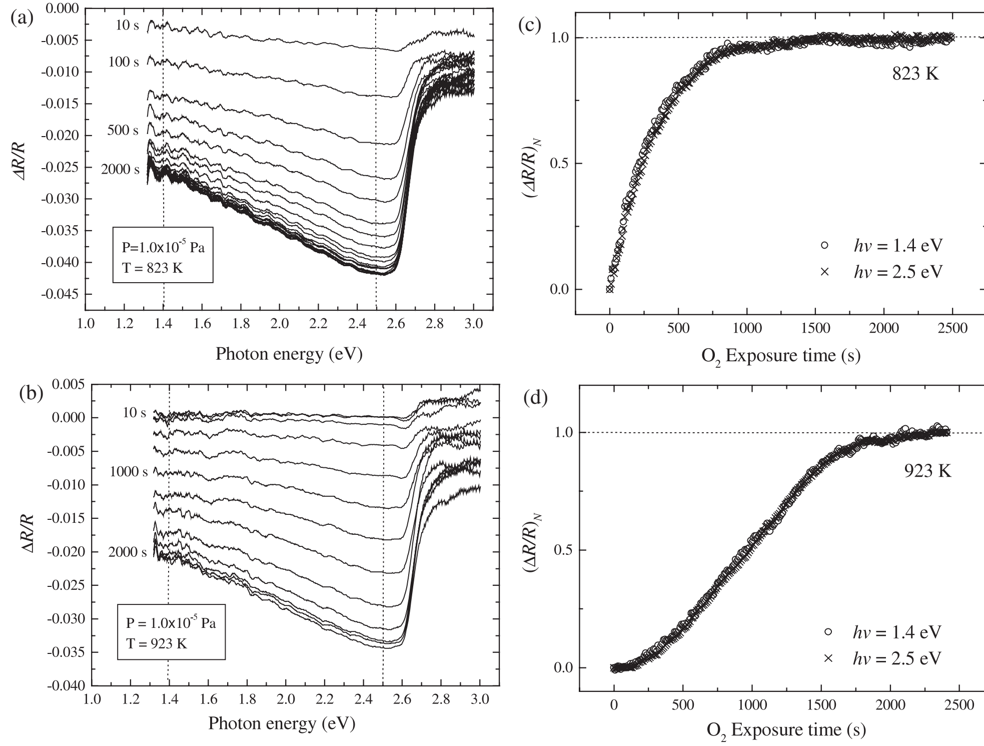

Figure 1. SDR spectra during oxidation at a pressure of 1.0×10^{-5} Pa at the temperature of (a) 823 K and (b) 923 K. The signal above 2.6 eV is filtered out to eliminate the effects of second-order light. Time courses of SDR intensity obtained at (c) 823 K and (d) 923 K. These curves are normalized so that the intensity converges to unity. There appears to be no significant photon energy dependence between 1.4 and 2.5 eV.

On the other hand, slight photon energy dependence was discernible at temperatures below 823 K, as shown in figures 2 and 3. The difference between the time courses at 1.4 and 2.5 eV appears to increase with decreasing temperature. All the normalized curves could be well fitted with a single-exponential function:

$$\theta = 1 - \exp(-\kappa_1 t), \tag{2}$$

where κ_1 represent the reaction rate during monolayer oxidation on Si(001)-(2 × 1). To obtain an activation barrier, we may postulate that

$$\kappa_1 = D_1 \exp\left(-\frac{\epsilon_1}{k_B T}\right). \tag{3}$$

The analysis using these relations is straightforward when θ represents the total oxygen coverage and is applied to the growth of two or more oxide layers on Si(001) [6]. Extended use of this relation to describe the partial coverages at different adsorption sites might be rather difficult, because partial oxygen coverages at saturation appear to be not well determined. However, it is reported that the time courses of O(2p) intensity of XPS remain almost constant at around 623–823 K [25]. Thus, we assumed that partial oxygen coverages at saturation do not show strong temperature dependence in this range. Therefore, we concluded that the photon energy dependence of the estimated activation energies is significantly associated with the reaction rates towards different adsorption sites.

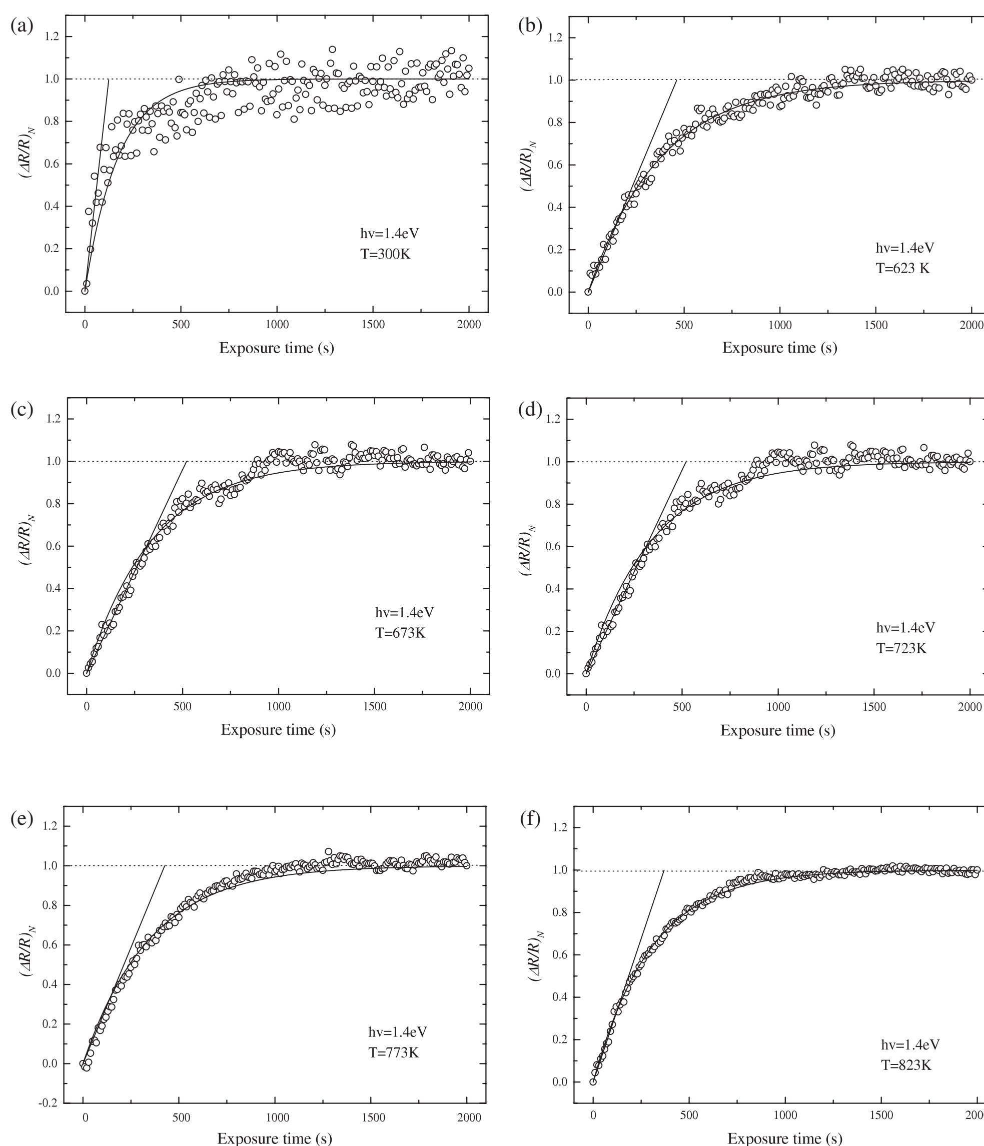

Figure 2. A series of time courses obtained at temperatures between 300 and 823 K at the photon energies of 1.4 eV. The uptake curves are normalized so that the intensities at the beginning and the end point are zero and one, respectively. Exponential curves represent the fitting for all the data points, while lines represent the fitting of the data satisfying $(\Delta R/R)_N \leqslant 0.3$.

Activation energies for monolayer oxidation (ϵ_1) at different photon energies were estimated from Arrhenius plots of the reaction rate, κ_1, in figure 2 for 1.4 and figure 3 for 2.5 eV. To investigate the coverage dependence of the activation energy, we also analysed the initial part of the time courses of SDR intensity. Arrhenius plots using the data plots satisfying $(\Delta R/R)_N \leqslant 0.3$ are shown in figure 4(b). The gradients obtained by the linear fitting represent the initial value of κ_1. The data plots at RT were apparently not located along the line obtained by the fitting of the high temperature data, and were excluded from the Arrhenius plots. Error

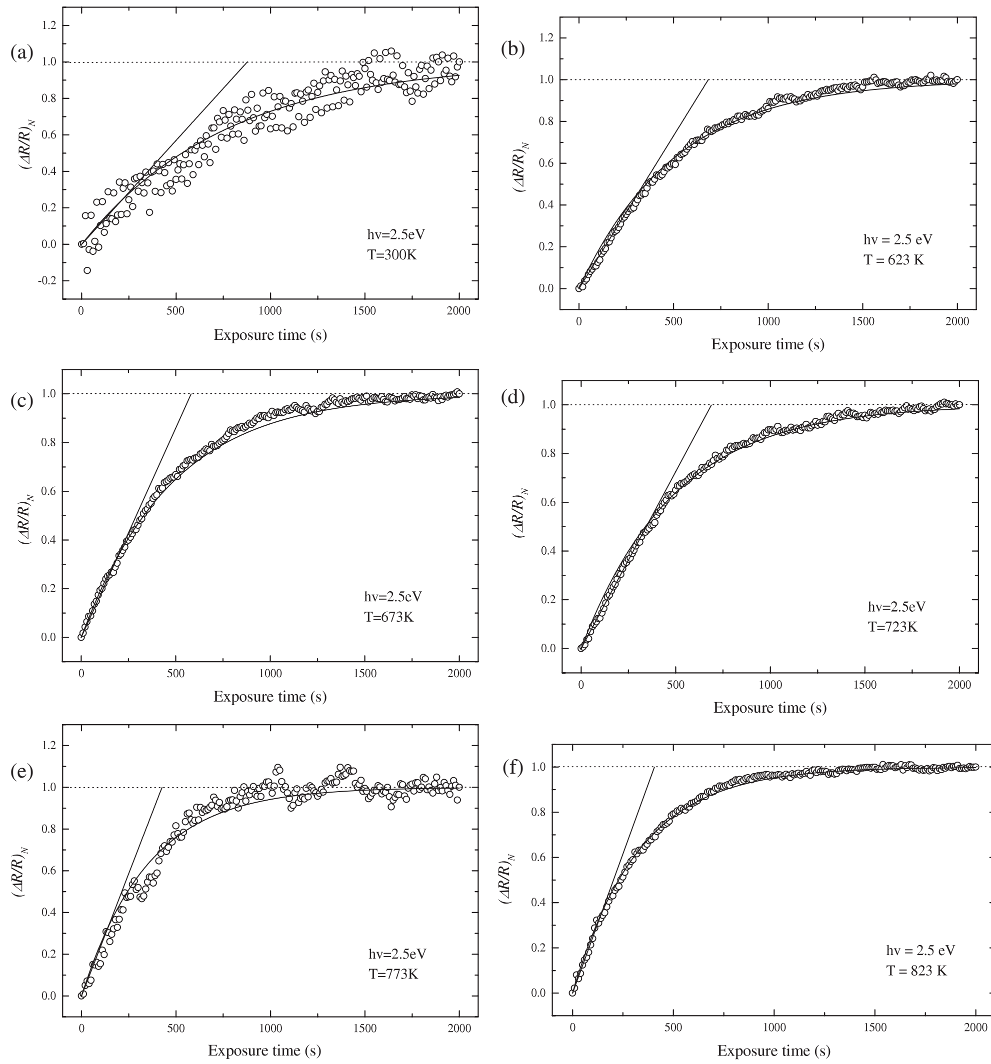

Figure 3. A series of time courses obtained at temperatures between 300 and 823 K at the photon energy of 2.5 eV. The uptake curves are normalized so that the intensities at the beginning and the end point are zero and one, respectively. Exponential curves represent the fitting for all the data points, while lines represent the fitting of the data satisfying $(\Delta R/R)_N \leqslant 0.3$.

bars in the plots in figure 4 were estimated considering statistical error in $\Delta R/R$ due to the optical set-up and the uncertainty in the sample temperatures. The estimated activation energies are summarized in table 1 for comparison with those obtained for thicker layers, as reported in the literature.

4. Discussion

The activation energies obtained over the temperature range of 623–823 K are estimated to be $\epsilon_\alpha = 0.04 \pm 0.02$ eV for 1.4 eV and $\epsilon_\beta = 0.11 \pm 0.02$ eV for 2.5 eV. A tentative notation is α-

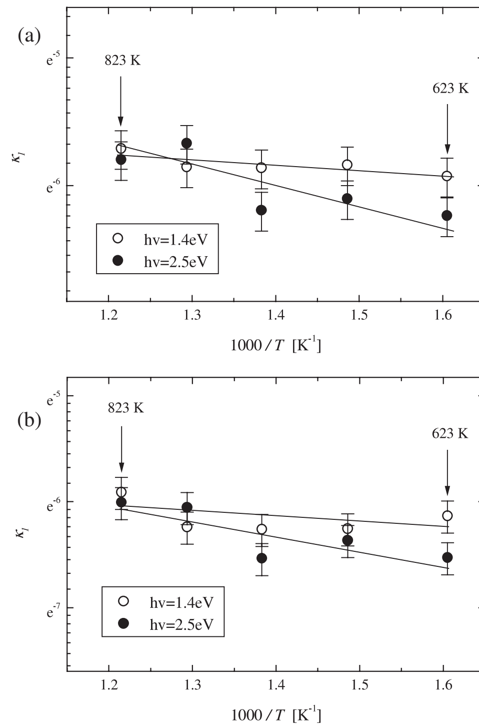

Figure 4. Arrhenius plots for the reaction rate κ_1 in monolayer oxidation; (a) obtained from the exponential fitting of all the data in figures 2 and 3, (b) obtained from the linear fitting of the initial slope that satisfies $(\Delta R/R)_N \leqslant 0.3$.

Table 1. Activation energies obtained in the present work for monolayer oxidation and those reported for layer-by-layer oxidation in the literature. (Note: the asterisk (*) indicates the activation energy at the early stage.)

Oxide layer i	Activation energy ϵ_i (eV)	Method
1st	$\epsilon_\alpha = 0.04 \pm 0.02$	SDR (This work)
1st	$\epsilon_\alpha^* = 0.04 \pm 0.02$	SDR (This work)
1st	$\epsilon_\beta = 0.11 \pm 0.02$	SDR (This work)
1st	$\epsilon_\beta^* = 0.12 \pm 0.02$	SDR (This work)
1st	$\epsilon_1^* = 0.0$	Calc. [20]
2nd	$\epsilon_2 = 1.2 \pm 0.3$	RDS [6]
2nd	$\epsilon_2^* = 0.3$	AES/SREM [21]
3rd	$\epsilon_3 = 2.0 \pm 0.2$	RDS [6]
4th	$\epsilon_4 = 2.2 \pm 0.2$	RDS [6]

state for $h\nu = 1.4$ eV and β-state for $h\nu = 2.5$ eV, and possible assignments will be presented later. The present results indicate that finite activation energies exist at high temperatures. A recent low temperature STM study on a stepped Si(001)-c(4 × 2) surface at 80 K suggested that mobile oxygen species with a long lifetime should exist on the terrace and migrate until they are adsorbed near the step edges [26]. This seems consistent with a finite activation energy for oxidation to occur at low temperatures. A recent theoretical study suggested that a rigorous

treatment of the role of triplet oxygen in the dissociation process may not be compatible with barrierless dissociation [27]. These studies also suggest that the simple barrierless dissociation model may be not adequate to explain the initial oxidation process on the same surface.

The obtained activation energies for monolayer oxidation, $\epsilon_{\alpha(\beta)}$ and $\epsilon^*_{\alpha(\beta)}$, are much smaller than the values reported for the growth of two or more oxide layers. This is reasonable, because the surface should be quite reactive when unsaturated dimers on Si(001)-(2 × 1) still remain in monolayer oxidation. The value for the growth of the second layer estimated by means of RDS was considered to be the average value, ϵ_2 [6]. The initial value ϵ^*_2 obtained with AES is much smaller [21]. The activation energy appears to increase markedly with increasing the oxygen coverage during the second-layer oxidation, and the values increase slightly more for the growth of the third and fourth layers. The initial value of the $\alpha(\beta)$-state, $\epsilon^*_{\alpha(\beta)}$, is almost the same as the averaged value of $\epsilon_{\alpha(\beta)}$. This coincidence suggests that the activation energy does not change with the oxygen coverage in terms of these states.

Finally, we should comment on the possible assignments for the α- and β-states. The time courses obtained above 823 K in figure 1 are in good agreement with the results obtained by real-time AES [8]. Thus, the SDR intensity is apparently proportional to the total oxygen coverage in both cases. On the other hand, there appears to be a significant difference in energy dependence in the time courses at 623–823 K, between the α-state and β-state. The difference is even larger at 300 K. This may suggest that partial coverage of the α-state is proportional to that of the β-state above 823 K, but not at lower temperatures. Our tentative assignment is that the α-state exclusively represents the backbond site and the β-state represents a mixture of the other possible adsorption sites, such as dimer interstitial sites, on-dimer sites, or bridge sites between neighbouring dimers [28, 29]. Our results indicate that the activation energy of the α-state is less than half of that of the β-state. This trend coincides well with a preferential adsorption of oxygen at backbond sites, as suggested by core level photoemission studies [30, 31]. The initial slope is distinctively steep for the α-state at 300 K. This means that preferential adsorption of oxygen at backbond sites is much more pronounced at room temperature than at high temperatures. A recent first-principles study showed that the oxygen-adsorbed structure with one missing Si dimer can be energetically the most stable at low coverage [32]. When Si dimer ejection occurs frequently, the position of oxygen on average should be closer to the surface. This picture is consistent with the slight increase of the work function originating from the surface dipole layer in the Langmuir-type adsorption regime [25]. In other words, oxygen atoms tend not to be adsorbed on the backbond sites underneath the Si dimers at high temperatures because of the enhanced mobility of Si. Such a kinetic feature at high temperatures could account for the significant photon energy dependence of the SDR time courses, and may explain the existence of finite activation energies towards various adsorption sites at high temperatures.

5. Summary

We have shown that SDR spectroscopy is able to resolve concomitant oxidation processes towards different adsorption sites. In the temperature range of Langmuir-type adsorption, we examined the activation energies of monolayer oxidation on Si(001)-(2 × 1) over the temperature of 623–823 K. Analysis of the initial part of the uptake curves indicated that finite activation energies exist even at low coverage. Our tentative assignment of the photon energy dependence of SDR spectra to different states is qualitatively consistent with previous reports of preferential adsorption of oxygen at backbond sites. Our results provide strong evidence that SDR is able to resolve site-specific reaction rates in the oxidation of Si(001)-(2 × 1).

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