Optical anisotropy of Ge(001)

H. Wormeester, D. J. Wentink, P. L. de Boeij and A. van Silfhout

Faculty of Applied Physics, University of Twente, P.O. Box 217, 7500 AE Enschede (Netherlands)

Abstract

The surface induced optical anisotropy in the electronic structure of clean Ge(001)2 × 1 was studied with an ellipsometer at normal incidence. The change in the reflection difference between light polarized parallel and perpendicular to the dimer bond at this surface upon either adsorption of molecular oxygen or Ar⁺ ion bombardment was recorded. Both procedures were found to give the same results. It was possible to obtain a qualitative agreement of the optical spectrum recorded and the position and parity of the occupied and unoccupied surface states known on the clean surface.

1. Introduction

The 2 × 1 reconstruction of Ge(001) is characterized by dimers aligned in rows [1], as shown for two surface unit cells in Fig. 1. The orientation of the dimers on this surface results in different electronic structures in the directions parallel and perpendicular to the dimer bonds, while the bulk is isotropic. This well-defined surface with a small surface unit cell provides a unique opportunity to study the surface induced optical reflection anisotropy and to compare spectra obtained experimentally with theoretical calculations. In the past decade the geometric and electronic structure of the clean Ge(001)2 × 1 surface has been studied with ultraviolet photo-electron spectroscopy (UPS) [2–7], characterizing the occupied surface states. Scanning tunneling microscopy (STM) has provided an additional tool for obtaining spectroscopic information on the electronic structure around the Fermi energy [8–10]. This paper shows that the anisotropy in the surface reflection provides an additional tool for the study of the electronic structure of surfaces.

An ellipsometer at normal incidence is used, which measures the difference in reflection for the two polar-
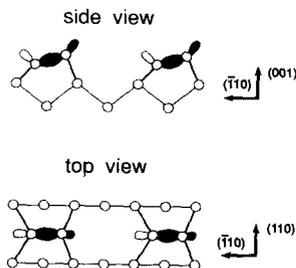
ization directions of light (polarized in the $(\bar{1}10)$ and (110) directions on Ge(001), the intrinsic axis of this surface). Because the bulk of the material is isotropic, no contribution of the region beyond the first few surface layers is expected. This anisotropic optical reflection is described by the complex anisotropic reflection ratio $\tilde{\rho}$ according to

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

We recorded the optical anisotropy change due to a modification of a clean Ge(001)2 × 1 surface, since such a relative measurement eliminates unknown influences of non-perfect components in the ellipsometer set-up [11]. In the past, the proposal by Meyer and Bootsma [12] to measure the properties of the clean surface by comparing it with a surface exposed to molecular oxygen up to saturation coverage has been applied successfully by several groups. In this procedure, it is assumed that exposure to oxygen results in a a surface with all surface states removed. However, in which region this assumption is valid is still a matter of debate. In our experimental set-up, we want to arrive at a modified surface that is optically isotropic. In our opinion, a prolonged Ar⁺ ion sputtering results in an isotropic surface, because several atomic layers can be removed, roughening of the surface occurs and an amorphous top layer results. This disorder effect has been reported with second harmonic generation measurements [13] for the Si(111)7 × 7 surface. The optical anisotropy change on modification (mo) of the clean (cl) surface is given by

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

side view

top view

Fig. 1. Side and top view of clean Ge(001)2 × 1.

The technique for measuring surface induced optical anisotropy we applied is comparable to reflectance difference spectroscopy. However, not only the change in amplitude ratio $\delta \tan(\psi)$ is measured, but also the phase change $\delta \Delta$. Because the change in $\tilde{\rho}$ is a complex quantity, causality gives a relation between the changes in the amplitude and the phase, the Kramers–Kronig relation. This relation provides an internal consistency check of the measurements.

2. Experimental details

We used a Ge(001) surface with a misorientation of 5° towards the (110) direction, which prohibits the formation of single atomic steps. At such a misorientation only double atomic steps occur (DB type), with a dimer orientation parallel to the step edge in both the upper terrace and the lower terrace, and a macroscopic well-defined single domain surface was obtained. The surface was cleaned before every experiment by Ar$^+$ ion bombardment (800 eV, dose $\approx 10^{13}$ ions cm^{-2} s^{-1}, 600 s), followed by simultaneous ion bombardment and resistive heating ($\sim$700 K, 1200 s) and finally resistive heating only ($\sim$800 K, 1 h) [14]. LEED measurements of the clean surface showed a single domain 2×1 reconstruction. Several LEED spots were doubled, consistent with regular terraces with DB steps at the surface [15, 16].

The optical experiments were performed with a standard spectroscopic rotating analyzer ellipsometer operated in the energy region 1.5–4.5 eV [11, 17]. Changes of $\sim 10^{-4}$ could be detected in the optical anisotropy during modification of the surface. In contrast to classical ellipsometry, the ellipsometer beam was near normal incidence on the Ge surface. This was accomplished by two aluminum mirrors that gave an extra phase retardation and therefore allowed a much better measurement of changes in Δ [11]. Also, a residue calibration becomes feasible in this configuration.

3. Results

The change in optical anisotropy induced by exposing clean Ge(001)2 × 1 to molecular oxygen up to saturation coverage is shown in Fig. 2(a). The solid lines are a fit to the data points, and form a Kramers–Kronig pair between $\delta \tan(\psi)$ and $\delta \Delta$. It has been a matter of debate whether such an oxidation process of a semiconductor surface completely removes the clean surface optical anisotropy. The naturally oxidized Si(110) surface was shown to have a considerable optical anisotropy which is intrinsic to the unreconstructed surface. We have therefore looked for another proce-
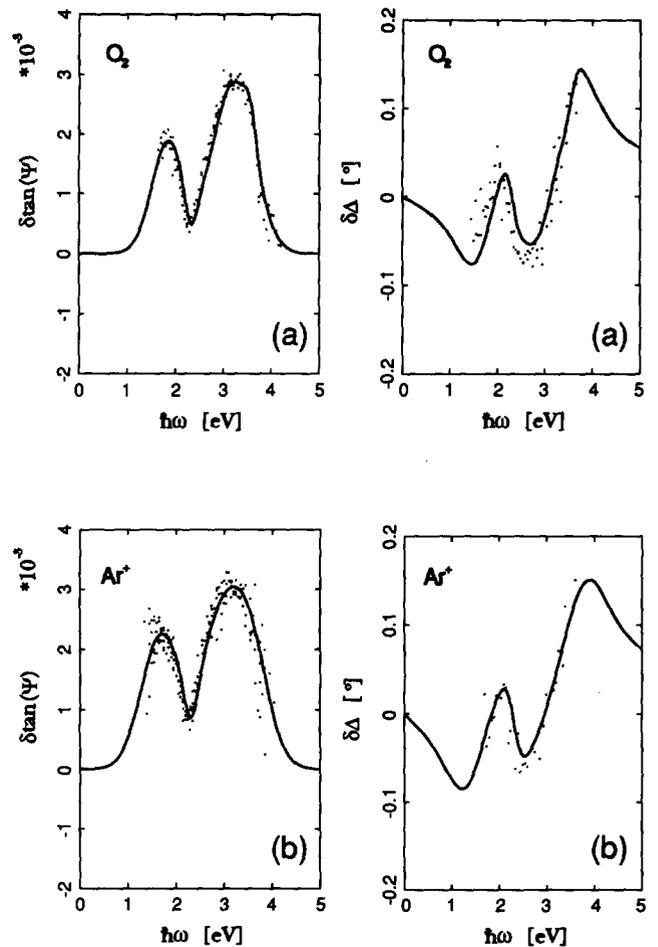

Fig. 2. Change in ellipsometric parameters of a clean single domain Ge(001)2 × 1 surface: (a) $\delta \tan(\Psi)$ and $\delta \Delta$ on exposure to molecular oxygen up to saturation coverage; (b) $\delta \tan(\Psi)$ and $\delta \Delta$ on Ar$^+$ ion bombardment (see text for details). Points show measurements; the solid lines are an approximation of the measurements, which also form Kramers–Kronig pairs between $\delta \tan(\Psi)$ and $\delta \Delta$.

dure to modify the clean Ge(001)2 × 1 surface into an isotropic surface. We bombarded the clean surface with Ar$^+$ accelerated to a kinetic energy of 800 eV and a dose of 10^{16} ions cm^{-2}. Our sputtering procedure results in 2–3 impacts per first layer atom, which will change the surface dramatically, probably with a random distribution of the atoms in the outermost layers. Figure 2(b) shows the anisotropy change of the clean surface upon Ar$^+$ ion bombardment. The changes in optical anisotropy upon Ar$^+$ ion sputtering are comparable to those obtained by exposure to molecular oxygen up to saturation coverage. We conclude, therefore, that exposure of clean Ge(001)2 × 1 to molecular oxygen indeed results in an isotropic optical surface response in the photon energy range in question. However, it is expected that, on oxidation, the incorporation of oxygen atoms in the Ge lattice will still give a residual anisotropic ordering of the atoms, certainly in the outer-

most layers. The energy states related to this anisotropic ordering are probably outside the photon energy region studied. UPS measurements [4] showed that the low binding energy features especially are changed into a structureless electron distribution on 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 [18, 19]. Thus we expect an ion-bombarded surface to provide an optical isotropic response over a larger photon energy region than the molecular oxygen exposed surface.

4. Discussion

The theoretical description of the optical reflection at a surface has been refined in two complementary ways, the continuous model [20] and the discrete dipole model [21]. With the discrete dipole model it has become possible to give an unambiguous link between the electronic and geometric structure of the surface region at 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 reflectance anisotropy depend on the actual surface reconstruction [22]. The local electric field on an atomic scale is highly sensitive to the geometric structure and has a large influence on the intensity of the optical anisotropy spectrum. In this work, our spectra are interpreted using a special version of the continuous model: the McIntyre–Aspnes model [23], which does not take the local fields into account. Thus, using a continuous model, our interpretation will provide an accurate prediction of surface state energy positions, but it cannot give quantitative information on intensities.

The changes in optical anisotropy are interpreted with the Bootsma–Meyer model [12] in terms of the anisotropy of the surface dielectric function. 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 by sputtering or molecular oxygen exposure. Because the new surface is isotropic, an effective two-layer system, consisting of bulk and vacuum, remains. Using this assumption, the relation between the change in reflection coefficient and the dielectric function of the surface area provided by ref. 23 can be applied. The change in the complex 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 $\Delta\tilde{\varepsilon}_{ss}$ [11]:

$$\Delta\tilde{\varepsilon}_{ss}d_{ss} \equiv (\tilde{\varepsilon}_{ss}^{(\bar{1}10)} - \tilde{\varepsilon}_{ss}^{(110)})d_{ss} = \frac{ic}{2\omega}(\tilde{\varepsilon}_b - 1)\left(\frac{\tilde{\rho}_{cl}^{ni}}{\tilde{\rho}_{is}^{ni}} - 1\right) \quad (3)$$

where c is the speed of light, ω is the angular frequency of the incident light and $\tilde{\varepsilon}_b$ is the bulk dielectric function, which is taken from ref. 24. The thickness d_{ss} cannot be separated experimentally from $\tilde{\varepsilon}_{ss}$. In this paper, we hence use the integrated dielectric function of the surface. The imaginary part ($\text{Im}(\Delta\tilde{\varepsilon}_{ss}d_{ss})$) of this function is shown as the points in Fig. 3, which is derived from Fig. 2(a) using eqn. (3).

The imaginary part of the dielectric function reflects the absorption of electromagnetic waves in a medium and can be related to the quantum mechanical properties of the system using the Bassani expression [25]:

$$\text{Im}(\tilde{\varepsilon}_{ss}) \approx \frac{1}{\omega^2}\sum_{i,f}|\langle\Psi_f|\mathbf{e}\cdot\mathbf{P}|\Psi_i\rangle|^2 F_{fi}(\hbar\omega) \quad (4)$$

where $|\Psi_{i(f)}\rangle$ is the initial (final) state, $\mathbf{e}$ is the polarization of the incident electric field (*i.e.* parallel to ($\bar{1}10$) or (110)) and $\mathbf{P}$ is the electron momentum operator. $F_{fi}(\hbar\omega)$ is the joint density of initial and final states, separated by photon energy $\hbar\omega$. We let $F_{fi}(\hbar\omega)$ determine the energy positions of optical transitions. It is assumed that the influence of the matrix elements and the joint density of states is independent, which results in the factorization used in eqn. (4). In this qualitative interpretation we let the matrix elements determine whether a transition is optically active or not, using the 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 $\mathbf{e}$
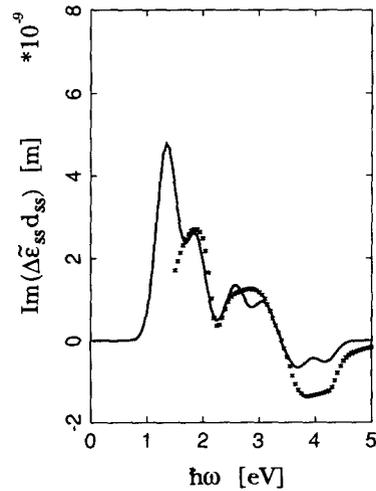

Fig. 3. $\text{Im}(\Delta\tilde{\varepsilon}_{ss}d_{ss})$: * calculated from Fig. 2(a), the solid line is obtained by application of symmetry-based optical selection rules as discussed in the text.

TABLE 1. Predominant symmetries of the various surface states along the (110) and ($\bar{1}$10) directions and their energy position 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

and equal symmetries perpendicular to e (both even or both odd) [25]. The difference in optical activity for polarization along the ($\bar{1}$10) and (110) directions determines the sign of $Im(\Delta\tilde{\epsilon}_{ss}d_{ss})$, and thus mimics the difference in electronic structure in the ($\bar{1}$10) and (110) 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 [2–6, 8, 26–30]. Table 1 gives the symmetry properties of surface states derived from these references and the energy positions used in this work for filled (empty) dimer states D_i (D_i^*), filled (empty) dangling bonds D_{up} (D_{down}) and backbonds B_1 and B_2. The energies given do not take 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 between $Im(\Delta\tilde{\epsilon}_{ss}d_{ss})$ calculated from eqn. (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 F_{f_i} and to account as a crude approximation for the dispersion of the states. Comparison of the experimental results with the solid line shows a striking resemblance for the energy position, the sign and the optical activity of the features. The parity of the wavefunctions associated with the B_1 state and both empty states result in forbidden transitions involving the B_1 state, and therefore no B_1 related feature should be observed experimentally. Transitions associated with the B_2 transition have a contribution with opposite sign in $Im(\Delta\tilde{\epsilon}_{ss})$ to the transitions associated with D_i and D_{up}. The position of the unoccupied D_{down} state was derived from theoretical work only. The comparison in Fig. 3 hence represents the first experimental observation of this surface state.

5. 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 in the position of the D_i, D_{up}, D_i and B_2 states was found. Also, the D_{down} state was determined experimentally for the first time 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 to molecular oxygen was found to hold in the photon energy range 1.5–4.5 eV, by comparing oxygen exposure up to saturation coverage with Ar$^+$ ion bombardment.

Acknowledgment

References

1 D. J. Chadi, Phys. Rev. Lett., 43 (1979) 43.
2 J. E. Rowe and S. B. Christman, J. Vac. Sci. Technol., 17 (1980) 220.
3 T. C. Hsieh, T. Miller and T. C. Chiang, Phys. Rev., 30 (1984) 7005.
4 J. G. Nelson, W. J. Gignac, R. S. Williams, S. W. Robey, J. G. Tobin and D. A. Shirley, Phys. Rev. B, 27 (1983) 3924.
5 S. D. Kevan, Phys. Rev. B, 32 (1985) 2344.
6 E. Landemark, R. I. G. Uhrberg, P. Krüger and J. Pollmann, Surf. Sci. Lett., 236 (1990) L359.
7 R. I. G. Uhrberg and G. V. Hansson, Solid State Mater. Sci., 17 (1991) 133.
8 J. A. Kubby, J. E. Griffith, R. S. Becker and J. S. Vickers, Phys. Rev. B, 36 (1987) 6079.
9 J. E. Griffith, G. P. Kochanski, J. A. Kubby and P. E. Wierenga, J. Vac. Sci. Technol. A, 7 (1989) 1914.
10 J. E. Griffith, J. A. Kubby, P. E. Wierenga, R. S. Becker and J. S. Vickers, J. Vac. Sci. Technol. A, 6 (1988) 493.
11 D. J. Wentink, H. Wormeester, P. L. de Boeij, C. M. J. Wijers and A. van Silfhout, Surf. Sci., 274 (1992) 270.
12 G. A. Bootsma and F. Meyer, Surf. Sci., 14 (1969) 52.
13 T. F. Heinz, M. M. T. Loy and W. A. Thompson, J. Vac. Sci. Technol. B, 3 (1985) 1467.
14 E. G. Keim, L. Wolterbeek and A. van Silfhout, Surf. Sci., 180 (1987) 565.
15 A. J. Hoeven, J. M. Lenssinck, D. Dijkkamp, E. J. van Loenen and J. Dieleman, Phys. Rev. Lett., 63 (1989) 1830.
16 E. Pehlke and J. Tersoff, Phys. Rev. Lett., 67 (1991) 1290.
17 H. Wormeester, A. M. Molenbroek, C. M. J. Wijers and A. van Silfhout, Surf. Sci., 260 (1992) 31.
18 A. G. B. M. Sasse, H. Wormeester, M. A. van der Hoef, E. G. Keim and A. van Silfhout, J. Vac. Sci. Technol. A, 7 (1989) 1623.
19 A. G. B. M. Sasse, H. Wormeester, M. A. van der Hoef and A. van Silfhout, J. Phys. (Condens. Matter), 1 (1989) 10175.
20 R. Del Sole and A. Selloni, Phys. Rev. B, 30 (1984) 883.
21 G. P. M. Poppe and C. M. J. Wijers, Physica B, 167 (1990) 221.
22 G. P. M. Poppe, H. Wormeester, A. Molenbroek, C. M. J. Wijers and A. van Silfhout, Phys. Rev. B, 43 (1991) 12122.
23 J. D. E. McIntyre and D. E. Aspnes, Surf. Sci., 24 (1971) 417.

24 D. E. Aspnes and A. A. Studna, *Phys. Rev. B*, 27 (1983) 985.
25 F. Bassani and G. Pastori Parravicini, in *Electronic States and Optical Transitions in Solids*, Pergamon, Oxford, 1975.
26 F. Meyer, *Phys. Rev. B*, 9 (1974) 3622.
27 H. J. W. Zandvliet and A. van Silfhout, *Surf. Sci.*, 211/212 (1989) 544.

28 H. J. W. Zandvliet, E. G. Keim and A. van Silfhout, *J. Vac. Sci. Technol. A*, 8 (1990) 2581.
29 P. Krüger, A. Mazur, J. Pollmann and G. Wolfgarten, *Phys. Rev. Lett.*, 57 (1986) 1468.
30 J. Pollmann, P. Krüger and A. Mazur, *J. Vac. Sci. Technol. B*, 5 (1987) 945.