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LETTER TO THE EDITOR

Real-time coverage monitoring of initial oxidation processes on Si(001) by means of surface differential reflectance

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Abstract
Initial oxidation processes on Si(001) have been studied by means of surface differential reflectance (SDR). The time courses of the SDR spectra measured during thermal oxidation at 820 and 920 K allowed two different growth modes, Langmuir-type adsorption and two-dimensional island growth, to be distinguished. No photon energy dependence was observed in the time course of the SDR intensity at either temperature. On the other hand, different uptake curves were observed at different photon energies for oxidation at 300 K. The difference between the oxidation mechanisms at 300 K and at high temperatures was qualitatively apparent from SDR results, because significant photon energy dependence was observed only at 300 K. Possible assignments of the spectral components in the SDR spectra are discussed.

1. Introduction

Ultrathin oxide film has been widely used as the gate dielectric layer in metal–oxide–semiconductor field effect transistors (MOS-FETs) [1, 2]. Silicon dioxide (SiO_2) film of a few nanometres works as a buffer layer to reduce the interface state density, when high k materials such as ZrO_2, HfO_2 are grown on a silicon surface [3]. Rigorous control of compositional homogeneity and the flatness of SiO_2 films is important in order to improve the switching rate and to reduce the critical leakage current.

Oxidation processes on Si(001) have been intensively studied using a variety of surface science techniques [4]. However, it is only recently that the initial growth modes have been identified on the basis of the rate of increase of oxide thickness in real time using Auger electron spectroscopy (AES) [5], ultraviolet photoemission spectroscopy (UPS) [6] and x-ray photoemission spectroscopy (XPS) [7]. There remains an issue associated with the probe beam effect on the oxidation. It is known that high energy electrons produced by an Auger electron gun promote enhanced oxidation on both Si(111) [8] and Si(001) [9]. Recently, the electronic

states of an oxide film were found to be greatly affected by low energy electron bombardment at 100 eV [8]. To reduce the effects of probe beams, it is desirable to employ low energy photons in the visible to near-ultraviolet range.

In the present letter, we report that different growth modes can be detected by means of surface differential reflectance (SDR) spectroscopy, which is a surface-sensitive optical tool designed to measure surface chemical processes in real time. Among the advantages of SDR are the capability to make measurements even during high pressure gas exposure and a rapid response time of the order of a few milliseconds. Of the available optical methods using low energy photons, SDR allows the measurement of different chemical reactions at various adsorption sites, separately and simultaneously, while reflectance difference spectroscopy (RDS) is more sensitive to the change of surface anisotropy. Both techniques are well recognized as powerful additions to conventional surface science techniques from many studies of semiconductor surfaces and metal surfaces [10]. Recent RDS studies of the initial oxidation processes on silicon surfaces showed a good agreement with theoretical calculations in terms of the processes of growth of two or more oxide layers [11]. Moreover, by combining RDS with imaging techniques, site-dependent chemical reactions and growth processes were examined at the resolution of 1–10 μm, providing insight into the evolution of the surface morphology during high pressure gas exposure [12].

In usual RDS measurements, an uptake curve is often measured at a fixed photon energy, namely, with monochromatic light. This can be disadvantageous unless the incident photon energy is known to be relevant to the specific bond type. On the other hand, the present SDR set-up [13], with a spectrometer in front of the detector, enables us to observe the whole spectrum. We and others have used SDR to examine the time course of partial coverage of hydrogen and halogens at different sites on Si(111)-7 $\times$ 7 at various temperatures [13, 14].

In SDR analysis, estimation of the partial coverages is possible when fitting coefficients can be obtained from the calculated spectral functions corresponding to the site-dependent adsorption. However, it is not always straightforward to discriminate between spectral components associated with the different adsorption sites, because each component may consist of several peaks. Moreover, each component in the optical reflectance may not change linearly with partial coverage of the adsorbates over the whole energy range. In other words, the use of linear decomposition to analyse the SDR spectra may be questionable, for example, if accumulated stress effects are induced by concomitant adsorption at various adsorption sites. With the aid of theoretically calculated SDR spectra, it is possible, though difficult, to decompose the spectra and estimate the partial coverages [13, 14]. In the case of RDS, both the adsorption sites and the anisotropy of the domain structures affect the spectral features. In addition, a recent RDS study of oxidized Si(001) surfaces has clearly shown the difficulty of estimating the site-dependent coverage, because typical spectral features in RDS appear around E_1 and E_2 critical points, which are predominantly ascribed to local strain effects [15]. This work suggested that RDS spectra of oxidized Si(001) do not directly reflect the electronic states of oxygen, but rather the lattice strain of the silicon substrate induced around the oxygen adsorption sites.

Considering these problems, it is important to compare the uptake curves obtained from SDR with those obtained by using well-established experimental methods. Correspondence between them may establish the reliability of SDR as a method of monitoring partial coverages at various adsorption sites. In the case of oxidation on Si(001), there are many possible adsorption configurations, which would make the SDR analysis rather complex. However, our present results show that uptake curves measured using SDR have the same precision as AES [5] for evaluation of thermal oxidation on Si(001), supporting the suitability of SDR for coverage measurements at the atomic level.

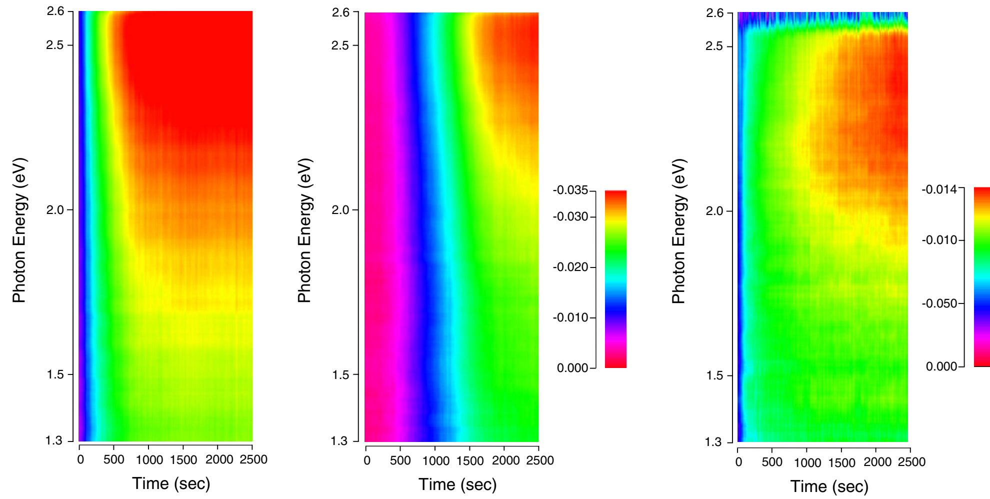

Figure 1. Time courses of the SDR spectra measured during oxidation at a fixed O_2 pressure of 1.0×10^{-5} Pa. The sample temperatures were (a) 820 K, (b) 920 K and (c) 300 K. The scale of the gradation is common to (a) and (b).

(This figure is in colour only in the electronic version)

2. Experimental details

Experiments were performed with an ultrahigh vacuum chamber, whose base pressure was under 2×10^{-8} Pa. The sample used was a p-type Si(001) single crystal with resistivity of 12.0–14.0 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. The sample was degassed for over 12 h at 870 K and cleaned by flashing at 1470 K. It was then subjected to oxidation with molecular O_2 at the temperature of 300, 820 or 920 K. An infrared pyrometer was used to measure the sample temperature above 820 K. The oxygen pressure was kept constant at 1.0×10^{-5} Pa.

The optical set-up has been described elsewhere [13]. A halogen lamp was used as the light source from the visible to near-ultraviolet region. The p-polarized light was applied to the surface with an incident angle of about 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 [16]. The reflected light from the sample was passed to a photodiode array through a monochromator. Intensity fluctuation of the halogen lamp was cancelled out by the use of the reference spectra taken through a beam splitter. As a grating was used in the monochromator, the reflected light had to be filtered to cut off the components above 2.6 eV in order to eliminate the second-order light.

3. Results

Figure 1 shows the two-dimensional plot of SDR spectra measured during oxidation at a fixed oxygen pressure of 1.0×10^{-5} Pa at (a) 820 K, (b) 920 K and (c) 300 K. The horizontal axis represents the time of oxygen exposure and the vertical axis represents the photon energy. The intensity of the difference spectra ($\Delta R/R$) is defined as

$$\frac{\Delta R}{R} = \frac{R_a - R_c}{R_c} \tag{1}$$

where R_c and R_a represent the reflectance of the clean surface and that of the oxygen adsorbed surface, respectively.

For the thermal oxidation at 820 K, as shown in figure 1(a), the SDR intensity decreases monotonically during oxygen exposure. The intensity decreases markedly at the beginning, and almost saturates at 1640 s. The uptake curve at each photon energy can be fitted with a single exponential function. As shown in figure 1(b), the intensity at 920 K initially decreases slowly, then decreases rapidly towards the end and is saturated at 2370 s. At a fixed photon energy, each uptake curve shows a sigmoid line shape. For oxidation at 300 K (figure 1(c)), the intensity curves are energy dependent and decrease rather gradually. The signal at the high energy side decreases very slowly and is not saturated even at 2500 s, while that on the low energy side changes rapidly, reaching saturation within 750 s.

4. Discussion

4.1. Oxide growth at high temperatures

We first demonstrate here the ability of SDR to discriminate between the two growth modes of Langmuir-type adsorption and two-dimensional island growth during thermal oxidation. To analyse the time course of the SDR intensity, values of $\Delta R/R$ at 1.4 and 2.5 eV were plotted as a function of O_2 exposure time, t (figure 2). These photon energies were chosen to allow comparison with the results at 300 K. In this figure, each spectrum was normalized so that $\Delta R/R$ takes the value zero at the initial point and the value one at the end point. No photon energy dependence was seen at 820 and 920 K.

The initial oxidation on Si(001) involves different types of growth mode, depending on the sample temperature and the O_2 pressure. Over the same pressure range as in figure 2, it has been shown by Takakuwa *et al* [5] that Langmuir-type adsorption takes place at 820 K, while two-dimensional island growth takes place at 920 K at similar oxygen pressures.

In Langmuir-type adsorption, dissociated oxygen atoms are considered to be adsorbed immediately on the surface without migration. The uptake curves in figure 2(a) can be fitted with

$$\theta_{\mathrm{oxide}} = 1 - \exp(-kt) \tag{2}$$

where θ_{oxide} represents the total O_2 coverage and k (s^{-1}) is the reaction coefficient. The fitted curve is shown as the solid line in figure 2(a). The fitted parameters were close to those obtained by AES [5]. This means that the change of $\Delta R/R$ both at 1.4 and 2.5 eV is proportional to the total oxygen coverage.

As for the two-dimensional island growth at 920 K, it was proposed [6] that the total oxygen coverage can be described as

$$\theta_{\mathrm{oxide}} = \theta_0 \frac{1 - \exp(-\kappa t/\tau_0)}{\theta_0 + \exp(-\kappa t/\tau_0)} \tag{3}$$

where θ_0 is the critical coverage at which the θ_{oxide} starts to show a rapid increase, τ_0 (s) is the inverse of the initial growth rate, and $\kappa = (\theta_0 + 1)/\theta_0$. The line shape is sigmoid, as shown in figure 2(b). The values of the fitted parameters are also consistent with the previous AES data [5]. The above function was derived from the autocatalytic model, in which both the dissociative adsorption of O_2 and the desorption of SiO species determine the oxidation kinetics. It has been confirmed that the time course of $\Delta R/R$ represents the total oxygen coverage during thermal oxidation, regardless of the growth mode. In the case of thermal oxidation on Si(001), spectroscopic analysis was not possible because of the lack of photon energy dependence after the normalization procedure within the range of 1.3–2.6 eV.

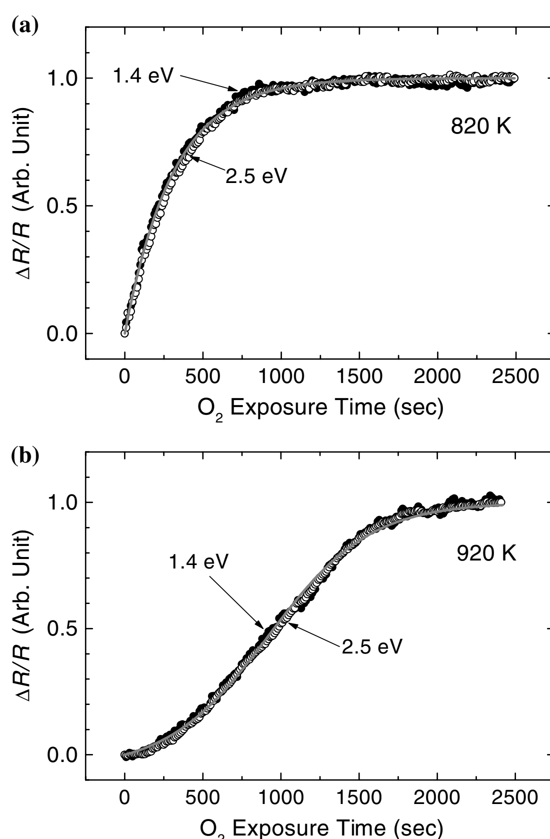

Figure 2. Time courses of the SDR intensity at the photon energies of 1.4 and 2.5 eV. The uptake curves are normalized so that the intensity converges to unity. (a) The sample temperature was 820 K and the fitting parameters were $k = 0.0032$ at 1.4 eV and $k = 0.0030$ at 2.5 eV. (b) The sample temperature was 920 K and the fitting parameters were $\tau_0 = 5806\ s^{-1}$, $\theta_0 = 0.0593$ at 1.4 eV and $\tau_0 = 6430\ s^{-1}$, $\theta_0 = 0.0516$ at 2.5 eV.

The good accordance in the uptake curves with AES implies that the extent of change of $\Delta R/R$ upon oxidation is not sensitive to the adsorption sites at high temperature in this energy range. The saturation of $\Delta R/R$ may correspond to complete coverage of the surface with an oxide monolayer, as indicated by AES [5]. The results indicate that SDR can be used to measure the oxygen coverage with the same precision as AES. However, the structureless features in the SDR spectra can not be simply explained by theoretical calculations, which would associate the spectral features with certain bonding states at the surface. Thus, thermal broadening or some kinetic effects at high temperature may influence SDR spectra.

4.2. Oxide growth at 300 K

In figure 3, the uptake curves for oxidation at 300 K are plotted for the incident energies of 1.4 and 2.5 eV. It is apparent that the line shapes are different, in contrast to the case at high temperatures. For hydrogen adsorption processes on Si(001) measured with SDR using s-polarized light, integrated SDR intensity was considered to represent the coverage of adsorbates [17]. Similarly, at high temperatures, it has been shown here that the integrated

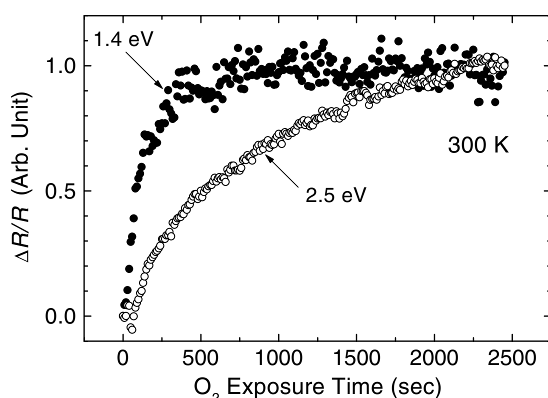

Figure 3. Time courses of the SDR intensity at the photon energies of 1.4 and 2.5 eV. The uptake curves are normalized so that the intensity at the beginning and the end point are zero and one, respectively. The sample temperature was 300 K and the fitting parameters were $k = 0.0064\ \mathrm{s}^{-1}$ at 1.4 eV and $k = 0.0013\ \mathrm{s}^{-1}$ at 2.5 eV.

SDR intensity in the visible to near-ultraviolet range represents the total coverage of oxygen, although no photon energy dependence was observed. On Si(111)-7 × 7, partial coverages of halogens were estimated from SDR with the aid of TDS [18] and STM [19]. The present results demonstrate the feasibility of site-dependent analysis in the case of Si(001), since the time courses at 300 K showed significant photon energy dependence.

According to first-principles calculations, dissociated oxygen tends to be adsorbed on the back-bond sites through barrierless processes [20]. Ultraviolet photoemission spectroscopy (UPS) measurements of the work function during oxidation indicate that oxygen tends to be adsorbed closer to the surface as the oxidation temperature increases [21]. A possible assignment consistent with these reports is that the features at 1.4 and 2.5 eV correspond to the back-bond site and dangling bond site of the silicon dimer, respectively. The rapid increase of $\Delta R/R$ intensity at 1.4 eV means that the oxidation occurs much faster at the back-bond sites than at the dangling bond sites at 300 K as suggested by the calculations. A comparison of Langmuir-type adsorptions at 300 and 820 K indicates that the reaction coefficient k decreases with temperature at 1.4 eV, while it increases with temperature at 2.5 eV. This is consistent with an increase of the work function due to the surface dipole layer at high temperatures.

The significant photon energy dependence recognized in the SDR spectra at 300 K indicates that the spectra could be decomposed into two or more components. This means that SDR may have the ability to discriminate between various surface bonding states simultaneously. Nevertheless, the correspondence may not be straightforward according to the early calculations for RDS spectra [22]. Recent RDS calculations based on the detailed band structure calculations showed that a dimer state related feature appears at 1.7 eV, while quenching of the RDS signal at 2.5 eV is due to the complete removal of surface states from the fundamental gap [23]. Thus, it is possible that the 2.5 eV uptake of SDR at 300 K may be related to the disappearance of the surface states. It should, however, be recognized that these calculations do not completely reproduce typical features observed in the previous RDS experiments, and it might be necessary to take disordered oxide structures into account to interpret the RDS spectra. Although a direct link between the SDR spectra and RDS spectra has been discussed [24], different assignments would be possible in the case of oxidation on Si(001), because of the many candidate adsorption sites. It was reported that

SDR measurements with s-polarized light can identify the breaking of the dimer bond [17]. Oxygen adsorption in the dimer interstitial site was also identified from the similarity of the spectrum to that of dihydride-covered Si(001). It is possible that s-polarized light is much more sensitive to the dimer bonds than to the dangling bonds and the back-bonds. If we fully utilize the polarization dependence and photon energy dependence of SDR, it should be possible to estimate the site-dependent coverages at different adsorption sites on Si(001) and other surfaces. To establish the SDR assignments, further experiments and theoretical calculations are needed, considering specifically the polarization dependence of the reflectance spectra.

5. Summary

We observed the initial oxidation process on a Si(001) surface by means of SDR. These real-time experiments were performed *in situ* at 300, 820 and 920 K. From the analysis of SDR results, two growth modes, i.e., the Langmuir-type adsorption and two-dimensional island growth, were distinguished in the same manner as in AES intensity analysis. Our results indicate that SDR is useful for real-time coverage measurements for the system in which there are various adsorption sites. Preliminary results at 300 K suggest the feasibility of site-dependent analysis of partial coverage during oxidation on Si(001).

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