Feature Article

Masao Horiba Award

Analysis of O$_2$, NO and CO Reaction Processes on Silicon Surfaces by Means of Surface Differential Reflectance Spectroscopy and Reflectance Difference Spectroscopy

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We developed a new apparatus by combining surface differential reflectance (SDR) spectroscopy and reflectance difference spectroscopy (RDS), which enables us to observe thickness at submonolayer regime and interface strain at the atomic level in nondestructive manner with high surface sensitivity. We applied this new technique to observe initial oxidation process on silicon surfaces in real-time, and could obtain novel information on the growth modes and activation energies. We further investigated ingredients of exhaust gas, such as carbon monoxide (CO) and nitric oxide (NO).

Introduction

Optical spectroscopic methods have great potential as a *in-situ* nondestructive probing method and are applicable for developing wide range of industrial applications such as device fabrication and catalytic materials. We newly developed combinative apparatus by utilizing two types of reflectance spectroscopy, namely, surface differential reflectance (SDR) spectroscopy and reflectance difference spectroscopy (RDS).

Reflectance spectrosocpy is classified as linear spectroscopy same as spectroscopic ellipsometry (SE). In the case of SE, all the reflected signals from the thickness regime comparable to the penetration depth of ligh (usually over 10 nm) are collected and analyzed. Hence, analysis of surface reactions at the atomic level is quite difficult although, precision of the thickness measuremet is high as much as 0.01 nm. To enhance surface sensitivity, reflectance spectroscopy was developed by some technical innovations to reduce signals from the bulk and to predominantly collect signals from the surface region. In 1980s, Aspnes *et al.* developed RDS technique, which was initially applied to investigate growth process of III-V semiconductors[1]. Kobayashi et al. developed SDR using p-polarized light at around 1990[2], which is also applied to Metal-organic chemical vapor deposition (MOCVD) process on compound semiconductors.

Intensive studies of silicon oxidation has been motivated by the theoretical work of Nakayama *et al.*, which predicted RD oscillations due to layer-by-layer growth[3]. This penomenon was experimentally confirmed by Yasuda et al.[4], andactivation energies for the oxide growth at two or more layers were estimated[5].
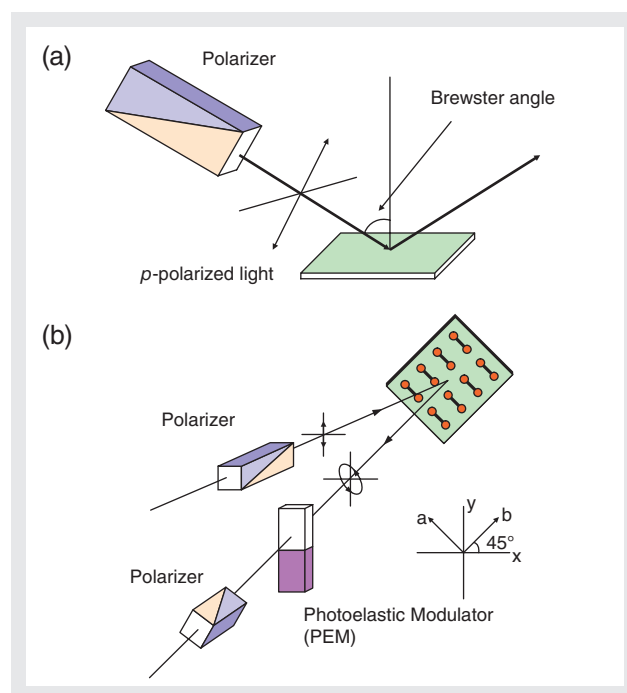

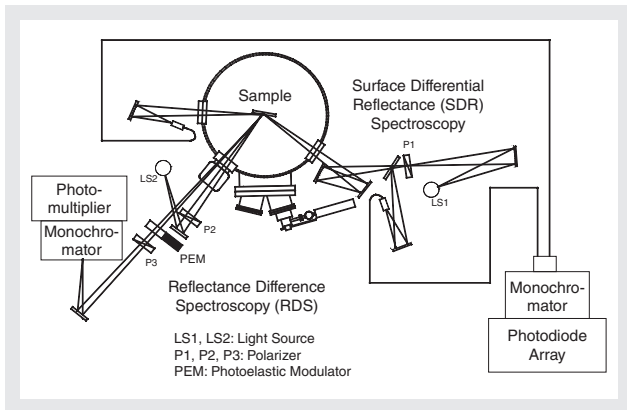Figure 1 (a) Schematic of SDR optics.
(b) Schematic of RDS optics.

Figure 2   Experimental setup for SDR and RDS.

Recently, high-k materials such as HfO_2 are dominantly used as the gate oxide but importance of SiO_2 ultrathin film is preserved due to its existence at the interface. We investigated initial oxidation process on silicon surface by combining SDR and RDS, especially in monolayer regime[6, 7, 8].

Surface Differential Reflectance (SDR) Spectroscopy and Reflectance Difference Spectroscopy (RDS)

Schemtatic of SDR optics is shown in Figure 1(a). Figure 2 depicts experimental setup for SDR and RDS newly developed by our group. In SDR measurements, photodiode array is used to observe each spectrum instantaneously and to detect changes of the reflectance signal at a high speed. Differential reflectance of SDR is defined as

$$\frac{\Delta R}{R} = \frac{Ra - Rc}{Rc}$$

where Ra and Rc are reflectances from adsorbed surface and clean surface. It was shown that reflectance signal from the bulk compared to that from the surface takes minimum at Brewster angle for p-polarized light[9]. Therefore, information on surface structures and surface states can be available by utilizing p-polarized light at Brewster angle.

Schematic of RDS optics is shown in Figure 1(b). Linearly polarized light is introduced almost normal to the surface. Elliptically polarized light is reflected from the surface due to anisotropy of the surface structure. The reflected light contains information on the difference of reflectances along mutually orthogonal a-axis and b-axis. We used a strain-free window to minimize optical anisotropy irrelevant to the surface structure.

The RD amplitude, $\Delta\tilde{r}/\tilde{r}$, is defined as

$$\frac{\Delta\tilde{r}}{\tilde{r}} = \frac{\tilde{r}_a - \tilde{r}_b}{(\tilde{r}_a - \tilde{r}_b)/2}$$

, which can be rewritten by anisotropy of the amplitude and phase Δr, $\Delta\theta$ as

$$\frac{\Delta\tilde{r}}{\tilde{r}} = \frac{\Delta r}{r} + i \cdot \Delta\theta$$

Real part $\Delta r/r$ or imaginary part $\Delta\theta$ can be measured by lock-in detection technique using photoelastic modulator (PEM). It is known that measurement accuracy is higher for the real part compared to imaginary part[1]. It is also noted that Kramers-Kronig relation holds between $\Delta r/r$ and $\Delta\theta$, which enables us to extract major information from analysis of the real part.

Real-Time Analysis of Initial Oxidation Process on Si (001)

Oxidation modes on Si (001) can be classified into two regimes: passive oxidation which promotes SiO_2 growth and active oxidation for which etching is the dominant process. Passive oxidation is further subdivided into Langmuir-type adsorption and two-dimensional island growth. In the former, dissociative adsorption of oxygen molecule occurs, while in the latter SiO desorption is also involved.

It was known that reflectance spectroscopy has enough surface sensitivity to detect adsorbates in submonolayer regime. However, it was not well recognized whether it is applicable to complicated reaction process involving both adsorption and desorption. Figure 3 shows normalized uptake curve of SDR intensity at 550 °C and 650 °C so that the initial point and the end point are zero and one, respectively. The results clearly represent that the line shape of the uptake curve is quite different. At 550 °C, it can be well fitted with a single exponential function while at 650 °C sigmoid curve is obtained.

The results are consistent with the uptake curves obtained with Ultraviolet Photoemission Spectroscopy (UPS)[10] and Auger Electron Spectroscopy (AES)[11], which reveals that SDR intensity is roughly proportional to the total oxygen coverage. The uptake curve at 550 °C corresponds to Langmuir-type adsorption while that at 650 °C corresponds to two-dimensional island growth. The uptake curve of Langmuir-type adsorption can be fitted with a single exponential function:
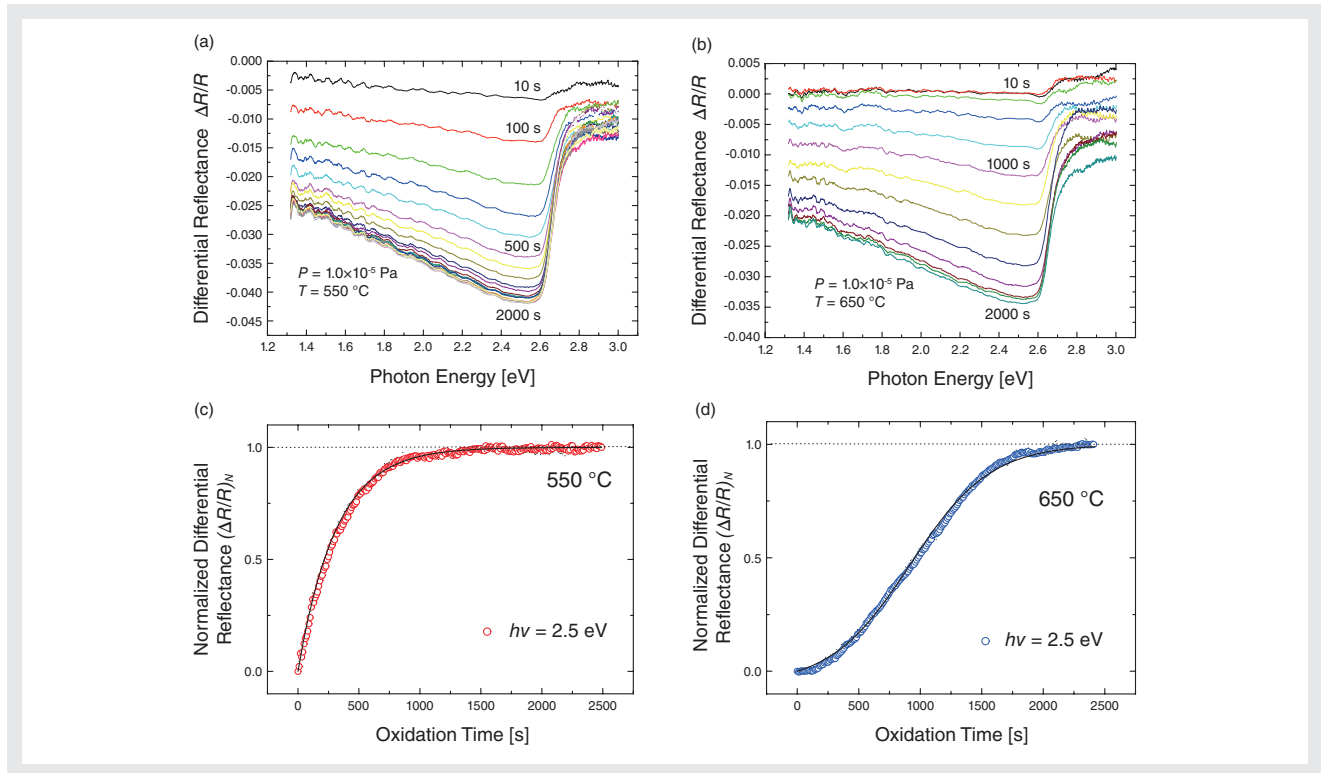
$$I(t) = 1 - exp(-kt)$$

Figure 3   (a) SDR spectral time course at 550 °C.
(b) SDR spectral time course at 650 °C.
(c) Normalized uptake curve of SDR intensity at hv=2.5 eV (550 °C).
(d) Normalized uptake curve of SDR intensity at hv=2.5 (650 °C)

where the signal is normalized as described above and k represents reaction coefficient. The uptake curve of two-dimensional island growth can be fitted with the following function:

$$I(t) = \theta_0 \frac{1 - exp(-\kappa t/\tau_0)}{\theta_0 + exp(-\kappa t/\tau_0)}$$

where θ_0 represents critical coverage at which growth speed largely increases, τ_0 is the inverse of the initial growth rate, and $\kappa = (\theta_0+1)/\theta_0$.
Figure 4 shows RD spectra for a clean Si (001) - (2×1) surface and oxidized surface by oxygen exposure at the pressure of 1×10⁻⁵ Pa at 583 K. The spectrum of a clean surface has negative peak at 3.2 eV and has shoulder structure at E1, E0' critical points (3.4 eV) indicative of a (2×1) single domain for a specimen with 4° off miscut[12]. Shape of the uptake curves is similar between Langmuir-type adsorption and two-dimensional island growth and well fitted with a single exponential function, which is marked difference compared with SDR. Hence, it is not possible to identify growth modes with the shape of the uptake curves when RDS is applied. In Figure 5, Arrhenius plots of the oxidation period are depicted in which minimum oxidation time corresponds to the
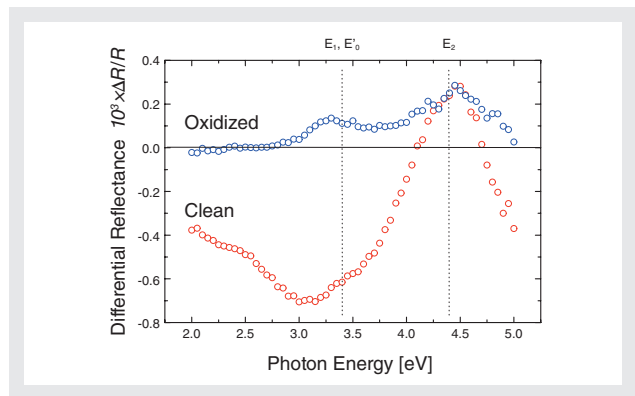

Figure 4   RDS spectra of a clear Si (001) surface and oxidized surface.
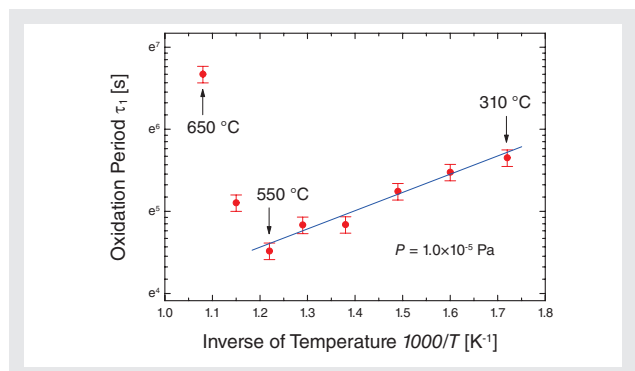

Figure 5   Arrhenius plots of the oxidation period obtained by RDS.

transition temperature of 550 °C.

In monolayer oxide, typical spectral features are positive peaks at E1, E0' critical points and E2 critical points (4.3 eV). First principles calculations by Fuchs et al. showed that the calculated spectrum when oxygen is inserted in the silicon lattice along (-110) or (110) direction well reproduces RD spectrum for oxidized surface. This means that the peak structures on the oxidized surface can be interpreted as due to interface strain induced by oxygen adsorption.

Finite activation energies are obtained from Arrheniu splots in the temperature range of Langmuir-tyep adsorption. In SDR measurements, the estimated values are ε (1.4 eV)= 0.04±0.02 eV, ε (2.5 eV)=0.11±0.02 eV while in RDS ε=0.16±0.03 eV was obtained. The results indicate that small but finite activation energy exists in monolayer regime. Activation energies at low coverage were estimated from the analysis of the initial slope of the uptake curves.

Recent low-temperature scanning tunneling microscopy (STM) showed that oxygen molecules dissociated on the terrace can migrate on the surface and preferentially adsorbed at the step edge[14]. The results suggest that finite activation energy exists on the terrace. First principles calculations predicted that a barrierless dissociative adsorption process of oxygen molecule takes place on the dimer of Si (001)[15]. A recent report claims that finite activation energy of 0.05-0.11 eV exists when incoming molecule is not perfectly parallel to the surface[16]. The values are consistent with our experimental results. It should be noted that interaction with one oxygen molecule on a clean Si (001) surface is considered in the theoretical work.

We demonstrated that reflectance spectroscopy is useful to investigate oxide growth mode on a Si (001) surface in monolayer regime, coverage estimation and detection of the interface stress. Nevertheless, reaction dynamics is still not well understood and should be further investigated by integrating information given by several experimental methods. We plan to perform real-time photoemission spectroscopy measurements at the synchrotron facility (SPring-8).

Based on the present findings, we are now investigating reaction with NO and CO molecules. Our preliminary results showed that similar transition of the growth modes occurs in the case of NO. These molecules are toxic and contained in exhaust gas. Finding effective catalyst to remove these species will greatly help to solve serious environmental problem.

Summary

In the present study, analysis of the initial time course of SDR and RDS intensity enabled us to identify Langmuir-type adsorption and two-dimensional island growth, and to estimate the transition temperature between them as well as activation energies. Details of surface reaction processes could be unraveled by utilizing two types of reflectance spectroscopy, namely, SDR and RDS in combination.

Reflectance spectroscopy has the advantage of applicability to the measurements not limited in ultrahigh vacuum condition but also atmospheric condition without losing surface sensitivity and as a nondestructive probe. It has, nevertheless, disadvantage in the element specific detection. Quite recently, element specific method such as X-ray photoemission spectroscopy (XPS) was applied to the high pressure regime up to 10^2 Pa[17]. Nevertheless, at more higher regime of 10^2-10^5 Pa (ambient pressure) will be exclusively observed by means of optical techniques in the future. There is still a gap between the fundamental research of reaction processes at the atomic level and industrial exploration for catalytic materials. We hope that highly sensitive nondestructive methods using optical technique are considered as promising means to overcome the difficulty.

Acknoledgement

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