

## Investigation of surface states on Si(001) and Si(111) surfaces –Photo-reflectance measurement and ab-initio calculation–

K.Inagaki<sup>a</sup>, K.Hirose<sup>a</sup>, K.Sugiyama<sup>a</sup>, K.Endo<sup>a</sup>, H.Goto<sup>b</sup>, T.Kataoka<sup>a</sup>, Y.Mori<sup>a</sup> and Y.Bessho<sup>a</sup>

<sup>a</sup>Department of Precision Science and Technology, Osaka University,  
2-1 Yamada-oka, Suita, Osaka, Japan

<sup>b</sup>Faculty of Engineering, Kyoto Institute of Technology,  
Matsugasaki, Sakyo-ku, Kyoto, Japan

Bulk Si is an optically isotropic material, but optical properties of the surface depend on surface states generated by truncation of material. Photo-reflectance spectrum measurement is a very sensitive method for evaluating surface properties. The observation reveals that the difference between spectra of Si(001) and Si(111) surfaces is larger than the magnitude of 1%. In order to explain this dependence on surface orientation, we have calculated the electronic structures of the surfaces by using ab-initio calculation method based on LDA (local density approximation). Calculated JDOS (Joint Density of States) is in good agreement with the experimental results.

### 1. Introduction

Optical properties of materials are closely related to their electronic structures. Surface defects such as steps, vacancies which exist on surface layer of material perturb considerably not only their surface electronic structures, but also their optical properties. The detection of the changes of the optical properties becomes one of surface characterization methods. Especially photo-reflectance spectrum is one of the nondestructively measurable optical parameter. We have developed the high precision photo-reflectance spectrometer in order to evaluate ultra-precision machined real surfaces. This spectrometer can detect the change in photo-reflectance spectra with errors in the range of 0.01% by means of differential photo-reflectance spectroscopy method[1]. This method also provides high surface sensitivity by the cancellation of the optical responses from the bulk states.

To separate many kinds of effects of the surface defects from experimentally obtained spectra, the data will be compared with theoretically calculated spectra of each model with defect.

In this paper, as a preliminary test of this direction, we have experimentally measured

the dependence of photo-reflectance spectrum on surface orientation which are not expected on bulk properties, and compared these data with the calculated ones.

### 2. Measurement

Differential photo-reflectance spectrum method was applied for precise quantitative evaluation of photo-reflectance spectra. Differential photo-reflectance  $\Delta R/R$  is defined as follows.

$$\frac{\Delta R}{R} \equiv \frac{R_A - R_B}{(R_A + R_B)/2} \cong \frac{R_A - R_B}{R_B} \quad (1)$$

Here,  $R_A$  and  $R_B$  are photo-reflectance of test and reference sample, respectively. Differential photo-reflectance spectrum measurement system is shown in Fig. 1. Unpolarized monochromatic light is near normal incident on a sample, and the reflected light is detected. The numerator in Eq.(1) is obtained by detecting the change of the photo-detector output through exchanging reference sample with test one.

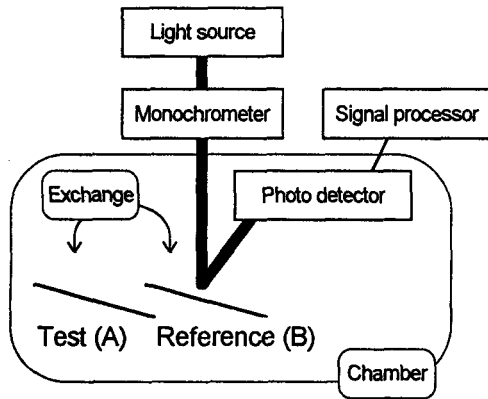


Figure 1 Measuring system for differential photo-reflectance spectrum.

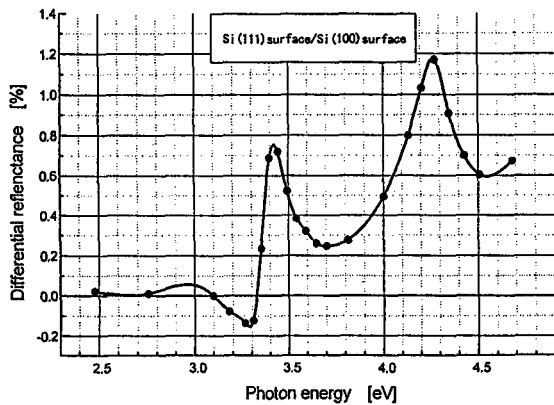


Figure 2 Differential photo-reflectance spectrum between Si(001) and Si(111) H-terminated surfaces.

The dependence of photo-reflectance on surface orientation is measured[2] to compare with calculation. In this experiment, the reference and test sample are Si(001) and Si(111), respectively. Each samples were etched off its oxide layer by HF cleaning method. Such surfaces have sudden truncation of bulk continuity with hydrogen atom termination[3]. Experimentally obtained photo-reflectance dependence on surface orientation is shown in Fig.2. Although the bulk Si has isotropic optical properties, Differential reflectance has big differential peaks of 1.2% at 4.3eV, 0.8% at 3.4eV and -0.2% at 3.3eV in the spectrum, therefore it is clear that the

surface state affects sensitively photo-reflectance spectra.

### 3. Calculation

The numerical calculation consists of two steps. The first step is the calculation of the surface states. This was performed within single-particle approximation and LDA. The second step is the calculation of optical properties from surface states.

The differential reflectance is evaluated as follows. First, this is separated into two terms by using differential reflectance between test (or reference) surface and 'bulk' reflectance.

$$\frac{R_{(111)} - R_{(001)}}{R_{(001)}} \cong \frac{R_{(111)} - R_{\text{Bulk}}}{R_{\text{Bulk}}} - \frac{R_{(001)} - R_{\text{Bulk}}}{R_{\text{Bulk}}} = \left( \frac{\Delta R}{R} \right)_{(111)} - \left( \frac{\Delta R}{R} \right)_{(001)} \quad (2)$$

Each differential reflectance is obtained from surface conductivity  $\sigma_i^{(s)}$  and bulk dielectric constant  $\epsilon$ [4],

$$\left( \frac{\Delta R}{R} \right)_i = 2\text{Re} \frac{\sqrt{\mu_0/\epsilon_0}}{\epsilon - 1} \sigma_i^{(s)} \quad [i = (111), (001)]. \quad (3)$$

Here,  $\mu_0$  is the magnetic permeability in vacuum and  $\epsilon_0$  is the dielectric constant in vacuum.  $\epsilon$  and  $\sigma_i^{(s)}$  contain only bulk and surface states effects, respectively.

Surface conductivity is calculated from Adler's representation [5].

$$\sigma^{(s)} = \frac{ie^2}{m\omega} \rho + \frac{ie^2}{4m^2\omega} \left[ \sum_{\mathbf{k}} \sum_{n,l} \frac{1}{E_n - E_l - \hbar\omega} (\Psi_{nl}^{\mathbf{k}})^* \Psi_{ml}^{\mathbf{k}} \right] \quad (4)$$

$e$ : charge of an electron,  $m$ : mass of an electron,  $\omega$ : angular frequency of light,  $\rho$ : charge density,  $\mathbf{k}$ : Bloch wave vector, B.Z: first Brillouin zone,  $E$ : energy level,  $n, l$ : band indices of conduction and valence bands, respectively,  $\hbar$ :  $h/2\pi$   $h$ : Planck's constant, and  $\Psi$ : transition magnitude.

The first term is related to plasma vibration and the second one to the transition be-

tween valence and conduction band. Main contribution to the reflectance is from the second term of (4). This term is separated to two parts, one is the first half of the summation which is called as JDOS (Joint Density of States) and the other is the rest of the term which is called as transition provability.

$$\text{JDOS} = \frac{1}{4\pi^3} \int_S \frac{dS}{|\nabla_k E_{cv}(\vec{k})|} \quad (5)$$

$$\Psi_{in}^k = i\hbar \int_{-\infty}^{\infty} d^3r \left( \frac{\partial \phi_i^*}{\partial y} \phi_n - \phi_i^* \frac{\partial \phi_n}{\partial y} \right) \quad (6)$$

Here,  $y$  indicates the direction of the electric field of incident light,  $\phi_i$  wave function of surface states. Consequently, optical response of a surface can be determined by wave function  $\phi$  and energy level  $E$ .

JDOS is the most important parameter for evaluating energy dependence of the optical properties, since JDOS contains the information of the energy dependence of the surface electronic states. In this work, the transition probability is approximate to unity value and differential reflectance spectra are compared with difference of JDOS.

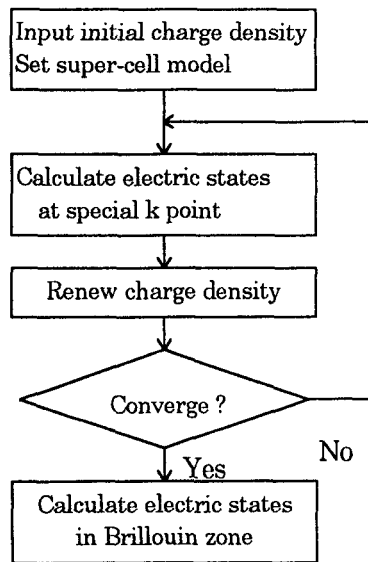


Figure 3 Flow chart for band calculation

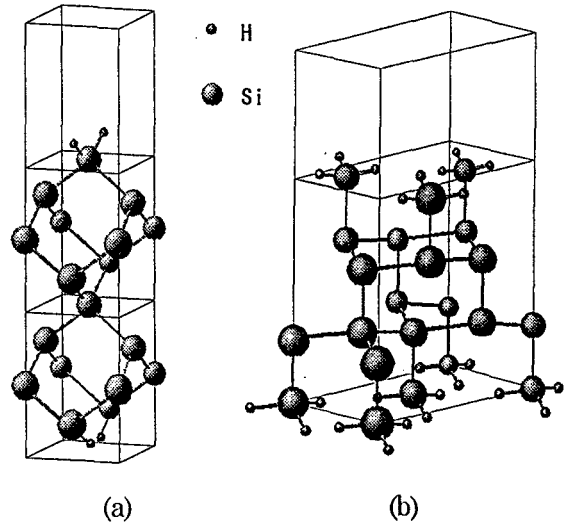


Figure 4 Super-cell models of H-terminated Si surfaces

In order to estimate of the wave function  $\phi$  and of the energy level  $E$ , we applied the first principles electronic state calculation. The band gap calculated in the framework of LDA is narrow compared to the experimental results, and the rigid shift of the conduction bands to higher energy level relative to the valence bands is a simple and effective correction method based on the quasi-particle calculations[6]. We adapted the rigid shift method.

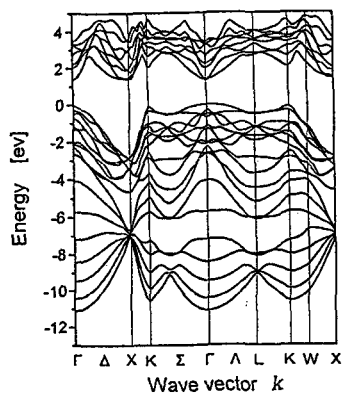
Calculating procedure is displayed in Fig. 3. Norm-conserving pseudopotential method for ion core representation (HSC pseudopotential[7]), and exchange-correlation function (Perdew and Zunger[8]), plain wave expansion and super-cell model were applied. Figure 4 shows the super-cell models. The Si(001) surface is constructed by 8-layer 8 Si atom slab model with di-hydride termination and vacuum gap, while Si(111) is by 6-layer 12 Si atom slab one with tri-hydride termination and vacuum gap.

Self-consistent calculation was executed with zero initial charge density assumption. Using this converged electronic density, the band structures are calculated and the results are indicated in Fig.5(a) for Si(001) di-hydride model and (b) for Si(111) tri-hydride model. Bloch wave length  $k$  is taken along special line as the same of bulk one.

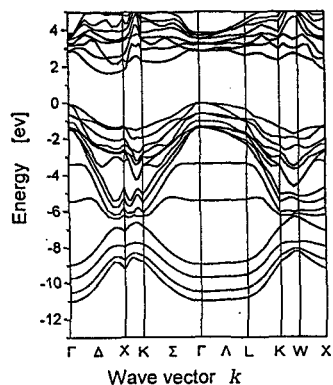
Figure 6 shows the JDOS calculated from 2D-band structure; (a) Si(001) and (111) band structures and (b) the difference between these spectra. In the approximation of disregarding transition probability, this difference of JDOS means the dependence of surface orientation of the reflectance spectra through Eq. (3) and (4) which consistent the observed one shown in Figure 2.

#### 4. Conclusion

We calculated the surface orientation dependence of surface band structure and JDOS within local density approximation. The difference of JDOS between two surface orientations is agree with the experimental result. But peak energies are not perfectly agree with one another. Further investigations, e.g. calculation of

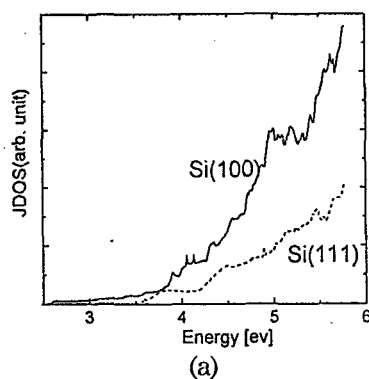


(a)

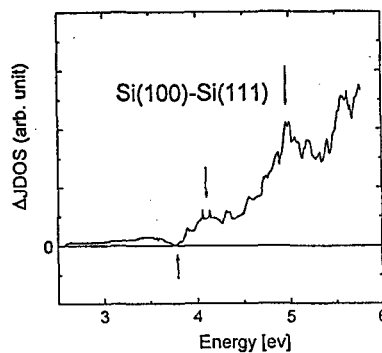


(b)

Figure 5 Surface Band structure of hydrogen terminated Si (a) Si(001) (b) Si(111)



(a)



(b)

Figure 6 JDOS of Si surfaces (a) JDOS spectra of Si(001) and Si(111) surfaces (b) differential JDOS spectrum between (001) and (111)

the transition probability or gap correction, are needed for more precise evaluation of the optical properties.

#### References

1. Y. Mori et al., J. Japan Soc. of Prec. Eng., 60,9(1994)1360
2. T. Kataoka et al., Proc. of Japan Soc. of Prec. Eng. Autumn Annual Meeting, (1993)629
3. Y. Morita et al., Jpn. J. of Appl. Phys. 1, 30 128 (1991) 3570
4. M. Nakayama, J. Phys. Soc. Japan, 39, 2 (1975) 265
5. S. L. Adler, Phys. Rev., 126 2 (1962) 413
6. J. E. Northrup, Phys. Rev. Lett. 76 (1996)
7. D. R. Hamann, et al., Phys. Rev. Lett. 43 (1979) 1494
8. J. P. Perdew and A. Zunger, Phys. Rev., B23 1981) 5048