SURFACE STATES ON CLEAN Ge(001) 2×1 SURFACES

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This paper describes a study concerning the interaction of oxygen with clean Ge(001) 2×1 surfaces in ultrahigh vacuum at 300 K. Surface conductance measurements, differential ellipsometry in the photon energy range of 1.5–4 eV and Auger electron spectroscopy have been used to monitor this solid–gas reaction. We observed in the joint density of states, as derived from ellipsometry, a peak at about 3.3 eV in addition to the optical transition at 1.8 eV reported earlier by Meyer. From the optical spectrum we show that the clean Ge(001) surface has at least three distinct surface states. Our results are essentially consistent with recent STM measurements and theoretical predictions. Moreover, we show that the distinct feature at 2.6 eV below the Fermi level as found with STM can be attributed to a surface state.

1. Introduction

The (001) surfaces of germanium and silicon are prototypical examples of systems possessing both a strong short-range reconstruction and a moderate-range, energetically weaker one. The basic (2×1) reconstruction is generally accepted to entail the formation of dimers, created through pairing of nearest-neighbour surface atoms [4]. Hence, the energy involved is due to chemical bond formation. If this was the only ordering mechanism, a (2×1) surface unit cell would result. Larger unit cells reported ($p(2 \times 2)$, $c(2 \times 2)$ and $c(4 \times 2)$) have usually been explained in terms of a longer-range, energetically weaker ordering of neighbouring dimers [5,6]. Symmetrical dimerization results in an odd number of unpaired electrons per surface atom, forming a half-filled band corresponding to a metallic surface.

High resolution angle-resolved photoemission studies of the Ge(001) surface show the existence of a metallic surface state near the centre of the surface Brillouin zone [6,16,17]. The state slowly disappears as the temperature is lowered from room temperature to 77 K. This metal–insulator transition is coincident with a recently predicted and observed transition from a disordered to an ordered $c(4 \times 2)$ structure [6]. However, asymmetric dimers are found as the main building blocks of the reconstruction at the surface [7,15,17]. First-principles electronic structure calculations by Krüger et al. [3] are in very good agreement with scanning tunneling measurements (STM) of Kubby et al. [2].

Using a local-density-functional formalism in a self-consistent scattering theoretical method, Krüger et al. determined the surface band structure for the Ge(001) surface consisting of asymmetric buckled dimers. Angle-resolved photoelectron spectroscopy investigations of surface states on the Ge reconstructed (001) surface [14,18,25] showed features at -0.5 eV (-0.6 eV), -1.3 eV [14,18] and -2.4 eV [25]. Our ellipsometric measurements are essentially consistent with STM measurements [2,11], angle-resolved photoelectron spectroscopy measurements [14,18,25] and theoretical calculations [3].

2. Experimental

The germanium sample ($30 \times 10 \times 0.52$ mm³) was made out of a 20Ω cm, n-type crystal in the (001) orientation, purchased from Hoboken. Prior to mounting the crystal was ultrasonically cleaned in ethanol. The sample could be resistively heated by the passage of a DC current. For the conductance measurements four titanium contacts were evaporated through a tantalum mask [12,13]. A current was sent through the outer pair of contacts of the sample, while the resulting potential was measured between the inner pair of contacts. In this way nonlinear behaviour of the metal–semiconductor contact is eliminated [12,13]. All experiments were performed in a stainless steel UHV system described previously [12]. The base pressure of this system was below 1.10^{-10} Torr. The ellipsometric measurements were performed with a rotating analyzer in the photon energy range 1.5–4 eV as described in refs. [12,19]. The Auger spectra were recorded using a primary current density of $\sim 1 \mu\text{A cm}^{-2}$, a modulation voltage of the energy analyzer 3–5 V_{pp} , a sweep rate of 1 eV/s, a lock-in time constant < 1 s and a primary energy of 2 keV.

A clean surface was obtained by cycles of sputtering (800 eV Ar^+ ions, $2 \mu\text{A cm}^{-2}$, 30 min, angle of incidence 45°) and annealing (850 K, 60 min) [6]. Also during sputtering the crystal was heated to ~ 700 K for about 15 min, followed by slow cooling. Auger spectra showed only a small residual carbon contamination of the surface [6,8]. We believe that this cleaning procedure results in a clean Ge(001)2×1 surface with a low density of defects; Alonso et al. [9] applied a similar surface cleaning treatment, called SIBA (simultaneous ion bombardment and annealing), to GaAs surfaces. Using the SIBA treatment Si surfaces reproducibly showed the best possible degree of perfection [10].

3. Results and discussion

The changes in the ellipsometric parameters $\delta\psi$ and $\delta\Delta$ upon oxygen adsorption were recorded as a function of photon energy. The results are given

Fig. 1. $\delta\psi = \psi(\text{O}_2) - \psi(\text{clean})$ as a function of photon energy.

in fig. 1 and 2. The $\delta\psi$ and $\delta\Delta$ versus E curves showed a significant structure. This structure was interpreted as due to a substrate change upon chemical adsorption, i.e., the saturation of the dangling bonds of the surface atoms. Chemisorption on clean germanium surfaces might cause a change in the (bulk) optical constants due to the Franz–Keldysh effect [27]. Nannarone et al. [28] mentioned that the change in reflectivity brought about by the oxide layer, cannot in principle be neglected. They say that such a term is very small

Fig. 2. $\delta\Delta = \Delta(\text{O}_2) - \Delta(\text{clean})$ as a function of photon energy.

Fig. 3. The imaginary part of the difference in complex dielectric constant $\text{Im}(\tilde{\epsilon}_{ss} - \tilde{\epsilon}_b)$ between the surface states layer and the bulk substrate for the clean Ge(001) surface as a function of the photon energy. (+) Without oxygen correction; (□) influence of an oxygen layer with a thickness of 1 Å.

except near critical points of the bulk structure and in germanium it is negligible below 3.5 eV [28].

The substrate effect has been described phenomenologically as the effective disappearance of a transition layer present at the clean surface [1,12,13]. This transition layer with an arbitrary chosen thickness of 5 Å (this value has no influence on the model) has optical constants ($\tilde{\epsilon}_{ss}$) different from the bulk ($\tilde{\epsilon}_b$), due to the difference in electronic structure between the surface layer (dangling bonds) and the bulk (sp^4 -type bonds). The effect of the thin oxide layer on the surface has been taken into account in both $\delta\psi$ and $\delta\Delta$. We have chosen an arbitrary thickness in our calculations of 1 Å. The relevant parameter for the transitions involving surface states is the difference between the imaginary part of the dielectric function of the surface layer and that of the bulk at corresponding photon energies, i.e. $\text{Im}(\tilde{\epsilon}_{ss} - \tilde{\epsilon}_b)$. The $\text{Im}(\tilde{\epsilon}_{ss} - \tilde{\epsilon}_b)$ curve for Ge(001) covered with one monolayer oxygen as a function of photon energy E is given in fig. 3; optical transitions at 1.8 eV and 3.3 eV are observed. These transitions would correspond to promotion of electrons from the filled surface states at -2.6 eV and -1 eV to the empty surface state at $+0.9$ eV (see STM measurements [2]). The difference in the transitions measured with the tunneling microscope and that measured by ellipsometry may arise from the difference in k space emphasized by these techniques; the 1.8 and 3.3 eV transitions are a threshold energy difference that needs not occur at the Γ point of the surface Brillouin zone, which is emphasized in the

tunneling spectrum. The filled state features have been determined by photo-emission [8,14,18,25]. The difference could also arise from the different ranges of $k_{\parallel}$ sampled by these different techniques. Nevertheless, the agreement is reasonable. We have assumed that the absorption in figs. 1 and 2 is mainly caused by transition between two subbands of surface states, although bulk state to surface state and vice versa may also contribute. The number of electrons contributing to the absorption should therefore be of the order of one electron per surface atom. In order to check the consistency of our data with this assumption we consider the f-sum rule

$$\int_0^{\infty} \omega \operatorname{Im}(\tilde{\epsilon}) d\omega = \pi \omega_p^2 / 2, \quad (1)$$

where $\omega_p^2 = 4\pi e^2 N / m$ is the plasmon frequency and N the number of electrons per unit volume. The effective number of electrons per surface atom involved in the surface absorption is given by

$$n_{\text{eff}} = (m / 2\pi^2 e^2 N) \int_0^{\infty} \omega \operatorname{Im}(\tilde{\epsilon}_{\text{ss}} - \tilde{\epsilon}_{\text{b}}) d\omega, \quad (2)$$

with $N = N_{\text{surface}} / d_{\text{ss}}$, where N_{surface} is the density of surface atoms and d_{ss} the thickness of the transition layer (5 Å). The effective number of electrons involved in the surface absorption (calculated from fig. 3) is somewhat greater than one. This value decreases when the influence of the oxide layer is taken into account. If at room temperature and at constant pressure (5×10^{-8} – $3 \times$

Fig. 4. Conductance changes and variation of the ellipsometric parameter ψ at the optical transition at 1.8 eV versus oxygen exposure.

Fig. 5. Conductance changes and variation of the ellipsometric parameter ψ at the optical transition at 1.8 eV versus oxygen exposure.

10^{-5} Torr) molecular oxygen was added, the p-type conductance decreased to a saturation value (figs. 4 and 5). Margoninski et al. [20,21], however, reported an initial increase of the surface conductance followed by a decrease. This type of result is also found by us after mild sputtering of the surface with Ar^+ ions (800 eV, 45° , $1 \mu\text{A}/\text{cm}^2$, 5 min) without annealing (see fig. 6). They further [20] report the presence of a unordered structure, i.e. an amorphous layer on the surface. The adsorption of oxygen on Ge(001) surfaces is both a pressure and an exposure dependent process (figs. 4 and 5). If we assume that the saturation value corresponds to the flat band situation (this is not completely correct, see e.g. ref. [22]) we can calculate the band bending at the cleaned Ge(001) surface. By definition the surface conductance σ_s is given by

$$\sigma_s = e(\mu_{ns} \Delta N + \mu_{ps} \Delta P), \quad (3)$$

where e is the elementary charge, μ_{ns} and μ_{ps} are the effective carrier mobilities at the surface and ΔN , ΔP the excess electron and hole concentrations per unit surface area. The surface is considered to be nondegenerate, no fast holes and fast electrons are assumed, ΔN is neglected, the sample is considered intrinsic, and μ_{ps} (surface mobility of holes) is replaced by the known value μ_p (bulk mobility of holes). The last assumption introduces errors of about 20%, see for example refs. [23,24]. Then it follows that the band bending is at least -340 mV (uncertainty about 10 mV), in good accordance with Margoninski et al. [20,21]. From the conductance measure-

Fig. 6. Conductance changes of lightly amorphous Ge surface versus oxygen exposure.

ments we can conclude that at first mainly acceptor surface states disappear followed by a stage where both acceptor and donor surface states are quenched. The final stage is characterized by the removal of mainly acceptor surface states. During the second stage of oxygen adsorption, the surface conductance is nearly constant but the Auger peak-to-peak height (O(510 eV)/Ge(1147 eV)) rises from 0.08 to 0.15. This means that the oxygen coverage increases from approximately 0.1 monolayer to 0.2 monolayer [26]. The changes in ψ and Δ measured at the optical transition at 1.8 eV also indicate an uptake of oxygen (figs. 4 and 5).

4. Conclusions

There appears to be a strong correlation between results obtained by ellipsometry and by STM measurements pertaining to the surface-states distribution on Ge(001) surfaces. The combination of surface conductance measurements and ellipsometry has proved to be a very powerful tool for investigation of gas adsorption on semiconductor surfaces.

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References

- [1] F. Meyer, *Phys. Rev. B* 9 (1974) 3622.
- [2] J.A. Kubby, J.E. Griffith, R.S. Becker and J.S. Vickers, *Phys. Rev. B* 36 (1987) 6079.
- [3] P. Krüger, A. Mazur, J. Pollman and G. Wolfgarten, *Phys. Rev. Letters* 57 (1986) 1468; M. Needels, M.C. Payne and J.D. Joannopoulos, *Phys. Rev. Letters* 58 (1987) 1765; J. Pollmann, P. Krüger, A. Mazur and G. Wolfgarten, in: *Proc. 18th Intern. Conf. on the Physics of Semiconductors*, Ed. O. Engström (World Scientific, Singapore, 1986) p. 81; see also J. Pollmann, P. Krüger and A. Mazur, *J. Vacuum Sci. Technol. B* 5 (1987) 945.
- [4] R.E. Schlier and H.E. Farnsworth, *J. Chem. Phys.* 30 (1959) 917.
- [5] J. Ihm, D.H. Lee, J.D. Joannopoulos and J.J. Xiong, *Phys. Rev. Letters* 51 (1983) 1872.
- [6] S.D. Kevan and N.G. Stoffel, *Phys. Rev. Letters* 53 (1984) 702.
- [7] D.J. Chadi, *Phys. Rev. Letters* 43 (1979) 43.
- [8] J.G. Nelson, W. Gignac, R.S. Williams, S.W. Robey, J.G. Tobin and D.A. Shirley, *Phys. Rev. B* 27 (1983) 3924.
- [9] M. Alonso, F. Soria and J.L. Sacedon, *J. Vacuum Sci. Technol. A* 3 (1985) 1598.
- [10] F.G. Keim, L. Wolterbeek and A. van Silfhout, *Surface Sci.* 180 (1987) 565.
- [11] R.S. Becker, B.S. Swartzentruber and J.S. Vickers, *J. Vacuum Sci. Technol. A* 6 (1988) 472.
- [12] H.J.W. Zandvliet and A. van Silfhout, *Surface Sci.* 195 (1988) 138.
- [13] H.J.W. Zandvliet and A. van Silfhout, *Solid State Commun.* 65 (1988) 1425.
- [14] T.C. Hsieh, T. Miller and T.-C. Chiang, *Phys. Rev. B* 30 (1984) 7005.
- [15] D.V. Froelich, A. Bowen and J.D. Dow, *J. Vacuum Sci. Technol. B* 2 (1984) 390.
- [16] S.D. Devan, *Phys. Rev. B* 32 (1988) 2344.
- [17] S. Kevan and N.G. Stoffel, *J. Vacuum Sci. Technol. A* 3 (1984) 1497.
- [18] J.G. Nelson, W.J. Gignac, R.S. Williams, S.W. Robey, J.G. Tobin and D.A. Shirley, *Surface Sci.* 131 (1983) 290; see also *Phys. Rev. B* 27 (1983) 3924.
- [19] A.H.M. Holtslag, Thesis, Twente University of Technology, 1986.
- [20] Y. Margoninski and L.G. Feinstein, *J. Appl. Phys.* 42 (1971) 4426.
- [21] Y. Margoninski and L.G. Feinstein, *Phys. Letters A* 31 (1970) 153.
- [22] A.H. Boonstra, Thesis, Eindhoven Technical University, 1967, *Philips Res. Rept.* 3 (1968).
- [23] A. Many, Y. Goldstein and N.B. Grover, *Semiconductor Surfaces* (North-Holland, Amsterdam, 1965).
- [24] R. Seiwatz and M. Green, *J. Appl. Phys.* 29 (1958) 1034.
- [25] J.E. Rowe and S.B. Christman, *J. Vacuum Sci. Technol.* 17 (1980) 220.
- [26] L. Surnev, *Surface Sci.* 110 (1981) 439.
- [27] L.V. Keldysh, *Zh. Eksperim. Theor. Fiz.* 34 (1958) 1138.
- [28] S. Nannarone, R. Chiaradia, F. Ciccacci, R. Memeo, P. Sassaroli, S. Selci and G. Chiarotti, *Solid State Commun.* 33 (1980) 593.