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Isotropic and anisotropic contributions to the optical reflection of Si(001)-2×1

H. Wormeester, D. J. Wentink, and A. van Silfhout
Solid State Division, Centre for Materials Research, University of Twente, The Netherlands

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Optical properties of the outermost layer of clean Si and Ge surfaces are different from the bulk, and can be changed by chemisorption. We show that on Si and Ge(001), in contrast to O_2, H is not capable of removing completely the optical activity of the outermost layer as usually is assumed. By ellipsometric measurements both near Brewster's angle and at normal incidence, we are able to separate surface dielectric tensor components parallel and perpendicular to dimers on clean Si(001). The tensor components consist of at least two parts: a large isotropic part and a much weaker anisotropic part. The isotropic part can be represented by an attenuation of the bulk dielectric function. [S0163-1829(97)02131-0]

A remarkable abnormal behavior of the change in optical reflection from clean Si and Ge surfaces upon gas exposure was observed by Bootsma and Meyer three decades ago.[1] Instead of the expected growth of a chemisorbed layer, their measurements revealed a surface layer with dielectric properties different from the semiconducting bulk. Later, the change in optical reflection of both Si and Ge surfaces upon gas adsorption was recorded.[2–8] Early work was seriously hampered by imperfect cleaning of the surface, leaving C and O on the presumably clean surface. Dielectric properties of the outermost surface layer were attributed to surface states present at the clean surface. The intuitive picture of optical transitions between surface states was challenged recently by Kelly, Zollner, and Cardona,[7] who pointed out that spectra obtained from differently oriented surfaces are quite alike, despite the difference in surface states. The surface dielectric function was interpreted as a surface-modified bulk dielectric function. However, a theoretical explanation from first principles of this effect is still lacking. Theoretical and experimental difficulties of standard optical measurements have led to investigations of optical anisotropy of semiconductor surfaces. The anisotropy is attributed to the reconstruction of the surface. The capability of anisotropy measurements[3] was demonstrated with the confirmation of Pandey's[9] chain model of the reconstruction of the Si(111)-2×1 surface. More recently, optical anisotropy measurements of Si(110),[10] Ge(001),[11–13] and Si(001) (Refs. 13–15) surfaces have been reported.

In this paper we will show that the optical anisotropy of clean Si(001) reflects only a part of the surface dielectric function. Surface optical properties are dominated by an isotropic part which is independent of the actual reconstruction. Absorption of H and O_2 leads to different results, showing that probably H either does not remove or introduces optical properties on the semiconductor surface.

The experiments were performed in an UHV system with base pressure below 10^{-8} Pa. Two different Si(001) substrates were used: one nominal (001)-oriented (10^{13} B/cm^3) and the other 4.4±0.2° toward [110] (10^{15} B/cm^3). The clean reconstructed surfaces of these substrates show two orthogonal domains or a single domain orientation of the dimers, respectively. A nominally oriented Ge(001) substrate was also used (10^{14} P/cm^3). Before and after introduction in the UHV chamber, the samples were carefully cleaned. At pressures above 10^{-7} Pa, heating to 600 K and above led to irreversible changes of the Si(001) surfaces, identified as facet formation due to etching.[16,17] Also, the flash heating cleaning procedure at low temperatures gives identical irreversible changes,[18] eventually resulting in lower optical signals. In our sample cleaning, we used sputter anneal cycles for cleaning the surface.[16,17]

The optical reflection was monitored with a rotating polarizer ellipsometer, operated in the 1.5–5-eV photon energy region. This instrument can be used for measurements near Brewster's angle of incidence (70°) and at normal incidence for isotropy and anisotropy measurements, respectively, and is described elsewhere.[16,19] Changes in $\tan(\Psi)$ and Δ are measured. They are related to the change in complex reflectance ratio $\rho = r_p / r_s$ before and after gas exposure of the clean surface, r_p and r_s being the reflection parallel and perpendicular to the plane of incidence, respectively,

$$\frac{\rho_{\mathrm{cl}}}{\rho_m} = [1 + \delta \tan(\Psi) e^{i\delta\Delta}]. \tag{1}$$

The indices cl and m refer to the clean and modified surface. At normal incidence, r_p and r_s are along the $[1\bar{1}0]$ and [110] azimuth, respectively.

Values of $\delta \tan(\Psi)$ near Brewster's angle for exposure of clean Si(001) and Ge(001) surfaces to O_2 and H are shown in Fig. 1. Also, measurements at normal incidence for Si(001) are shown. Measurements near Brewster's angle were performed on the two-domain surface. Hence one averages from both domains in the surface dielectric function. The single-domain sample was used for measurements at normal incidence, and provides the anisotropy of the surface dielectric function. These figures show that near Brewster's angle there is a difference between the adsorption of O_2 and H. Between 1.5 and 3 eV, Si(001) shows a difference in curvature. For oxidized Ge(001), a clear negative signal is observed at 2.5 eV as well as a smaller signal between 3 and 3.5 eV. At normal incidence, the anisotropy spectrum of Si(001) shows an additional peak at 3.8 eV for H. Both oxidation and hydrogenation of semiconductor surfaces have been used for removing the optical activity of the clean surface.[2–8] The chemisorbed layer was considered to have negligible activ-

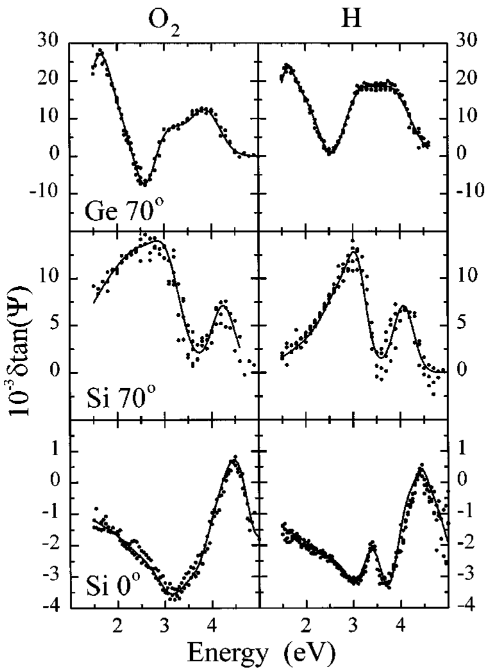

FIG. 1. The change in tan(Ψ), e.g., $\delta\tan(\Psi)$, upon oxidation and hydrogenation of double domain Ge(001)-2×1 at Brewster's angle (70°) and for double and single domain Si(001)-2×1 at Brewster's angle and at the normal angle of incidence respectively.

ity, and a bulk-terminated surface was expected after exposure. Our measurements clearly show that at least exposition to either O_2 or H does not completely remove the optical activity of the surface layer. By comparing the results at normal incidence with anisotropy measurements made during ion sputtering, we found that anisotropy can be completely removed by oxygen exposure for both Si (Ref. 17) and Ge.[12] This suggests that exposition to H does not lead to an optically bulk-terminated Si or Ge surfaces, and puts into question experiments which neglected residual optical activity after hydrogenation.[7] Although no direct proof exists that oxidation renders an optically bulk-terminated surface, we believe that this is most likely the case. Pinning of the Fermi level at the surface is removed,[20] and ultraviolet photoelectron spectroscopy also shows no occupied levels in the energy range contributing to the optical spectrum.

The change in anisotropy upon oxidation can be compared with reflectance difference spectroscopy data of Yasuda *et al.*[13] However, features might be different, as they reported a gradual change in optical anisotropy after sample cleaning. A gradual hydrogen contamination of the surface was suggested. This is probably true, because, after oxidation on the surface, they could still see a 2×1 low-energy electron-diffraction pattern. In many diffraction experiments performed after oxidation of Si(001)-2×1, no reconstruction of the surface has been observed by us. Also, a large discrepancy in size is observed as compared with measurements by Yasuda *et al.*[13] Both hydrogen contamination and the smaller misorientation angle of the Si substrate may be the reason for this, as a larger misorientation angle yields a more single-domain surface. Compared with the work of Kipp *et al.*,[14] we observe an identical spectrum. The difference in height can again be attributed to the amount of single-domain surface area.[16,17]

The interpretation of measured surface optical spectra is usually done by calculating the surface dielectric function, using a so-called three-layer model.[21] The clean surface is represented by a semi-infinite bulk crystal, a thin layer with thickness d representing the surface properties, and the vacuum forms the third layer. After oxidation, only the semi-infinite bulk crystal remains effectively a two-layer model. After hydrogenation the surface still shows optical activity, i.e., a three-layer situation. However, we can calculate the dielectric function of the H-terminated surface by using oxidation measurements, since in our experiments we measure the ratio of the complex optical reflectance ρ before and after chemisorption [Eq. (1)]:

$$\frac{\rho_{\mathrm{H}}}{\rho_{\mathrm{O}_2}}=\frac{\rho_{\mathrm{H}}}{\rho_{\mathrm{cl}}}\frac{\rho_{\mathrm{cl}}}{\rho_{\mathrm{O}_2}}. \tag{2}$$

Dielectric properties of the surface layer, the so-called surface excess, can be calculated according to Ref. 7 as

$$\left(\frac{\rho_{123}}{\rho_{13}}-1\right)\frac{i\hbar c}{2eE}\,\frac{\varepsilon_B-1}{\cos(\theta)}=\frac{\varepsilon_B}{\dfrac{\varepsilon_B}{\tan(\theta)^2}-1}\,d\Delta\varepsilon^{\mathrm{iso}}+d\Delta\varepsilon^{\mathrm{an}}. \tag{3}$$

Here, ρ_{123} and ρ_{13} represent the complex reflectance ratio of clean or hydrogen-covered surfaces and the oxidized surface, respectively. θ is the angle of incidence and the dielectric function of the Si bulk, and ε_B is taken from Aspnes and Studna.[22] At normal incidence, the term preceding the isotropic surface excess $d\Delta\varepsilon^{\mathrm{iso}}$ vanishes, and only the anisotropic component $d\Delta\varepsilon^{\mathrm{an}}$ remains. In our setup, the anisotropic surface excess measured at single-domain samples equals the difference in dielectric tensor components parallel to the surface:

$$d\Delta\varepsilon^{\mathrm{an}}=d(\varepsilon_{[110]}-\varepsilon_{[\bar{1}10]}). \tag{4}$$

Near Brewster's angle, the term preceding the isotropic surface excess makes this term dominant. As we have used a two domain sample for measurements near Brewster's angle, the isotropic surface excess is denoted as

$$d\Delta\varepsilon^{\mathrm{iso}}=d\left(\frac{\varepsilon_{[110]}+\varepsilon_{[\bar{1}10]}}{2}-\varepsilon_B+\varepsilon_B(\varepsilon_{[001]}^{-1}-\varepsilon_B^{-1})\right). \tag{5}$$

Both isotropic and anisotropic surface excesses are shown in Fig. 2. Clearly, for the clean surface, the isotropic and anisotropic surface excess are of equal strength, despite large differences in δ tan(Ψ). In fact, the isotropic spectrum mimics $|d\Delta\varepsilon^{\mathrm{an}}|$, with features at energies of bulk characteristic points.[22] This suggests a model in which the features are due to light absorption in the [110] ([$\bar{1}$10]) direction at 3.2 eV (4.1 eV), i.e., perpendicular and parallel to the dimer direction, respectively. The two critical points for semiconductors with a diamond lattice have been assigned to absorption in two perpendicular bond directions.[23] This would also explain the qualitative resemblance between the isotropic surface excess and the bulk dielectric function. However, for the hydrogen-covered surface, the isotropic signal has become quite small, in contrast to the anisotropic part. The idea of absorption in two orthogonal directions parallel to the sur-

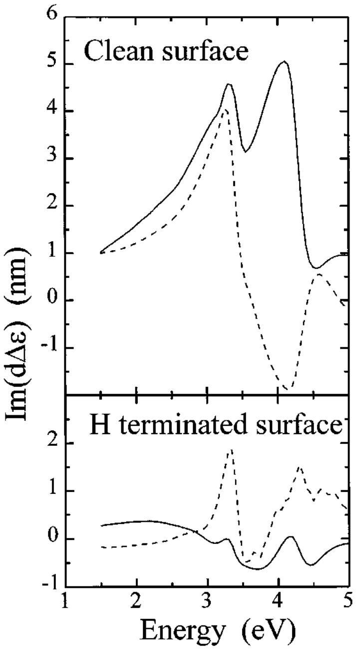

FIG. 2. The isotropic (solid line) and anisotropic (dashed line) surface excess of clean Si(001)-2×1 and H-terminated Si(001).

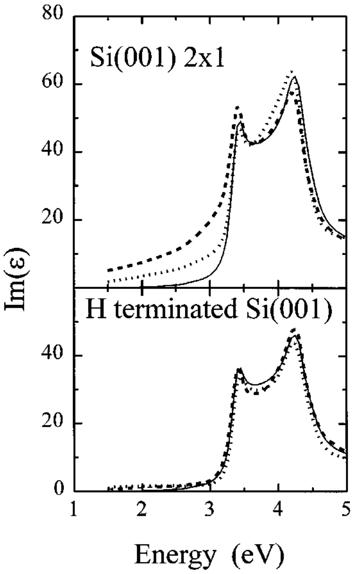

FIG. 3. (a) The dielectric function of the surface layer of a clean Si(001)-2×1 surface, in the [110] (dotted line) and [110] (dashed line) directions. Also, the bulk dielectric function is shown (solid line), multiplied by $\alpha = 1.35$. (b) H-terminated surface, [110] direction (dotted line), and [110] direction (dashed line). The bulk dielectric function (solid line) is shown for comparison. For both spectra a thickness of $d = 3$ Å for the surface layer was used.

face fails to describe the H-passivated surface. The presence of a large anisotropy on H-terminated Si(001) is not surprising. Although dimers present on the clean surface are removed with H, the H-Si-H bond and the dimer direction are in the same plane, and an anisotropic surface remains after H exposure. Near Brewster's angle, only isotropic properties are probed, which have almost completely been removed.

The surface excess has been computed since the surface layer thickness is unknown, and the three orthogonal components of the surface dielectric function cannot be evaluated separately. However, as already noted, the isotropic surface excess shows a large resemblance with the bulk dielectric function, as was also noted in Ref. 7. If the three orthogonal components of the surface dielectric function also have a large resemblance to the bulk dielectric function, the contribution of the term containing $\varepsilon_{[001]}$ to the isotropic surface excess becomes negligible. It is then possible to extract the two surface dielectric tensor components parallel to the surface by combining Eqs. (4) and (5). The thickness of the surface layer is set at 3 Å. Other values do not change line shapes or relative intensities. The dielectric function component parallel and perpendicular to the dimer bond can be determined from the combination of the normal incidence and near Brewster's angle measurement. Separately, they only give a differential or averaged dielectric function [see Eqs. (4) and (5)], but not the component itself. Figure 3 shows dielectric tensor components in the [110] and $[\bar{1}10]$ directions for clean and H-covered Si(001). This shows that the surface dielectric function looks quite like ε_B. The two orthogonal components of the H-terminated surface are about equal to ε_B, implying that both oxidized and hydrogenated surfaces show the same isotropic optical behavior. The difference between the dielectric tensor components in the two orthogonal directions is dwarfed by the common isotropic part for both clean and hydrogen-terminated surfaces. The idea of two different light absorption directions fails to provide an explanation for the observed isotropic and anisotropic optical reflection behavior. Instead, the surface dielectric function of the clean surface in a direction i parallel to the surface can be well represented by $\varepsilon_i = (1+\alpha)\varepsilon_B + \delta\varepsilon_i$. The isotropic part shows an enhanced optical density compared to the bulk dielectric function by a factor $\alpha \approx 0.35$ for $d = 3$ Å, while the anisotropy is introduced by an additional factor $\delta\varepsilon_i$. Both oxidation or hydrogenation of the Si(001) surface remove the enhanced optical density α. In contrast, the anisotropic part is removed by oxidation (as established from the resemblance in anisotropy spectrum of the oxidized and Ar^+-sputtered surface), while hydrogenation only modifies the anisotropic part, but is incapable of removing it. This implies that at least two processes are active in the optical response of semiconductor surfaces. The study of the anisotropy effect alone, cannot explain the behavior observed by Bootsma and Meyer.[1]

The existence of two processes at semiconductor surfaces, leading to isotropic and anisotropic optical behavior, is not surprising. On metal surfaces, a difference in the electronic structure in two orthogonal directions at a surface will lead to anisotropic reflection phenomena. However, ellipsometric changes observed upon oxidation of Cu(001) can only be explained by growth of a CuO layer.[24] A clean surface layer with different optical properties cannot be observed. These experiments on metal surfaces also make an explanation of the surface optical effect in terms of surface states unlikely, since these are also present on Cu and Ag(111) and (001).[25] A comparison with a metal like Cu can be quite illustrating because in the optical region, the metallic Drude contribution plays only a minor role.

Figure 3 shows that the enlarged optical density at the surface can be described by an attenuation of the bulk dielectric function with a factor α, i.e., the critical points of Si play a prominent role. An increase of the thickness of the layer d reduces α, but the shape remains the same. The total difference in optical density obtained from integrating the excess dielectric function from the surface down to the layer thickness d, given by αd, remains the same. The anisotropy is related to the bulk dielectric function as its intensity is increased at 3.4 eV and decreased at 4.2 eV for the [110] direction, and vice versa for $[\bar{1}10]$. The large influence of critical points also explains the resemblance between optical spectra taken at semiconductor surfaces with different crystal orientations.[7] The mechanism behind the isotropic part, the enhanced dielectric function (α) for the clean Si surface remains unclear. The different behavior of semiconductor and metal surfaces points to a semiconductor characteristic effect, like the Franz-Keldysh effect,[26] although the strength of this effect is a factor 10 too small. However, such a nonlinear effect would explain the vanishing of the isotropic contribution upon oxidation or hydrogenation, and the noted resemblance with surface conduction measurements.[5,20] Also the strong peak in the anisotropic dielectric function of Ge(001) after exposure to N_2O (Ref. 12) is exactly at a critical point, and has a large resemblance to electroreflectance measurements performed on Ge(001).[27]

In summary, we have shown that oxidation and hydrogenation of clean Si(001)-2×1 leads to optically different responses. Measurement at both normal incidence and near Brewster's angle is necessary for obtaining the surface dielectric function parallel or perpendicular to the dimer bond. The total optical response of a surface layer has to be divided into two parts: an isotropic part that shows an enhanced optical density that explains the observation of Bootsma and Meyer,[1] and a surface-structure-related anisotropic part. The isotropic part of the surface dielectric function is removed by both exposure to O_2 and H for Si(001). For the Ge(001)-2×1 surface we even found a substantial isotropic optical activity after H exposure. The anisotropic part of the dielectric function is only modified upon H exposure. This result indicates that exposure to H cannot be used for obtaining optically bulk-terminated semiconductor surfaces. In a theoretical calculation of the optical response of semiconductor surfaces, both components will have to be considered.

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