First-principles optical-response calculations of oxidized and strained Si structures are presented. Local Si lattice deformations accompanying the oxidation of Si bulk bonds cause pronounced optical anisotropies that account very well for the reflectance difference signal measured during oxide growth [Yasuda et al., Phys. Rev. Lett. 87, 037403 (2001)]. In contrast, calculations for various energetically favored (4 × 2) and (2 × 2) reconstructed overlayer structures fail to reproduce the experiment.

DOI: 10.1103/PhysRevB.72.075353 PACS number: 78.68.+m, 78.66.Db, 81.65.Mq

II. METHODOLOGY

The calculations are performed using the Vienna \textit{ab initio} simulation package (VASP) implementation\textsuperscript{10} of the gradient-corrected\textsuperscript{11} density functional theory (DFT-GGA). The electron-ion interaction is described by the projector augmented-wave (PAW) method.\textsuperscript{12,13} We expand the valence wave functions into plane waves up to an energy cutoff of 30 Ry. The Si(001) surface is modeled with symmetric, periodically repeated supercells consisting of 12 atomic Si layers including oxidized layers and a vacuum region equivalent in thickness to eight atomic layers. Sets corresponding to 64 and 256 \textit{k} points in the full \((1 \times 1)\) surface Brillouin zone are used to calculate the ground-state electronic structure and the optical response, respectively. In order to avoid an artificial bias due to the \textit{k}-point set for the calculation of the strained Si sample, we employed 200 000 random points in this case. The reflectance anisotropy is calculated according to the scheme devised by Del Sole\textsuperscript{14,15}

\[
\frac{\Delta r_i}{r} (\omega) = \frac{8 \omega \pi}{c} \text{Im} \left\{ \frac{\sigma_i^{\text{th}}(\omega)}{\epsilon_i(\omega) - 1} \right\},
\]

where the slab polarizability \(\alpha\) and the bulk dielectric function \(\epsilon_b\) are obtained in independent-particle approximation, i.e., neglecting excitonic and local-field effects.\textsuperscript{16}

In order to actually compute the polarizability, momentum matrix elements \(p_{NM} = \langle \Psi_N | \hat{p} | \Psi_M \rangle\) between \(M\)th and \(N\)th electron state need to be calculated. In the PAW method the all-electron wave functions \(\Psi_N\) are related to pseudo-wave functions \(\tilde{\Psi}_N\) by means of the linear transformation\textsuperscript{12,13}

\[
|\Psi_N\rangle = |\tilde{\Psi}_N\rangle + \sum_i \left( |\psi_i\rangle - |\tilde{\psi}_i\rangle \right) (\tilde{p}_i |\Psi_N\rangle),
\]

where the index \(i\) denotes atomic site, the angular momentum quantum number and the reference energy of the all-electron and pseudo atomic partial waves \(\psi_i\) and \(\tilde{\psi}_i\). The projectors \(\tilde{p}_i\) are dual to the pseudo partial waves. Accordingly, we calculate the momentum matrix elements using the expression\textsuperscript{17,18}

\[
p_{NM} = \langle \tilde{\Psi}_N | \hat{p} | \Psi_M \rangle + \sum_{i,j} \langle \tilde{\Psi}_N | \tilde{p}_i \rangle (\psi_i | \hat{p} | \psi_j) - (\tilde{\psi}_i | \hat{p} | \tilde{\psi}_j) (\tilde{p}_i | \Psi_M \rangle).
\]

The scissors operators\textsuperscript{19} with an energy shift of 0.5 eV is used to account for the band-gap underestimation in DFT. RDS spectra are difference spectra, which are furthermore
normalized to the bulk dielectric function [Eq. (1)]. Therefore, calculations within the independent-particle approximation reliably reproduce experimental data for a wide range of semiconductors.20,21

Extensive tests on the slab dimensions, the number of \( k \) points and the basis set size were performed to ascertain the numerical reliability of our calculations.22

III. RESULTS AND DISCUSSION

To model the initial stage of Si\((001)\) surface oxidation, we consider energetically favored surface structures (cf. Fig. 1) where oxidation occurs in the uppermost and the second Si surface layer. For these structures we determine adsorption energies with respect to spin-triplet atomic oxygen that are very close to the values predicted in Ref. 23. To be specific, the adsorption energies per oxygen atom obtained here are always 0.1–0.2 eV lower than those calculated by Yamasaki et al.23 The calculated RDS spectra of the structures used to model the oxidation of the uppermost atomic layer together with our results for the clean Si\((001)c(4 \times 2)\) surface are shown in Fig. 2. The optical anisotropy of the clean surface shows a strong, dimer-state related minimum for photon energies of 1.7 eV.4,24 The measured spectra for oxidized Si\((001)\) show little anisotropy for energies below 2.5 eV.2

The 1.7 eV feature is quenched, due to the saturation of the Si-dimer states. Submonolayer oxidation at room temperature leads to an overall positive anisotropy signal, apart from a small negative feature near the \( E_1 \) CP (cf. 298 K spectrum in Fig. 2). Of all the low-coverage structures considered here, i.e., models 1A-1F, only models 1E and 1F show a remotely similar feature in the calculated RDS.

Oxidation at about 1000 K for 8 s changes the measured spectrum, giving rise to positive anisotropies for all photon energies considered, with maxima close to the \( E_1 \) and \( E_2 \) CPs and at about 5.3 eV (cf. uppermost curve in Fig. 2). Yasuda et al.2 assigned this spectrum to the complete oxidation of the first atomic monolayer. Of all the structures investigated computationally, only 1G gives rise to an optical anisotropy that is positive throughout the photon energy range probed. The simulated RDS spectra in comparison with experiment thus support earlier findings25 indicating that the backbonds of the lower Si dimer atom are attacked first by oxygen, before it is inserted into the remaining Si-Si bonds at the surface. However, the deviations in line shape between the calculated spectra and the data measured for room and high temperature oxidation are considerable. Obviously, at no

FIG. 1. Top view of the models used to describe oxidation of the first (1A–1G) and the uppermost two Si\((001)\) layers (2A–2E). Dark and grey symbols indicate O and Si atoms, respectively. Small arrows indicate O atoms hidden below Si atoms.

The calculated positions of the \( E_1 \) and \( E_2 \) energies are indicated.

FIG. 2. RDS spectra \([\text{Re}((\eta_{110}−\eta_{110})\eta_{\bar{r}})]\) calculated for the oxidized Si\((001)\) configurations shown in Fig. 1 are compared with results for the clean surface and measured data from Ref. 2. The calculated positions of the \( E_1 \) and \( E_2 \) energies are indicated.

075353-2
time during the oxidation the surface is completely ordered with a symmetry corresponding to one of the structural models probed here.

The calculated RDS spectra for models where both the first and the second Si layer are oxidized are compared with the experimental data assigned to the oxidation of the second monolayer in Fig. 3. Experimentally, nearly an inversion of the signal is observed, compared to the spectrum assigned to the oxidation of the first monolayer. This inversion occurs repeatedly during the progression of the oxidation. Negative anisotropies occur for photon energies close to the Si bulk CPs and above 4.5 eV. Clearly, none of the calculated spectra reproduces the overall negative anisotropy, strong deviations from experiment occur in all cases.

High-energy electron diffraction data and scanning tunneling microscopy images of Si(001) surfaces exposed to oxygen indicate that the oxidation causes considerable surface disorder. Therefore, it may be questionable to model the Si surface oxidation with translationally invariant models such as shown in Fig. 1, in particular when optical spectra are averaged over a large part of the sample surface. In addition, the repeated oscillations of the RDS signal during Si oxidation seem hardly compatible with an effect originating from ordered surface structures.

Bulk Si is optically isotropic. If the disorder of the oxide film above the interface would render this film optically isotropic too, the only source of optical anisotropy were oxygen atoms inserted into Si-Si bulk bonds directly at the interface. We model this effect by studying the optical anisotropy induced by oxygen inserted into bulk Si bonds. For compatibility with the surface calculations, we use an orthorhombic supercell with $2 \times 2 \times 20$ periodicities along the $[\bar{1}10]$, $[110]$, and $[001]$ directions, respectively. (Test calculations with $4 \times 2 \times 20$ and $1 \times 1 \times 20$ periodicities resulted in similar features as discussed below.) The difference of the calculated bulk polarizability components is normalized such as to compare with the reflectance anisotropy from Eq. (1). The results are shown in Fig. 4. They show that oxygen inserted into Si-Si bonds in the $[\bar{1}10]$ plane indeed reproduces the features measured after oxidation of the first monolayer, whereas the oxidation of the second monolayer can be modeled by calculations for oxygen inserted into bulk bonds in the $(110)$ plane (the sign change is obvious for symmetry reasons). Given the simplicity of this idealized model, the agreement between calculation and measurement is impressive. Obviously, the measured RDS oscillations can be explained by assuming that (i) the oxidation occurs layer-by-layer and (ii) the silicon oxide directly above the abrupt interface does not contribute substantially to the optical anisotropy. Figure 4 shows that the simple interface model accounts better for the 2 ML experiment than for the 1 ML signal. This indicates the decrease of the RDS contributions from ordered surface structures with increasing oxide thickness.

After having reproduced the experimental data, we analyze the origin of the measured anisotropies in more detail. Yasuda et al. pointed out that their data cannot be explained by model calculations using the Si piezo-optic tensor. On the other hand, earlier measurements of the Si-SiO$_2$ interface...
optical properties have often been interpreted in terms of strain-induced shifts of the Si bulk CP energies.\textsuperscript{27–29} We perform model calculations for four layers of bulk Si uniformly compressed by 2\% along [\text{110}], a value that roughly accounts for the lattice deformation around an oxygen atom inserted into a Si(001) (2 $\times$ 2) interface unit cell. As seen from the inset of Fig. 4, the optical anisotropy induced by such a macroscopic strain has the same sign and roughly the same magnitude as the measured signal, but does not reproduce the line shape. Therefore, either specific Si-O bond distances are somewhat similar to the oxygen inserted case. This indicates that strain-perturbed Si bulk wave functions cause the optical anisotropy. However, it is important to account for the local deformation pattern around the defect. An uniform compression such as assumed by Yasuda and co-workers\textsuperscript{2} indeed does not explain the measurements. Figure 5 illustrates the complexity of the Si bulk deformation around an oxidized Si bond.

IV. SUMMARY

In conclusion, we calculated the atomic geometries and optical response of a large number of oxidized Si(001) surface structures as well as oxidized and strained silicon bulk systems from first principles. Comparison of the simulated optical spectra with experiment indicates that the oxidation-induced local strain pattern is causing the measured oscillations of the optical anisotropy in one-to-one correspondence to the layer oxidation, while the oxide layers directly above the interface, due to their disorder, contribute relatively little to the optical anisotropy.

ACKNOWLEDGMENTS

We thank Tetsu Yasuda for suggesting this project and critically reading the manuscript as well as Kaori Seino for numerous discussions. Grants of computer time from the Leibniz-Rechenzentrum München and the Höchstleistungsschwerpunkt Stuttgart are gratefully acknowledged. Financial support was provided by the Deutsche Forschungsgemeinschaft (SCHM-1361/6) and the EU Network of Excellence NANOQUANTA (Contract No. NMP4-CT-2004-500198).

\textsuperscript{1} J. Dabrowski and H.-J. Müßig, \textit{Silicon Surfaces and Formation of Interfaces} (World Scientific, Singapore, 2000).
\textsuperscript{11} J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R.