

Change of the surface induced optical anisotropy of the clean Si(110) surface by oxidation

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Normal incidence ellipsometry has been used to measure the change in the complex anisotropic reflectance ratio $\tilde{\rho}$ upon oxidation of the clean Si(110) 16×2 surface. The spectroscopic change in the amplitude of $\tilde{\rho}$ ($\tan(\Psi)$) shows a broad maximum of height 1.4×10^{-3} in the high energy region above 2.5 eV. No phase shift difference for the reflectance coefficients belonging to the surface principal optical axes has been measured. A Kramers–Kronig transformation of the amplitude ratio showed that a change in the phase is not expected. The change in $\tan(\Psi)$ indicates that the change in reflection upon oxidation in the optical region is mainly in the $(\bar{1}10)$ direction.

1. Introduction

In the last decade surface induced optical anisotropy (SIOA) has become a tool of fundamental interest in the study of the geometric and electronic structure of semiconductor surfaces. Reflectance anisotropy measurements of the clean Si(111) 2×1 surface clarified the geometric reconstruction of this surface and rejected undoubtedly the buckled row model in favour of the π -bonded chain model [1]. After this initial success of optical anisotropy measurements the interpretation of SIOA signals from other semiconductor surfaces has not been as straightforward. One of the main reasons for this is beyond doubt the contradicting experimental results obtained from different experimental techniques on the (110) surface of III–V compounds. In the experimental configuration used by Selci et al. [2], the reflection of a surface before and after oxidation is compared. Changing the polarization of the incident optical beam gives the reflectance anisotropy of the clean surface, presuming that the oxidized surface behaves optically isotropic. Berkovits et al. [3] have tried to circumvent this presumption by making use of a rotating polar-

izer for the determination of the SIOA signal and avoiding oxidation. The elimination of anisotropic optical components in this configuration has to be thorough and may lead to errors in the absolute anisotropy recorded. Unfortunately, comparing the measurements of Selci et al. [2] and Berkovits et al. [3], a different SIOA signal is obtained and neither of them corresponds with theoretical results [4]. From the measurements of Berkovits et al. [3] it is also clear that the presumption that the oxidized surface does not show optical anisotropy is questionable. In case of the elementary semiconductor surfaces Aspnes and Studna [5] showed that the naturally oxidized (110) surfaces have a substantial optical anisotropy above 3 eV. Poppe et al. [6] have shown recently that this optical anisotropy is a combination of the difference in surface polarizability along the two surface principal axes combined with the local field effect, the latter being sensitive to the actual reconstruction. Recently Aspnes et al. [7] described a few experimental configurations for the observation of the change in optical anisotropy in UHV. These experimental configurations differ from the setup of Berkovits et al. [3], in this sense that the incident beam does not

contain optical components that change the polarization state of the incident beam during the experiment, thereby avoiding influences of the anisotropic components like UHV windows and “searchlight” effects due to wobbling on the surface of the incident beam [7]. The application of these spectroscopic configurations was shown in case of the growth of III–V materials [7,8] and at the He–Ne wavelength for these materials by Koch et al. [9]. In this paper we will use an experimental configuration to detect changes in optical anisotropy similar to the one used by Aspnes et al. [7] and Koch et al. [9], based upon a rotating analyzer ellipsometer (RAE) instead of a photoelastic modulator. The virtue of this technique compared to Berkovits et al. [3] is that the rotating component is situated in the final part of the instrument. This configuration also allows us, if present above the S/N ratio, to record the phase shift difference between the two reflection coefficients of the surface principal axes, a quantity usually neglected in SIOA. In this paper the influence of an oxygen top-layer on the SIOA signal of the clean Si(110) surface is investigated as well.

2. Experimental

The reconstruction of the Si(110) surface has been reported to show a large variety of possible configurations [10]. Slight contamination of the surface with Ni, even below the detection limit of Auger electron spectroscopy, has been reported to be responsible for this large number [11,12]. The clean Si(110) surface in the experiment reported in this article, showed a 16×2 reconstruction as determined by LEED. The LEED pattern of this clean surface showed also that this reconstruction has two domains with an angle of 70° with respect to each other. This direction of 70° is reported to be a result from the different directions of the up and down terraces possible on this surface [13]. The LEED measurements were used to determine the principal crystal axes of the Si(110) surface, the (001) and $(\bar{1}10)$ directions. The SIOA signal originates mainly from the differences in geometric and electronic struc-

ture between these two directions. After oxidation of the surface with $\sim 10^5$ L (1 L = 10^{-6} Torr · s) molecular oxygen no LEED pattern could be distinguished from the uniform background. The surface was cleaned by simultaneous ion bombardment and annealing [14].

The complex anisotropic reflectance ratio $\bar{\rho}$ of a surface is defined as the quotient of the complex reflection coefficients of the two optical axes and can be written in terms of a real and imaginary component:

$$\bar{\rho} = \bar{r}_y / \bar{r}_x = \tan(\Psi) \exp(i\Delta). \quad (1)$$

The indices x , y refer to light polarized parallel to either of the two intrinsic axes of the surface, respectively the $(\bar{1}10)$ and (001) direction. This ratio is different from unity for an anisotropic surface. Ellipsometry can be used to determine this ratio as this technique is based on the difference in reflection of linear polarized light in two orthogonal directions. In off-normal incidence reflection from a surface these are the well known s- and p-directions. The experimental configuration is therefore described by standard RAE formalism, replacing the usual s- and p-components for oblique incidence by the reflection in x and y direction of the normal incident s-polarized light. A change in the ratio $\bar{\rho}$ is directly related to a change in anisotropy of the surface. If $|\bar{\rho}| \approx 1$ this ratio is easily related to the frequently used relative differential reflectivity quantity $\Delta R/R$,

$$\frac{\Delta R}{R} \approx 1 - \frac{R_y}{R_x} \approx 1 - \tan^2(\Psi) \approx 2 \delta(\tan(\Psi)). \quad (2)$$

The experimental configuration is shown in fig. 1. A parallel, monochromatic, linear polarized beam from a 75 W xenon light-source is split by a beamsplitter. The normal incident beam (s-type polarized) is reflected and passes through a window made of quartz and tilted 5° with respect to the plane of polarization of the incoming light wave. It reflects on the sample in the UHV chamber, and is transmitted by the window and the beamsplitter. The polarization state is analyzed with a rotating analyzer at a frequency $\omega = 67$ Hz. The alignment of the ellipsometer is

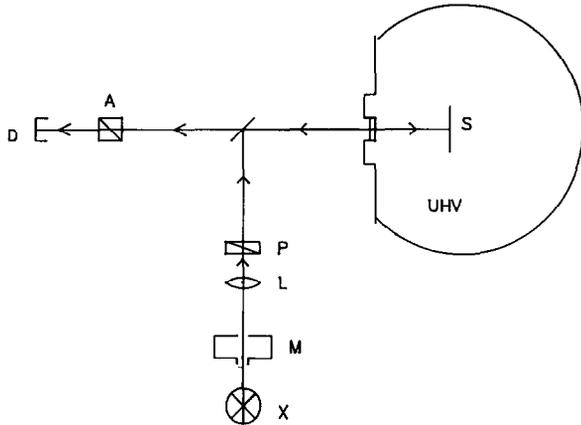


Fig. 1. Experimental configuration for normal incidence ellipsometry. (X) 75 W xenon lamp, (M) Oriel 7240 monochromator, (L) $f = 250$ mm lens, (P) polarizer, (S) sample, (A) rotating analyzer, (D) EMI 9659 QB-S20 photomultiplier.

easily established by minimizing the $\omega/2\omega$ and $3\omega/2\omega$ Fourier components in the sinusoidal signal. We have only considered the perfect ellipsometer and have given no attention to the influences of imperfect windows, polarizers or beamsplitters [15]. This is justified as we perform only relative measurements, i.e., the change of the anisotropy upon oxidation. No absolute value of the reflectance anisotropy of the clean nor the oxidized silicon surface will be presented. The (normalized) intensity at the detector for this ellipsometer can be written as a function of the time t :

$$I_N = 1 + a(p) \cos(2\omega t) + b(p) \sin(2\omega t). \quad (3)$$

p is the polarization angle of the incident beam with respect to the x -axis. The prefactors $a(p)$ and $b(p)$ are determined by means of Fourier analysis. The ellipsometric parameters $\tan(\Psi)$ and $\exp(i\Delta)$ can be expressed in these Fourier coefficients $a(p)$ and $b(p)$:

$$\tan(\Psi) = \frac{1}{|\tan(p)|} \left(\frac{1 + a(p)}{1 - a(p)} \right)^{1/2}, \quad (4)$$

$$\cos(\Delta) = \text{sign}(\tan(p)) \frac{b}{(1 - a^2(p))^{1/2}}.$$

The polarization of the normally incident optical beam is not rotated throughout the experiment,

avoiding unknown possible influences of the beamsplitter or window. The x -axis of the sample is positioned at an angle $p = -\pi/4$ rad with respect to the polarization direction of the normally incident optical beam. The analyzer offset angle is calibrated in such a way as to give $\tan(\Psi) \cong 1$ as we expect only a small anisotropy in the reflection coefficient (order of 1%) for this initial value. This procedure for determining the RAE calibration parameters has to be used, as the standard calibration procedures (residue and phase) are not allowed for a combination $\tan(\Psi) \approx 1$ and $\cos(\Delta) \approx 0$ [15]. The ellipsometric configuration was checked by measuring the changes caused by rotation of the sample to an angle of $p = \pi/4$ with respect to the polarisation direction of the incident light beam. The change of $\tan(\Psi)$ at this angle upon oxidation was exactly opposite to the change at $p = -\pi/4$, as in this case the change in $1/\tan(\Psi)$ is measured. From this equation it can also be deduced that if the incident beam is polarized parallel to one of the optical axes of the sample surface ($p = 0$ or $p = \pi/2$), no change in the optical anisotropy will be observed. Measurements at these axes confirmed that the principal crystal axes (001) and $(\bar{1}10)$ are also the optical axes at the Si(110) surface investigated. The stability of the ellipsometer configuration for $\tan(\Psi)$ is $\pm 10^{-4}$ from 2.0 upto 4.1 eV. Occasionally drift occurs, but this has been corrected. The stability of $\cos(\Delta)$ is a factor of 2 worse and is quite sensitive to the signal strength. Long term stability of $\cos(\Delta)$ at both ends of the optical spectrum is not easy to achieve.

3. Change in $\tan(\Psi)$ upon oxidation

In fig. 2 the change of $\tan(\Psi)$, $\delta(\tan(\Psi))$, upon exposing the clean Si(110) surface to molecular oxygen at saturation coverage is given as a function of photon energy. No change in $\cos(\Delta)$ due to oxidation could be detected in this photon energy range. These measurements show that over the whole energy region observed $\Psi_{\text{cl}} < \Psi_{\text{ox}}$. This results in $(r_{\text{ox}}/r_{\text{cl}})_x < (r_{\text{ox}}/r_{\text{cl}})_y$. Spectroscopic differential reflectometry (SDR) [14,16] showed that upon oxidizing clean Si surfaces the reflectance

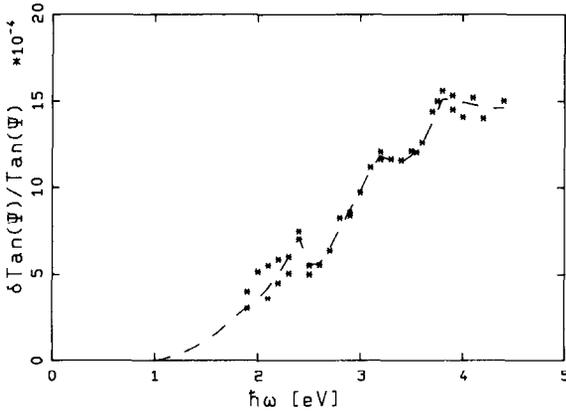


Fig. 2. Difference in $\tan(\Psi)$ as a function of the photon energy ($\hbar\omega$) before and after exposing the clean Si(110) 16×2 surface to molecular oxygen at saturation coverage, (*) measured points, broken line is the approximation used in the Kramer-Kronig transformation. The incident light-beam is polarized at an angle of -45° with respect to the $\langle 001 \rangle$ surface axis.

decreases, i.e., $r_{\text{ox}}/r_{\text{cl}} < 1$. The change in reflectance upon oxidation is, therefore, largest for light polarized in the $(\bar{1}10) = x$ -direction. These SDR measurements, performed at the 5×1 reconstructed surface, exhibited features at 3.2 and 3.8 eV similar to the photon energy positions in fig. 2. In the geometric reconstruction model of the Si(110) surface proposed by Wormeester and Keim (WK) [17,18] these optical transitions are assigned to originate from a filled state at about 2.4 eV below the Fermi level. This filled state was originally measured with UPS by Mårtenson et al. [19] on the 5×1 reconstructed surface as well as on the so-called X-faceted surface, the latter reconstruction was identified as $\langle 17\ 15\ 1 \rangle$ planes. It has been shown that this is the same as the 16×2 reconstruction. As reported by Mårtenson et al. [19] the main features of the 5×1 and X-structure at binding energies larger than 1.5 eV are comparable.

The WK model was developed for the Ni induced family of reconstructions. The 16×2 reconstructed surface used in this experiment, is in contrast to this family dominated by the formation of up and down terraces as resolved by RHEED [13] and is not based on missing rows in the (001) direction. In addition STM measure-

ments [20,21] and the models proposed by Ampo et al. [22] derived from their LEED measurements, make a reconstruction on the basis of missing chains and the related structures of adatoms and rest-atoms questionable for the 16×2 case. However, the next nearest rows thought to be responsible for the filled state at 2.4 eV in the WK model are present on the 16×2 surface. The absence of the missing chains on the 16×2 reconstruction and accordingly of the structure of rest-atoms as proposed by WK, also explains the almost zero change of the anisotropy in the low photon energy range (< 2.4 eV) as also UPS [19] measurements show a filled surface related feature at 0.8 eV, which in the SDR measurements [19] are thought to be the origin of the low photon energy transitions. Moreover the UPS measurements presented were taken for \vec{k} parallel to the $\bar{1}10$ direction, in which direction the feature at a binding energy of 2.4 eV clearly disappeared upon coverage of the clean 5×1 reconstructed surface with hydrogen. The largest change of the reflection in the $(\bar{1}10)$ direction as derived from fig. 2 is consistent with these UPS measurements.

4. Change in $\cos(\Delta)$ upon oxidation

Upon oxidation of the Si(110) surface no change in the phase shift $\cos(\Delta)$ could be recorded. This means that the changes in phase shift in the optical region studied is less than the S/N ratio of 10^{-4} . An estimate of the expected phase shift in $\bar{\rho}$ can be obtained using the Kramers-Kronig relation between the amplitude and phase of the complex reflection, i.e., the pair $\tan(\Psi)$ and Δ [23] as a function of the photon frequency ω :

$$\begin{aligned} \Delta(\omega) &= \frac{2\pi}{\omega} \\ &\times \int_0^\infty \frac{\ln[\tan(\Psi(\omega'))] - \ln[\tan(\Psi(\omega))]}{(\omega')^2 - \omega^2} d\omega' \\ &= J(\tan(\Psi)). \end{aligned} \quad (5)$$

With $\delta(\tan(\Psi)) = \tan(\Psi_{cl}) - \tan(\Psi_{ox})$, the expected change in Δ is, ($\tan(\Psi_{ox}) \approx 1$)

$$\begin{aligned} \delta\Delta &= \Delta_{cl} - \Delta_{ox} \\ &= J(\tan(\Psi_{ox}) + \delta(\tan(\Psi))) - J(\tan(\Psi_{ox})) \\ &= J(\delta(\tan(\Psi))). \end{aligned} \quad (6)$$

Therefore the calculated value of $\delta\Delta$ depends only on the difference in phase of the clean and oxidized surface. At the low photon energy side an extrapolation to the isotropic value of $\delta(\tan(\Psi))$ is made as necessary in the calculation and shown in fig. 2. The usual problem in evaluating the integral J is the asymptotic continuation in the high energy region, where experimental data are not available. We have evaluated several possibilities, but none of them affected the structure of Δ . The height of Δ however may change considerably due to the shape of the extrapolation. A maximum value of the height of the change in phase shift upon oxidation is determined by extrapolating the $\delta(\tan(\Psi))$ curve at the maximum change of $\delta(\tan(\Psi))$ observed ($\sim 1.5 \times 10^{-3}$). In fig. 3 Δ is presented when $\delta(\tan(\Psi))$ is in this way extrapolated upto 100 eV, which is a good indicator for the maximum possible change in Δ . From this it is clear that the maximum change in Δ (0.08°) expected is well below the detection limit of 0.6° of the experimental configuration used.

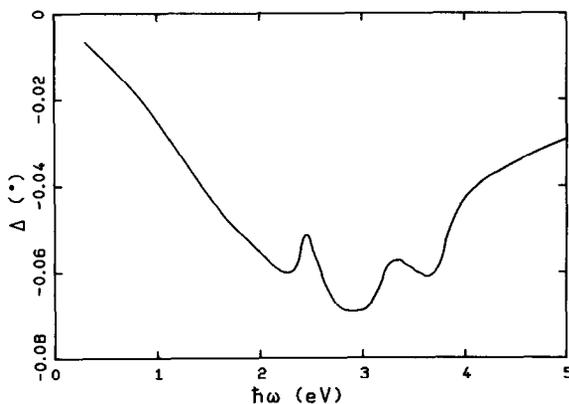


Fig. 3. Difference in Δ as a function of photon energy ($\hbar\omega$) as obtained from a Kramers–Kronig transformation of the difference in $\tan(\Psi)$ of fig. 2.

5. Conclusion

Summarizing, the reflectance anisotropy of the Si(110) 16×2 surface changes upon oxidation, although the changes are small in the photon energy region studied. The virtue of this method is that intensity fluctuations are compensated automatically. The surface principal axes are unambiguously identified (no change in the ellipsometric parameters). The normal incidence ellipsometer provides not only the change in reflection amplitude, but also the phase between the two components. The features observed in the change of the amplitude ratio correspond in energy position to the transitions observed with SDR on the 5×1 reconstructed surface above 2.5 eV, and are probably due to a transition from a filled state at 2.4 eV, which was resolved with UPS. The largest change in reflectivity of the Si(110) surface is observed in the $(\bar{1}10)$ direction. A change in phase shift upon oxidation was not recorded and by using Kramer–Kronig relations it was shown that the phase shift expected is well below the detection limit.

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