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# Measurement and calculation of the differential reflectance spectrum of hydrogen-terminated silicon surfaces having different crystal orientations

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## Abstract

The differential reflectance spectrum between the (001) and the (111) hydrogen-terminated Si surfaces without native oxidation is investigated. Careful measurements using developed apparatus and an ultra-clean process are performed. The measured spectrum is compared with the reported one (Chongsawangvirod and Irene 1991 *J. Electrochem. Soc.* **138** 1748–52), and is shown to be roughly identical even though a native oxidation effect exists. The theoretical calculation based on density-functional theory (DFT) and local density approximation (LDA) is also performed. The peak positions in the calculated and the measured spectra are in good accordance with each other, while the magnitudes of the peaks are in relatively worse agreement. Although the inclusion of advanced approximations would provide more accurate results, a qualitative reproduction is achieved in this study as well. It is concluded that the origin of the spectrum is mainly in the deformation of the bulk states induced by surface perturbation.

## 1. Introduction

The silicon (001) surface has been widely used as the substrate for electronic devices, because good insulating films can be easily formed simply by oxidizing the surface. Nowadays, much attention is being paid to other crystal orientations for the purpose of applying their special physical properties: the (111) surface is capable of being formed as an atomically flat surface by using the wet process [1], and the (011) surface possesses a higher hole mobility to improve the electronic devices [2]. Understanding the characteristics of the surface electronic properties of such kinds of crystal orientation, which exist even in isotropic materials, is becoming increasingly important.

In this paper, we investigate the difference of the surface electronic properties between the (001) and the (111) hydrogen-terminated silicon surfaces by means of optical measurement

and first-principles calculations. We adopt the method of the differential reflectance spectrum (DRS) as the optical evaluation [3, 4]; it is defined by

$$\frac{\Delta R}{R} = \frac{R_{111} - R_{001}}{R_{001}}, \quad (1)$$

where  $R_{111}$  and  $R_{001}$  indicate the reflectance of the (111) and the (001) surfaces as functions of the incident photon energy, respectively. The DRS, which measures the relative reflectance difference, enables us to perform a highly sensitive detection of the reflectance difference. In this method, no polarization techniques are utilized.

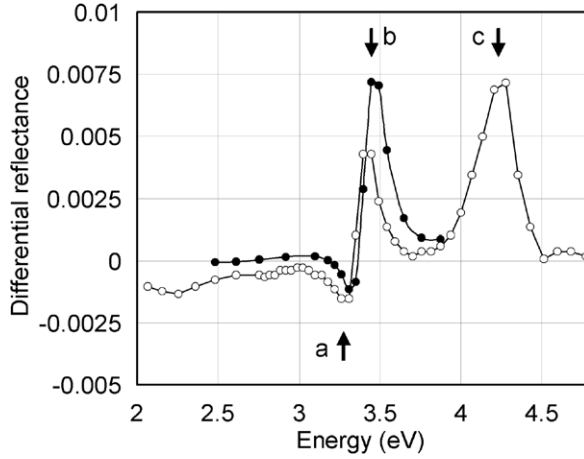
Chongsawangvirod *et al* [5] have already reported the measurement of the DRS between those surfaces treated by fluorinated acid, but the native oxidation effect is not negligible in their surface cleaning processes. In our investigation, the native-oxidation-free hydrogen-terminated surfaces are utilized by making use of ultrapure water with reduced dissolved oxygen concentration in the cleaning process.

The first-principles calculations of DRS were also performed based on density-functional theory (DFT) [6]. The calculated DRS is in qualitatively good agreement with the measured one. The origin of the spectrum is mainly in the deformation of the bulk states induced by surface perturbation in consideration of the peak position of the spectrum.

## 2. Experimental details

The apparatus for DRS is homemade; it has a near-normal incidence and mechanical sample exchanges [4]. The vacuum chamber is evacuated to about  $10^{-5}$  Pa so as not to oxidize or contaminate the sample surfaces. In measuring the DRS, the tilt angle of the samples is controlled within  $10^{-6}$  rad to maintain the stability of the optical path. The noise level and the repeatability of the system are both  $2 \times 10^{-5}$ . The samples are p-type Si(001) with  $140 \Omega \text{ cm}$  and p-type Si(111) with  $4 \Omega \text{ cm}$ . The sample cleaning process applied in this study is that proposed by Ohmi [7]. The impurity concentrations of oxygen and the total organic carbon dissolved in the ultrapure water are both controlled to be lower than 1 ppb, which is a key to obtaining atomically unoxidized and clean surfaces [7, 8]. The processed surfaces have been proven to be clean, so the atomic structure of hydrogen termination can be easily observed by scanning transmission microscopy (STM) without any additional cleaning but by loading into the vacuum chamber [8]. Moreover, the DRS between two nominally identically prepared samples is very small (typically within a few  $10^{-4}$ ). It should be noted that more stable optical properties can be obtained by the method mentioned above than by the usual treatment using buffered HF and  $\text{NH}_4\text{F}$  solution [9].

The measured DRS between the (001) and the (111) hydrogen-terminated silicon surfaces is shown in figure 1. A distinctive peak b at 3.4 eV with a magnitude of 0.007 is observed. The zero spectrum in the visible region (2.5–3 eV) indicates that no gap states exist on the sample surfaces, which is reasonable for hydrogen-passivated silicon surfaces. The spectrum is very similar to the reported one [5], but some discrepancies are observed: a featureless difference in the visible region (2.5–3 eV) and the height of peak b. We consider that the discrepancies arise from two reasons. The first is in the native oxidation of the samples in the cleaning process. It is revealed that the silicon surfaces which are covered by a nanometre-level surface oxidized layer generate a relatively large reflectance change of the order of 0.01, particularly in the region over 3.4 eV [10], and that native oxidation of silicon surfaces occurs easily during the ultra-pure water rinse in the sample cleaning process unless the oxygen impurity concentration in the utilized water is substantially reduced [11]. The difference of the heights of peak b is considered to be affected by this unintentional oxidation. The second is from



**Figure 1.** DRS between the (001) and the (111) hydrogen-terminated surfaces. Solid and open circles indicate the spectra obtained in this study and by Chongsawangvirod [5] respectively. Arrows indicate obvious peaks.

the worse accuracy in the measurement, which can be seen from the fact that unreasonable non-zero differences are observed in the region below the direct gap of 3.4 eV in [5]. Thus the DRS obtained in this study can be understood to be more accurate. In spite of these differences, the schematic features of these two DRSs are similar. Moreover, another reported DRS result between the oxidized surfaces [5] is also similar. Therefore, the main feature of the DRS is formed not by the microscopic surface structure such as surface oxidation, surface roughness, surface contamination etc [12] but by the difference of the surface/bulk electronic states depending on surface orientation.

### 3. First-principles calculation of differential reflectance

The differential reflectance is calculated based on a long-wavelength approximation (thin-film approximation) [13] in which a thin dielectric surface layer is assumed to be suspended on the bulk substrate. First, the bulk-reference DRS is defined as

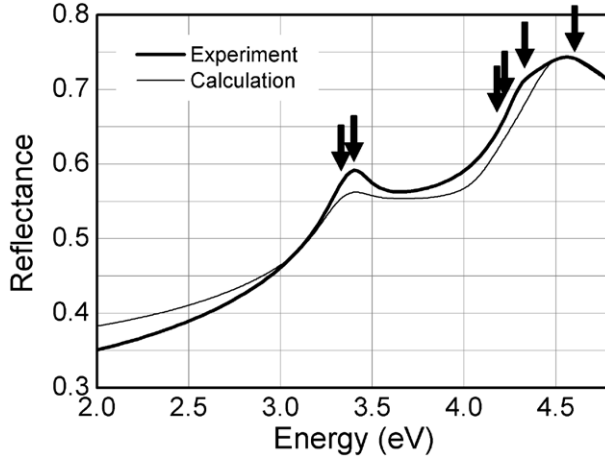
$$\frac{\Delta R}{R} = \frac{R_s - R_B}{R_B} \approx -\frac{8\pi L_z}{\lambda} \text{Im} \frac{\chi_s}{\chi_B}. \quad (2)$$

Here,  $R_s$  and  $R_B$  indicate the reflectance of the surface and the Fresnel reflectance, respectively,  $\chi_s$  and  $\chi_B$  the surface dielectric susceptibility and the bulk dielectric susceptibility, respectively,  $L_z$  the thickness of the surface layer, and  $\lambda$  the wavelength of incident light in vacuum. Since the bulk contribution is automatically removed from  $\chi_s$ , the differential reflectance is not seriously affected by the choice of the thickness  $L_z$ . The formulation (2) was obtained by analysing the reflectance of the ‘vacuum–thin-surface–bulk’ structure using electromagnetism. Second, the differential reflectance between the (001) and the (111) surfaces can be calculated by subtracting the above-mentioned bulk-reference differential reflectance values.

$$\begin{aligned} \frac{R_{111} - R_{001}}{R_{001}} &\approx \left( \frac{R_{111} - R_B}{R_B} \right) - \left( \frac{R_{001} - R_B}{R_B} \right) \\ &= \left( -\frac{8\pi L_z}{\lambda} \text{Im} \frac{\chi_{111}}{\chi_B} \right) - \left( -\frac{8\pi L_z}{\lambda} \text{Im} \frac{\chi_{001}}{\chi_B} \right). \end{aligned} \quad (3)$$

This procedure is equivalent to that described in [14].

The remaining unknown quantities are the bulk and the surface dielectric susceptibilities,  $\chi_{001}$ ,  $\chi_{111}$  and  $\chi_B$ , which can be calculated based on quantum mechanical theory by employing



**Figure 2.** Calculated and measured absolute reflectance spectra of silicon. The calculation is performed using (4) and the general Fresnel formula. Experimental data are taken from [17]. Arrows indicate the critical points measured by the electro-reflectance method [18].

**Table 1.** Calculation parameters.

|                                    | Bulk            | (001)              | (111)              |
|------------------------------------|-----------------|--------------------|--------------------|
| Number of atoms                    | 8(Si)           | 19(Si) + 4(H)      | 32(Si) + 4(H)      |
| Super cell size (au <sup>3</sup> ) |                 | 7.25 × 7.25 × 87.0 | 12.6 × 7.25 × 87.0 |
| Cut-off energy (Ryd)               |                 | 12.3               | 12.3               |
| Number of divisions in the BZ      | 100 × 100 × 100 | 50 × 50            | 50 × 50            |
| Rigid shift (eV)                   | 0.65            | 0.65               | 0.65               |

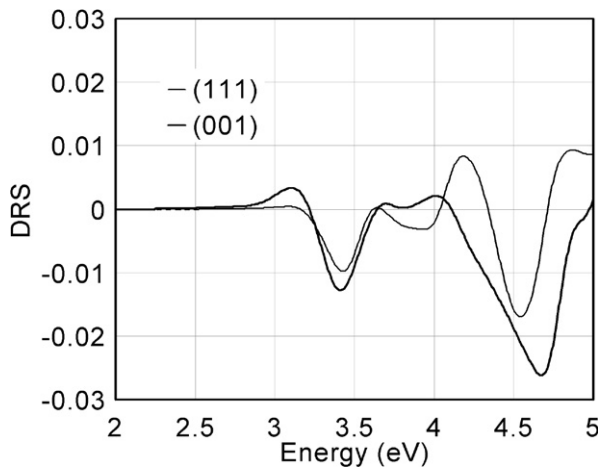
the Kubo formula,

$$\chi(E) = \sum_{\substack{n:\text{valence band} \\ m:\text{conduction band}}} \int_{\text{BZ}} \frac{d^3\vec{k}}{\pi^2} \frac{1}{E^2 - E_{nm\vec{k}}^2} \frac{1}{E_{nm\vec{k}}} |\langle \psi_{n\vec{k}} | \hat{p}_x | \psi_{m\vec{k}} \rangle|^2, \quad (4)$$

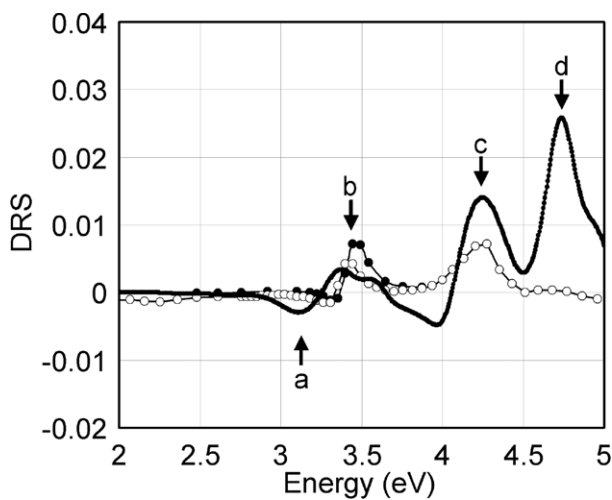
where  $\chi(E)$  indicates  $\chi_B$ ,  $\chi_{001}$  or  $\chi_{111}$ ,  $E$  the energy of incident light,  $\vec{k}$  Bloch's wavevector,  $\hat{p}_x$  the momentum operator parallel to the direction of the electric field of the light,  $\psi_{n\vec{k}}$  and  $\psi_{m\vec{k}}$  the wavefunctions of the valence and the conduction bands, respectively, and  $E_{nm\vec{k}}$  the energy gap between the states  $\psi_{n\vec{k}}$  and  $\psi_{m\vec{k}}$ . This formula can be utilized in cases of both the bulk and the surface calculations. However, in the surface calculation this value is divided by a factor of two because a slab structure contains two surfaces. The wavefunctions of the bulk and the surface structures are calculated by the ordinary DFT calculation [6]. We apply the LDA [15], norm-conserving pseudopotential [16] and plane-wave expansion methods.

The calculations are performed in the bulk model, the hydrogen-terminated 19 silicon layer (001) slab model and the hydrogen-terminated 16 silicon layer (111) slab model. The surface atomic structure is optimized by using molecular dynamics. The calculation parameters are summarized in table 1. The integration over the Brillouin zone (BZ) was performed so that the calculation points were restricted irreducible ones. The calculated spectra are shifted towards higher energy by 0.65 eV to compensate for the small energy gap in the LDA calculations.

The calculated and experimental reflectance spectra of bulk silicon are depicted in figure 2. The calculated spectrum is in rather good agreement with the experimental one [17] on taking into account the calculation method being based on the DFT-LDA method. The spectrum peak structure is predominantly constituted by the critical point structures of bulk silicon, which



**Figure 3.** Bulk-reference DRS of (001) and (111) hydrogen-terminated silicon surfaces.



**Figure 4.** Calculated and experimental DRS between (001) and (111) hydrogen-terminated silicon surfaces. The thick line indicates the calculated spectrum. Open and filled circles are the same as in figure 1. The peak positions of the DRS are indicated by arrows.

are indicated by arrows in the figure [18]. The agreement between the calculated and the experimental spectra implies the correctness of the band calculation. The bulk-reference DRSs of the (001) and (111) surfaces are shown in figure 3. It can be seen that no spectral difference is observed in the region below the direct band gap (3.4 eV), and in contrast, a large spectral difference is observed in the region near the critical points at 3.4 eV and 4.3 eV. These facts suggest that the contribution of the hydrogen-terminated surface on the reflectance spectrum is mainly in the change of the bulk originated states.

Figure 4 shows the DRS between the (001) and the (111) surfaces. Two major peaks at 3.4 and 4.3 eV are observed and no difference is also observed in the region below the direct gap. These results are qualitatively in good agreement with the experimental result in figure 1. However, several discrepancies are also observed. The peak b indicated in figure 4 at the 3.4 eV peak shows a rather small splitting feature. The magnitude of peak c in the 4.3 eV peak is larger than the experimental one. Moreover, peak d is hardly observed in the experimental data. The reasons have not been fully analysed, but considering that the implementation of advanced theories such as local-field effect, excitonic effect and GW approximation has been shown to be required for obtaining accurate result [19], there is quite a possibility that the inaccuracy

observed in figure 4 is overcome. In addition to this, one needs to measure the DRS in the high-energy region, excluding the oxidation effect. Nevertheless, it is, however, obvious that the peaks come from the change of the bulk electronic states, because the energy positions of the peaks are closely related to the bulk critical points.

In summary, the differential reflectance spectrum between the (001) and the (111) hydrogen-terminated Si surfaces without native oxidation has been investigated by experimental and theoretical methods. Careful measurements using developed apparatus and an ultra-clean process have been performed. The measured spectrum indicates considerable disagreement with the reported one [5], in which native oxidation is not negligible, but is roughly identical. A theoretical calculation based on density-functional theory (DFT) and the local density approximation (LDA) has also been performed. The peak positions in the calculated and the measured spectra are in good accordance with each other, while the magnitudes of the peaks are not. Although the inclusion of more sophisticated approximations is required to obtain more accurate calculations, qualitative reproduction is achieved. It is considered that the origin of the spectrum is in the difference between the electronic states and mainly in the deformation of the bulk states induced by surface perturbation.

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