Surface states of the clean and oxidized Ge(001) surface studied with normal-incidence ellipsometry

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With an optical probe, the anisotropy in the electronic structure of the clean, single-domain Ge(001)2×1 surface was studied by recording the change in optical response upon either adsorption of molecular oxygen or upon Ar^+-ion bombardment. Both methods were shown to result in an optically isotropic surface. It was possible to associate the measured surface dielectric function with the energy positions and wave-function parities of the occupied and unoccupied surface states known on the clean surface. The unoccupied D_{down} state has been observed experimentally and it is positioned 0.4 eV above the Fermi level. Comparing the changes in the anisotropy of the surface electronic structure upon O_2 and N_2O saturation exposure, it has been possible to deduce an unoccupied state at 0.7 eV above E_F on the monolayer oxygen-covered surface after N_2O exposure. This state is assigned to a bridge bond between germanium and oxygen atoms in the first layer. Furthermore, we present evidence that in the initial stage of molecular-oxygen adsorption one of the two oxygen atoms is immediately incorporated in a subsurface position.

I. INTRODUCTION

A. Optical response of surfaces

Since the construction of the ellipsometer,[1] this technique has provided a useful tool in the study of bulk and surface material properties. Using ellipsometry, Meyer[2] provided an indication about the electronic structure of Ge(001)2×1; an optical transition between an occupied and an unoccupied surface state at 1.7 eV was found. More recently, Zandvliet and co-workers[3,4] performed measurements over a wider energy range and reported transitions around 3 eV. Nevertheless, linear optical techniques have had only limited application in surface science, mainly for two reasons. First, the large penetration depth of light compared to the thickness of the actual surface gives a response of mainly bulk character. Modification of the surface by gas adsorption, as done by Meyer[2] and Zandvliet and co-workers,[3,4] provides an actual sampling depth for linear optical methods down to a few monolayers. In this article, the problem of the large penetration depth is overcome with a technique which is only sensitive to the anisotropy induced by a surface or interface upon an isotropic bulk. Second, the interpretation of the optical signal is not straightforward. Neither direct chemical information nor direct energy positions of surface states can be determined. Our experiments firmly establish that features of atomic scale at the surface influence the macroscopic optical response. The applicability of optical methods in surface science has been demonstrated further in the unraveling of the Si(111)2×1 surface reconstruction.[5] For III-V compound semiconductors, Aspnes and Studna[6] showed the anisotropy change during growth, going from a gallium top layer to an arsenic top layer. These experiments clearly demonstrated the scientific and technological importance of optical techniques as a nondisturbing monitor of *in situ* deposition processes.

In order to unravel further the surface-induced optical response, we studied one of the simplest known reconstructed semiconductor surfaces, the 2×1 reconstruction of Ge(001). It is characterized by parallel dimers aligned in rows,[7] as depicted in Fig. 1(a). The orientation of these dimers on the surface results in an electronic structure which is different in the directions parallel and perpendicular to the dimer bonds. Using a vicinal surface with a misorientation of 5° towards the (110) direction, double steps are found on the surface. This assures a macroscopically anisotropic surface. The electronic states associated with the Ge(001)2×1 surface reconstruction are characterized by both their symmetries and their energies relative to the Fermi level. In this experiment we probe the symmetries and energies of these states through the difference in the complex reflection coefficient parallel and perpendicular to the dimer bond. The results allow us to make a firm connection between the optical
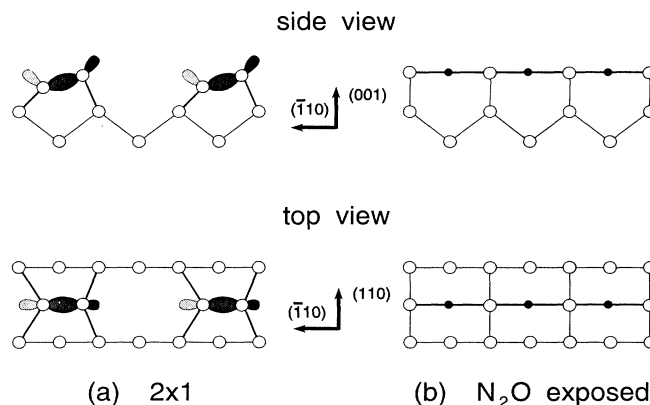
side view

top view

(a)   2x1   (b) N_2O exposed

FIG. 1. Side and top view of (a) clean Ge(001)2×1 and (b) the same surface after exposure up to saturation coverage with N_2O. Open circles are germanium atoms, filled circles represent oxygen atoms.

response of a surface, surface states predicted theoretically, and those observed with ultraviolet-photoelectron spectroscopy (UPS) and scanning tunneling microscopy (STM).

B. Normal incidence ellipsometry

In "classical" ellipsometry, with light incident at Brewster's angle, the reflection of s and p polarized light is compared. In such an experimental setup, the p polarized light has a component perpendicular to the surface and will hence be influenced by the component of the dielectric function in this direction. By measuring at normal incidence, we can eliminate this influence on the optical signal and concentrate on the anisotropy in the dielectric function parallel to the surface. The difference in reflection for the two polarization directions of light (s and p in classical ellipsometry) is replaced by the difference in optical reflection coefficient of light ($\tilde{r}$) polarized in the $(\bar{1}10)$ and (110) directions on Ge(001). This anisotropic optical reflection is described by the complex anisotropic reflection ratio $\tilde{\rho}$ according to

$$\tilde{\rho} \equiv \frac{\tilde{r}^{(\bar{1}10)}}{\tilde{r}^{(110)}} \equiv \tan(\Psi)e^{i\Delta} \ . \tag{1}$$

Because the anisotropy in the optical reflection at the surface is relatively small, we recorded the optical anisotropy change due to a modification of a clean Ge(001)2×1 surface. Such a measurement of a difference signal eliminates unknown influences of nonperfect components in the ellipsometer setup,[8] inherent to absolute measurements. The optical anisotropy change upon modification (mo) of the clean (cl) surface is given by

$$\frac{\tilde{\rho}_{cl}}{\tilde{\rho}_{mo}} = \frac{\tan(\psi_{cl})}{\tan(\psi_{mo})}e^{i(\Delta_{cl}-\Delta_{mo})} \equiv [1 + \delta \tan(\psi)]e^{i\delta\Delta} \ . \tag{2}$$

This technique for measuring surface-induced optical anisotropy is comparable to reflectance difference spectroscopy. However, not only is the change in amplitude ratio $\delta\tan(\psi)$ measured, but the phase change $\delta\Delta$ is also obtained. Because $\tilde{r}$ is a complex quantity, causality gives a relation between $\tan(\psi)$ and Δ and thus also for changes in these quantities. The resulting Kramers-Kronig relation[8] between the pair $\delta\tan(\psi)$ and $\delta\Delta$ provides an internal consistency check of the measurements and as a result only one independent quantity should result. However, only a limited photon energy region is measured. The Kramers-Kronig relation involves an integration over all photon energies and can therefore only be used with spectra recorded over a sufficient wide photon energy range. Measuring both quantities allows a further analysis of the optical signal in terms of the complex surface dielectric function. The anisotropy of the clean Si(111)2×1 surface has been revealed by measuring the anisotropy change due to heavy oxidation of the surface.[5] In this experiment it was presupposed that an isotropic surface results after this modification of the clean surface. In order to check the validity of this assumption, we will compare the results obtained by O_2 exposure with the change in anisotropy due to ion bombardment of

the surface. The latter process is rather different compared to oxidation. We expect that prolonged sputtering results in an isotropic surface, because several atomic layers are removed, roughening of the surface occurs, and an amorphous top layer results. This disorder effect has been reported with second-harmonic generation (SHG) measurements[9] on the Si(111)7×7 surface.

C. Theoretical description of the optical response

The theoretical description of the optical response of a surface has been refined in two complementary ways, the continuous model[10] and the discrete dipole model.[11] With the discrete dipole model it has become possible to give an unambiguous link between the electronic and geometric structure of the surface region on an atomic scale and the optical response of a surface. Recent calculations, applying the discrete dipole model to the Si(110) surface, have shown that the optical reflectivity and especially the reflection anisotropy depend on the actual surface reconstruction.[12] We have shown that the local electric field on an atomic scale is highly sensitive to the differences in the geometric structure of the unreconstructed and the 2×1 and 5×1 reconstructed surfaces. The particular strength of the local electric field has a large influence on the intensity of the features in the optical anisotropy spectrum. On the other hand, the energy positions of optical features are directly linked to the electronic structure of the surface and are not changed if the atoms are arranged differently. Because the dipole model needs a full evaluation of the geometric and electronic structure of the surface region, which lies far beyond the scope of this article, we will interpret our spectra using a continuous model. The effect of the particular surface reconstruction on the optical response is not as straightforward implemented in a continuous description. Although a continuous model provides an accurate prediction of surface-state energy positions and symmetry, such an analysis will not give quantitative information about intensities because the local electric field is not taken into account properly.[12] In our measurements, the difference in reflection at Ge(001)2×1 of light polarized in the $(\bar{1}10)$ and (110) directions is ascribed to the anisotropy in the electronic structure of this surface. This is done by transferring the measured change in optical anisotropy into a difference in the surface dielectric function in the $(\bar{1}10)$ and (110) directions, using the McIntyre-Aspnes model.[13] The anisotropic surface dielectric function calculated can be compared with the optical absorption spectrum expected from the energy positions and parity of the surface states known to be present on Ge(001)2×1. Hence the influence of the microscopic nature of the dimer reconstruction on the macroscopic optical response can be studied.

The experimental details are discussed in Sec. II. Next we will discuss the change in optical response upon modification of the clean anisotropic surface to an isotropic surface in Sec. III. In this section also an interpretation of the optical anisotropy spectrum in terms of the position and symmetry of surface states present on clean Ge(001)2×1 will be given. In Sec. IV we will show the

influence of N_2O adsorption on the anisotropy of the sur-
face. Although at first glance the adsorption of N_2O
seems quite similar to molecular oxygen, only the first
layer atoms are involved in an oxygen bond.[14] A well-
defined modified surface which is still anisotropic then re-
sults, as depicted in Fig. 1(b). From the difference in the
initial stage of exposure of the two gases, the kinetics of
the oxidation process is described. In Sec. V conclusions
will be given.

II. EXPERIMENTAL

The clean Ge(001)2×1 surface has a reconstruction
with a unit cell containing one dimer. The stress and
strain induced by the formation of these dimers is re-
lieved by single atomic steps (SA or SB type) on the sur-
face at which the orientation of the dimers is rotated over
90°.[15–17] This leads to two domains at the surface with
mutual perpendicular dimer orientation and a terrace
width of 100 nm maximum. The optical anisotropy is op-
posite in the two domains and is hence averaged out on a
macroscopic scale. We used a Ge(001) surface with a
misorientation of 5° towards the (110) direction. At such
a misorientation angle only double atomic steps occur
(DB type), with a dimer orientation parallel to the step
edge in both the upper and lower terrace. A single
domain surface which has a macroscopic well-defined an-
isotropy was obtained by Ar^+-ion bombardment (800 eV,
dose $\approx 10^{13}$ ions/cm²s, 600 s), followed by simultaneous
ion bombardment and resistive heating ($\approx$700 K, 1200 s),
and finally resistive heating only ($\approx$800 K, 1 h).[14] Low-
energy electron diffraction (LEED) measurements of the
clean surface showed a single domain 2×1 reconstruc-
tion. Several LEED spots were doubled, indicating regu-
lar terraces with DB steps present at the surface.[16,17]

The optical experiments were performed with a stan-
dard spectroscopic rotating analyzer ellipsometer, as de-
scribed previously, operated in the energy region between
1.5 and 4.5 eV.[8,18] Changes of about 10^{-4} could be
detected in the optical anisotropy. In contrast to classi-
cal ellipsometry, the light beam was near normal in-
cidence on the Ge surface. This was accomplished by
two aluminum mirrors which gave an extra phase retar-
dation and therefore allowed a much better measurement
of changes in Δ.[8] Also a residue calibration becomes
feasible in this configuration. Before exposing the clean
Ge(001)2×1 surface to N_2O, this gas was distilled at 80
K and during gas exposure the inlet system was held at
120 K. This distillation procedure minimizes uncon-
trolled exposure of the surface to reactive species like O_2
and H_2O, present as minorities in the 99.999%
guaranteed pure N_2O gas.

III. CHANGE TO AN ISOTROPIC SURFACE

A. Oxidation versus ion sputtering

The change in optical anisotropy, induced by exposing
clean Ge(001)2×1 to molecular oxygen up to saturation
coverage, is depicted in Figs. 2(a) and 2(b). A curve, de-
picted as the solid line in Fig. 2(a), consisting of several

Gaussians of variable widths with no physical meaning,
was fitted through the experimental results of $\delta\tan(\Psi)$.
The quality of this fit is determined from two parameters:
a minimum in the summed squared deviation between ex-
periment and fit and the Kramers-Kronig transformation
of the fitted $\delta\tan(\Psi)$ should give a good comparison to
the measurements of $\delta\Delta$ in Fig. 2(b), as determined by the
eye. It has been a matter of debate whether such an oxi-
dation of a semiconductor surface completely removes all
surface optical anisotropy. The naturally oxidized Si(110)
surface was shown to have a considerable optical anisot-
ropy which is intrinsic to the unreconstructed (bulk-
terminated) surface. We have therefore looked for anoth-
er procedure of modifying the clean Ge(001)2×1 surface
into an isotropic surface. From SHG experiments, in
which the 7×7 reconstruction of Si(111) was attacked by
adsorption of O_2 and Ar^+ ion bombardment, it is known
that this surface is disordered by either of these
methods.[9] Thus a thorough destruction of the geometric
ordering in the surface area, and consequently the anisot-
ropy, is expected by an ion bombardment of the clean
surface. In another experiment we bombarded the sur-
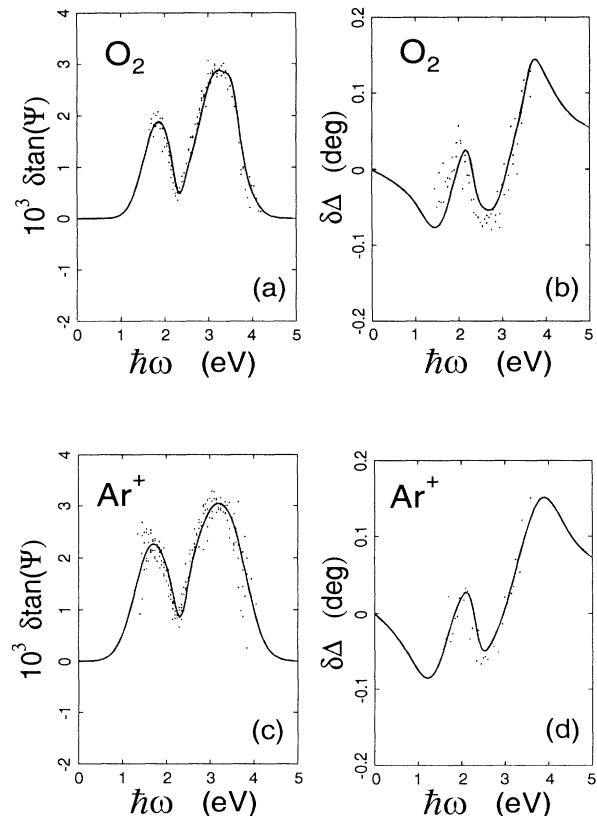face with Ar^+ accelerated to a kinetic energy of 800 eV

FIG. 2. Change in ellipsometric parameters of a clean single
domain Ge(001)2×1 surface (a) $\delta\tan(\Psi)$ and (b) $\delta\Delta$ upon expo-
sure to molecular oxygen up to saturation coverage and (c)
$\delta\tan(\Psi)$ and (d) $\delta\Delta$ upon Ar^+-ion bombardment, see text for
details. (●) measurements; the solid lines are an approximation
of the measurements which also form Kramers-Kronig pairs be-
tween $\delta\tan(\Psi)$ and $\delta\Delta$.

and a dose of 10^{16} ions/cm^2. From low dose ion bombardment studies on the similar Si(001)2×1 surface, it is known that a single collision roughens an area of approximately 25 Å^2.[19,20] A similar effect is expected for the Ge(001)2×1 surface. Our sputtering procedure results in 2 to 3 impacts per first layer atom, which will change the surface dramatically with, most likely, a random distribution of the atoms in the outermost layers. In Figs. 2(c) and 2(d) the anisotropy change induced by such an Ar$^+$ ion bombardment of the clean surface is depicted; the solid lines are best fits obtained as outlined above. These changes are comparable to the ones obtained by exposure to molecular oxygen up to saturation coverage. We conclude, therefore, that both exposure to molecular oxygen and Ar$^+$-ion bombardment of clean Ge(001)2×1 result in an optically isotropic surface after either of these treatments in our experimental photon energy region. UPS measurements of Nelson *et al.*[21] showed that especially the low binding-energy features are changed into a structureless electron distribution upon adsorption of molecular oxygen. Auger electron spectroscopy measurements clearly indicated that additional states were found at higher binding energies due to oxygen exposure on the comparable Si(001) surface.[22,23] The incorporation of oxygen atoms in the Ge lattice is therefore expected to give an anisotropic ordering of the atoms, certainly in the outermost layers. The energy states related to this anisotropic ordering are most probably outside the photon energy region studied. In summary, an ion bombarded surface will provide an optical isotropic response over a larger photon energy region than the molecular-oxygen-exposed surface.

B. Anisotropic surface dielectric function

The changes in optical anisotropy will be interpreted in terms of the anisotropy of the surface dielectric function with the Bootsma-Meyer approach.[24] This model assumes that the clean surface can be represented by three layers, the vacuum layer, the surface layer, which in this case has an anisotropic dielectric function, and the isotropic bulk layer. As shown, the anisotropic surface is changed into an isotropic layer, upon sputtering or molecular-oxygen exposure. Because the new surface is isotropic and optically transparent, it can be neglected in this analysis. Then an effective two layer system, consisting of bulk and vacuum, remains. Using this approach, McIntyre and Aspnes[13] provided the relation between the change in reflection coefficient upon modification of the surface and the dielectric function of the surface area. With this relation, the change in the complex anisotropic reflection ratio $\tilde{\rho}$, going from the clean (cl) to the isotropic (is) surface can be translated to the difference in surface dielectric function in the directions parallel $(\bar{1}10)$ and perpendicular (110) to the dimer bond, $\Delta\tilde{\varepsilon}_{SS}$:[8]

$$\Delta\tilde{\varepsilon}_{SS}d_{SS} \equiv (\tilde{\varepsilon}_{SS}^{(\bar{1}10)} - \tilde{\varepsilon}_{SS}^{(110)})d_{SS}$$

$$= \frac{ic}{2\omega}(\tilde{\varepsilon}_b - 1)\left[\frac{\tilde{\rho}_{cl}}{\tilde{\rho}_{is}} - 1\right]. \qquad (3)$$

In this, c is the speed of light, ω is the angular frequency

of the incident light, d_{SS} is the thickness of the anisotropic surface layer, and $\tilde{\varepsilon}_b$ is the bulk dielectric function, which is taken from Aspnes and Studna.[25] Calculations, using the discrete dipole model, have shown that the optical anisotropy is insensitive to the profile of the polarizability perpendicular to the surface, as long as the integrated value of this polarizability profile in the direction normal to the surface remains constant[26] It is exactly this phenomenon which allows us to use the McIntyre-Aspnes approach successfully, i.e., why the rectangular profile of thickness d_{SS} and strength $\tilde{\varepsilon}_{SS}$ for the surface dielectric function assumed in this approach can be used. Hence, the thickness d_{SS} becomes rather arbitrary and an experimental separation between the dielectric function of the surface layer and its thickness, not to mention the variation of $\tilde{\varepsilon}_{SS}$ with depth, has not yet been feasible. Calculations of the nonlinear optical response of a surface do show a dependence on the actual shape of the polarizability profile and an estimated value of d_{SS} may be determined from such a measurement.[26] In this paper we will use the imaginary part of the integrated dielectric function of the surface Im$(\Delta\tilde{\varepsilon}_{SS}d_{SS})$ depicted as the points in Fig. 3, derived from the solid lines in Figs. 2(a) and 2(b) using Eq. (3).

C. Optical properties of surface states

In the past decade the geometric and electronic structure of the clean Ge(001)2×1 surface has been studied using various methods. First of all UPS (Refs. 21 and 28–31) was used for characterizing the occupied surface states. The assignment of experimental features to surface states with UPS is carried out by verifying one or more of the following three criteria;[32] (i) the energy position lies in the forbidden bulk zone, (ii) no energy dispersion upon variation of the incident photon energy is not-
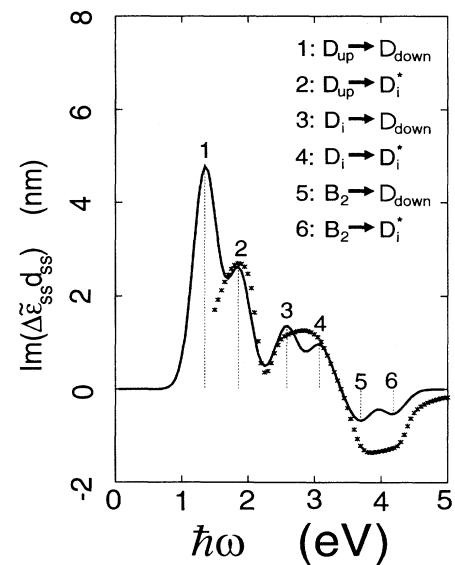

FIG. 3. Im$(\Delta\tilde{\varepsilon}_{SS}d_{SS})$, (*) calculated from Figs. 2(a) and 2(b). The solid line is obtained by applying symmetry-based optical selection rules as discussed in the text.

ed, and (iii) the change of the spectrum upon adsorption of a gas. The overlap between the bulk electronic structure and surface states, sometimes in combination with large surface resonances, often leads to difficulties in applying these criteria. The first two criteria, especially the first one, are very often not adequate in UPS measurements. The third criterion, however, is very often treated with much skepticism since an adsorbed overlayer not only changes the electronic structure in the surface region, but also influences bulk features due to different scattering of transmitted electrons. This criterion can be more successfully applied in linear optical techniques. In contrast to UPS, non-surface-state-related features as a result of scattering and the small penetration depth of the detected electrons do not blur the spectrum. Inverse photon-emission spectroscopy is needed to provide similar knowledge to UPS about unoccupied surface states. Both techniques have the advantage of being able to sample dispersion of surface states. STM has provided an additional tool for obtaining spectroscopic information about the electronic structure around the Fermi energy.[15,33,34] Opposed to UPS, STM can address both empty and filled surface states simultaneously, but it has the drawback of being insensitive in a small energy region around the Fermi level and it probes the Γ point in reciprocal space only. The normal incidence ellipsometry measurements presented in this article characterize transitions from occupied to unoccupied surface states on Ge(001) and provide additional insight into the electronic structure of this surface, especially its anisotropy as the result of the dimer formation.

The imaginary part of the dielectric function depicted in Fig. 3 images the macroscopic absorption of electromagnetic waves in a medium. Following the Bassani expression,[27] we can write

$$\text{Im}(\bar{\varepsilon}_{SS}) \sim \frac{1}{\omega^2} \sum_{i,f} |\langle \Psi_f | \mathbf{e} \cdot \mathbf{P} | \Psi_i \rangle|^2 \mathfrak{I}_{fi}(\hbar\omega) , \qquad (4)$$

in which $|\Psi_{i(f)}\rangle$ is the initial (final) state, $\mathbf{e}$ is the polarization direction of the incident electric field [i.e., parallel to $(\bar{1}10)$ or (110)], and $\mathbf{P}$ is the electron momentum operator. $\mathfrak{I}_{fi}(\hbar\omega)$ is the joint density of states of initial and final states, separated by photon energy $\hbar\omega$, and it determines the energy positions of optical transitions. It is assumed that the influence of the matrix elements and $\mathfrak{I}_{fi}(\hbar\omega)$ is independent, which results in the factorization used in Eq. (4). From UPS measurements it is quite obvious that this is a very crude approximation, as dispersion may alter peak positions by several tenths of eV in reciprocal space. This approximation provides a qualitative picture of the electronic structure in the surface region with an estimate of surface-state energy positions. Furthermore, Eq. (4) is derived for the bulk of a crystal. At a surface or interface, the exact magnitude of the local electric fields is not well determined. In such cases one must turn to another method, where the quantum-mechanical properties are expressed on the scale of the fluctuations of the local electric field, i.e., the atomic scale. In the application of Eq. (4) to surface optics, information about the exact magnitude of the local features is hence lost. A more rigorous analysis with a direct rela-

tion between a calculated electronic structure and the optical response is necessary for the evaluation of the actual intensities.[11,12] Our approach for determining a qualitative picture of the macroscopic optical response consists of letting $\mathfrak{I}_{fi}(\hbar\omega)$ determine the energy of a transition while the matrix elements govern the possibility of a transition qualitatively by using symmetry properties of the initial and final states. Thus, a matrix element equals zero unless the wave function of the initial and final states have unequal symmetries (i.e., even and odd) along the polarization direction $\mathbf{e}$ and equal symmetries perpendicular to $\mathbf{e}$ (both even or both odd).[27] The difference in optical activity for polarization directions along the $(\bar{1}10)$ and (110) directions determines the sign of $\text{Im}(\Delta\bar{\varepsilon}_{SS}d_{SS})$, defined in Eq. (3), and thus reflects the difference in electronic structure along these directions.

The electronic structure of the clean Ge(001)2×1 surface in the vicinity of the Fermi level is known from a number of theoretical and experimental investigations.[2−4,21,28−31,33,35,36] In Table I we have listed the symmetry properties of surface states derived from these articles. Also the energy positions used in this work of filled (empty) dimer states D_i (D_i^*), filled (empty) dangling bonds D_{up} (D_{down}), and backbonds B_1 and B_2 are listed. The properties of these surface states will be discussed extensively below, especially the energy positions depicted in Table I compared to those found in literature. The energies listed are without taking the dispersion of the energy position of a surface state into account. These data were used in the calculation of the solid line in Fig. 3, representing the difference in the surface dielectric function $\text{Im}(\Delta\bar{\varepsilon}_{SS}d_{SS})$ calculated with Eq. (4) and scaled to the experimentally observed transition at 1.7 eV. In this calculation we used a Gaussian of 0.25-eV width to represent $\mathfrak{I}_{fi}$ to account for a crude approximation for the dispersion of the states. The position of the surface states in Table I compared to those found in literature will now be discussed.

The parity of the wave function associated with the B_1 state and both empty states results in forbidden transitions involving the B_1 state and therefore no B_1-related feature should be observed experimentally. Transitions associated to the filled B_2 state have a contribution with opposite sign in $\text{Im}(\Delta\bar{\varepsilon}_{SS})$ to the transitions associated with D_i and D_{up} states. Hence a discrimination between these three occupied states can be made.

The energy positions of the unoccupied states D_i^* and D_{down} are derived from a theoretical calculation[31,35] that shows an energy separation of 0.5 eV. From STM measurements an unoccupied state at 0.9 eV is known.[33] This position is assigned to the D_i^* state as there is no struc-

TABLE I. Predominant symmetries of the various surface states along the (110) and ($\bar{1}$10) directions and their energy positions relative to the Fermi level.

	D_i^*	D_{down}	D_{up}	B_1	D_i	B_2
(110)	even	even	even	odd	even	odd
($\bar{1}$10)	odd	odd	even	even	even	odd
E (eV)	0.9	0.4	−1.0	−1.3	−2.2	−3.3

ture at higher energy and hence D_{down} must be located at 0.4 eV. Due to the insensitivity of spectroscopic STM measurements in the vicinity of the Fermi level, the D_{down} state can easily be overlooked. In theoretical calculations, the energy positions of the empty states are found closer to the Fermi energy as determined experimentally. This discrepancy is not surprising and can be ascribed to the local-density approximation used in the theoretical evaluation. The band gap in such calculations is typicaly 30–50 % smaller than the actual band gap, a problem extensively addressed by Hybertsen and Louie[37] for the band structure of solids and unreconstructed surfaces. Their results suggest that the unoccupied states could have a substantial self-energy correction.

The D_{up} state is located by us at -1.0 eV while previous UPS measurements[21,29,30] resolved this feature between -0.5 and -0.8 eV. Because in UPS D_{up} is seen as a shoulder on the very intense transition of the B_1 state, it has been hard to establish its position accurately, although at low photon energies the p-type character of the D_{up} state helped to resolve it. With STM, a broad structure is seen at -1 eV that comprises both the D_{up} and B_1 states. Because the B_1 state is located between the first and second layer atoms, a decreased sensitivity of this electron distribution to spectroscopic STM measurements is expected and hence the D_{up} state should be more pronounced. Although in some calculations the D_{up} state is hardly visible,[33,36] other presentations of these calculations[31,35] do show a state at -0.8 eV. Ellipsometry measurements have located a transition at 1.7 eV,[3,4] which is in agreement with the transition observed in this work assigned to the $D_{up} \rightarrow D_i^*$ transition. A possible transition $B_1 \rightarrow D_{down}$ cannot be ruled out from these experimental results as this transition would also give rise to a feature with a transition energy of 1.7 eV that cannot be discriminated from the $D_{up} \rightarrow D_i^*$ transition. However, both previous optical characterizations of the surface states as well as this work do not show a transition $B_1 \rightarrow D_i^*$ at 2.2 eV, making any contribution in the spectrum originating from the B_1 state unlikely, let alone that a transition involving B_1 is optically not allowed according to selection rules.

Theoretical calculations[31] show a very weak and broad feature at -2.3 eV, associated with the D_i state. The low intensity of this feature makes it very hard to observe with UPS, and only Rowe and Christman[28] report a feature at -2.4 eV which they assign to this state. Hsieh, Miller, and Chiang[29] and Nelson *et al.*[21] associate this feature in their UPS measurements to a bulk state. However, a well-resolved feature at -2.6 eV is seen in spectroscopic STM measurements,[33] indicating a more surfacelike phenomenon. Our measurements predict a state at -2.2-eV binding energy as a result of the positive peak in Fig. 3. This peak is assigned to a combination of a transition at 2.5 eV ($D_i \rightarrow D_{down}$) and 3.0 eV ($D_i \rightarrow D_i^*$). The latter of these transitions is also well resolved in the ellipsometric measurements of Zandvliet and van Silfhout.[3] The difference in energy positions of this surface state might arise from the fact that various parts of k space are sampled by the various techniques and the broadness of the feature seen in the calculations.

At 3.5 eV, $\mathrm{Im}(\Delta \tilde{\varepsilon}_{SS} d_{SS})$ in Fig. 3 changes in sign. This is caused by a transition involving the B_2 state located at -3.3 eV, which has opposite parity in both directions compared to the D_{up} and D_i state. Although UPS measurements of Rowe and Christman[28] and Kevan[30] do indicate a feature at this energy, they attributed it to a bulk structure. The UPS measurements of Landemark *et al.*, as well as calculations,[31] quite clearly resolve a state at -3 eV attributed to a backbond, with a state density maximum at the second layer of Ge atoms. In the classical ellipsometry setup used by Zandvliet and van Silfhout,[3] the sum and not the difference of the components of the surface dielectric function along the surface is measured. Also there is a contribution from the component of the surface dielectric function normal to the surface. This is observed as a broad maximum in the photon energy range from 2.8 to 3.8 eV, comprising transitions from both D_i and B_2.

Summarizing, we have found an excellent agreement between our optical anisotropy measurements and the known energy positions and parities of surface states. A number of transitions is measured directly and it is clear why we do not see any B_1-related transition. D_{down} is determined experimentally at 0.4 eV.

IV. MONOLAYER OXYGEN-INDUCED SURFACE STATES ON Ge(001)2×1

A. Anisotropy of the N₂O exposed surface

Exposing clean Ge(001)2×1 to N_2O, this molecule will dissociate at the surface in gaseous N_2 and atomic oxygen at room temperature.[14] The atomic oxygen is adsorbed in a bridge bonded configuration with the first layer Ge atoms as depicted in Fig. 1(b), i.e., a one monolayer oxygen-covered surface results. This is confirmed by LEED measurements of the N_2O exposed surface which shows a sharp 1×1 pattern with a clear spot splitting due to regular spaced terraces. In contrast, the adsorption of molecular oxygen also gives insertion of oxygen atoms in backbonds on both Ge (Refs. 3 and 4) and Si (Refs. 14 and 38) surfaces. N_2O exposure up to saturation coverage will modify the subsurface B_1 and B_2 states of the clean surface, but certainly not as much as molecular oxygen. In the latter case the Ge-Ge bond between the first and second layer is replaced by a Ge-O-Ge bond. The anisotropy, associated with the remaining backbond states after N_2O exposure, is expected to still be observable. Both the initial clean surface and the monolayer oxygen-covered Ge(001) surface, obtained with N_2O, are well-defined surfaces. In Fig. 4 the change in ellipsometric parameters upon N_2O exposure is depicted. Comparison of these results to those of Figs. 2(a) and 2(b) shows a clear difference with exposure to molecular oxygen. The most obvious one is the negative value in Fig. 4 of $\delta \tan(\psi)$ at 2.2 eV. The analysis of the anisotropy change in terms of a surface dielectric function anisotropy is not as straightforward as in the case of molecular-oxygen adsorption or Ar^+-ion bombardment, where an isotropic surface is obtained after modification. We will
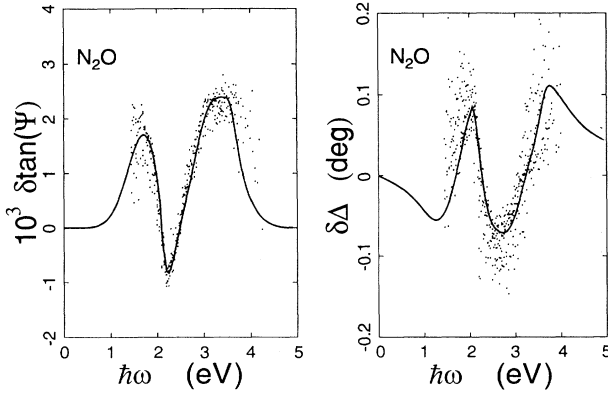
FIG. 4. Change in ellipsometric angles of a clean, single domain Ge(001)2×1 surface upon saturation exposure to N_2O. (●) measurements, the solid lines are again an approximation of the measured points, forming a Kramers-Kronig pair.

therefore interpret this change with the aid of the change upon exposure to molecular oxygen from Sec. III. This allows for a similar analysis as done before. The change from an anisotropic surface to an isotropic one is now defined as going from the anisotropic N_2O exposed surface, the initial monolayer oxygen-covered stage, to the isotropic final state, the molecular-oxygen saturated surface:

$$\delta\Delta_{N_2O\to O_2} = \Delta_{N_2O} - \Delta_{O_2} = \delta\Delta_{cl\to O_2} - \delta\Delta_{cl\to N_2O} ,$$

$$\delta\tan(\psi)_{N_2O\to O_2} = \frac{\delta\tan(\psi)_{cl\to O_2} - \delta\tan(\psi)_{cl\to N_2O}}{1+\delta\tan(\psi)_{cl\to N_2O}}$$

$$\approx \delta\tan(\psi)_{cl\to O_2} - \delta\tan(\psi)_{cl\to N_2O} .$$

(5)

In Fig. 5 the anisotropy in the surface dielectric function $\Delta\tilde\varepsilon_{N_2O}d_{N_2O}$ of the Ge(001) surface exposed to N_2O, calcu-
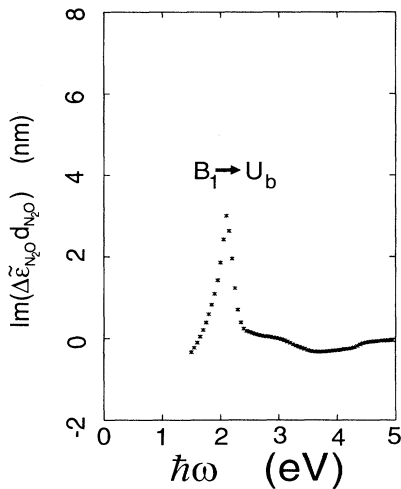
FIG. 5. $Im(\Delta\tilde\varepsilon_{N_2O}d_{N_2O})$, calculated from Fig. 2(a) and Fig. 4 as explained in the text.

lated using Eqs. (3) and (5) and Figs. 2(a), 2(b), and 4, is shown. A sharp transition at 2.0 eV is found.

B. Initial oxidation of Ge(001)2×1

Following $\delta\tan(\psi)$ at 2.2 eV during exposure to either O_2 or N_2O reveals that already in the initial stages differences occur. During O_2 exposure, $\delta\tan(\psi)$ is immediately positive, opposite to N_2O exposure, where it is always negative. Therefore, already in the initial stage of the reaction, different adsorption processes occur. As will be explained hereafter, the difference concerns the immediate incorporation of oxygen into backbonds during O_2 exposure. This difference in reaction already in the initial stage was also noted by surface conductance measurements (SCM) on both the Ge(001)2×1 surface[3,4] and the quite similar Si(001)2×1 surface.[38] For silicon the difference was most obvious since in this case a difference in sign of the change in surface conductance was reported. For germanium this is less obvious, but also in this case the initial stage of the adsorption of nitrous oxygen is marked with a lesser removal of acceptor states compared to adsorption of molecular oxygen. The backbond states B_1 and B_2 may precisely be these non-removed acceptor states. Molecular oxygen reacts with both Si(001)2×1 and Ge(001)2×1 as a decomposition at the dimer bond of the molecule with one of the oxygen atoms reacting with the dimer bond. The remaining oxygen atom should react with an adsorption site in the vicinity of the decomposition site. Possibility sites are the long dimer site (a combination of a dangling bond up and down), another dimer site, or the backbond. The long dimer site is not likely as the optical transition related to this site shows a delay with respect to the optical transition related to the dimer site.[3,14] The difference in adsorption recorded with SCM between exposure to N_2O and O_2 and the opposite sign in the change in $\delta\tan(\psi)$ at 2.2 eV, as noted by us, suggests that in the initial stage the second atom of the decomposed O_2 molecule does not react with another dimer site. Incorporation between the first and second layer atoms attacking both the B_1 and B_2 site is the only remaining possibility.

The optically observed difference between molecular and nitrous oxygen is also found in classical optical experiments. Both Keim, Wolterbeek, and van Silfhout[14] and Zandvliet, Keim, and van Silfhout[4] observed on the Si(001)2×1 and the Ge(001)2×1 surface, respectively, that exposure of these surfaces towards nitrous oxygen up to saturation coverage leads to a spectrum with more structure compared to the spectrum obtained with molecular oxygen. Zandvliet, Keim, and van Silfhout saw a splitting of the low photon energy peak of the change in $\tan(\psi)$, recorded upon exposure to O_2, into a transition at 1.7 and 2 eV and an additional shoulder at 2.3 eV upon exposure to N_2O. These transitions are due to a mix of the surface states seen on the clean and the atomic oxygen-covered surface, the latter states are seen in their work as the transition at 2 eV. The clean and adsorbed surfaces are therefore both three-layer systems with their respective surface dielectric functions, a situation which makes the analysis of their spectra complex. In the high photon energy range the optical transition at 3.3 eV was

seen to split into two contributions at ≈ 3 and 3.5 eV. In this case also a mix of the transitions at the clean surface and the N_2O exposed surface is a possible explanation for the observed transitions. However, in the exposure-dependent measurements of the change in the optical response at selected energies, no obvious difference between the adsorption of N_2O and O_2 is seen with an ellipsometer incident at Brewster's angle or a differential reflectometer and a comparable reaction mechanism was suggested for these two gases in the initial stage. In our setup the difference in reaction between the two gases is obvious from the change at 2.2 eV.

The occupied state involved in the transition in Fig. 5 has to be either the B_1 or B_2 states, as these states are present on the surface exposed to nitrous oxide gas, while on the molecular-oxygen-exposed surface they are removed. Both states will have changed on the N_2O exposed surface, compared to the clean surface, because the geometrical position of the outer layer atoms has changed. The general feature of these states, however, is to our opinion preserved. The photon energy of 2.0 eV, associated with the transition, indicates that the most likely candidate of the two backbonds is the B_1 state. With the B_1 state being the occupied state, also an unoccupied state U_b has to be involved in order to get an optical transition. This unoccupied state cannot be present at the clean surface, as in this case we should also have seen a transition $B_1 \rightarrow U_b$ upon exposure of the clean surface towards molecular oxygen, which is not the case. Therefore U_b has to be the result of the bridge bonded oxygen atoms between the first layer atoms, with a position ≈ 0.7 eV above the Fermi energy. Because we observed a strong transition related to the B_1 state with a positive sign in $Im(\bar{\epsilon}_{N_2O})$ in Fig. 5, the wave function of the unoccupied state U_b should be odd in both the $(\bar{1}10)$ and the (110) direction. This symmetry of U_b also explains why no $B_2 \rightarrow U_b$ transition is observed.

V. SUMMARY

We have used a spectroscopic ellipsometer at normal incidence which provides a straightforward interpretation of the measured optical response. For Ge(001)2×1, the reflection anisotropy, induced by the anisotropy of the electronic structure in the surface region, was recorded and interpreted in terms of the surface states known to exist on this surface. Thus a general agreement with UPS, STM, and theoretical calculations and the observed energy positions of the D_i^*, D_{up}, D_i, and B_2 states was found. Also the D_{down} state has been determined experimentally and estimated to be positioned 0.4 eV above the Fermi level. The assumption that an optically isotropic surface is obtained by exposing a clean semiconductor surface towards molecular oxygen was found to hold in the photon energy range between 1.5 and 4.5 eV, by comparing oxygen exposure up to saturation coverage with Ar^+-ion bombardment. Exposing the clean Ge(001)2×1 surface to N_2O resulted in an optically anisotropic surface. For an explanation of the remaining anisotropy the recorded change in optical anisotropy upon N_2O exposure was compared with that upon exposure to molecular oxygen. From this comparison we could deduce that the incorporation of oxygen atoms in a bridge bonded configuration between the first layer germanium atoms should result in an unoccupied surface state U_b at 0.7 eV. We also found that the reaction of molecular oxygen is of a dissociative nature, already in the initial stage, in which one oxygen atom is inserted in a first layer bridge bonded configuration, while the other is incorporated simultaneously in the backbonds.

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