Dissociative H₂O adsorption on the Si(100)2×1 and Ge(100)2×1 surfaces

C U S Larsson and A S Flodström, *Materials Science, Royal Institute of Technology, S-100 44 Stockholm, Sweden*

Core-level spectroscopy and valence band photoelectron spectroscopy were used to study H₂O adsorption on the Si(100) and Ge(100) surfaces. We find that H₂O dissociates into H and OH on both surfaces at 300 K. The H and OH are adsorbed in on top positions on the surface. The OH group is tilted with respect to the surface normal on the Si(100) surface. We consider two possible interpretations for the results from the H₂O dosed Ge(100) surface at 300 K. Either a similar model as for the Si(100) surface or a model based on two adsorption sites.

1. Introduction

There has been a number of studies of H₂O adsorption on the Si(100) and Ge(100) surfaces. This is a function of the importance of the wet oxidation process in the semiconductor industry. The majority of recent investigations agree that H₂O adsorbs dissociatively on the Si(100)2 × 1 (refs 1–5) and the Ge(100)2 × 1 (refs 6–8) surfaces at 300 K. However, the interpretation of the results from photoelectron spectroscopy, core-level and valence band spectra is still not agreed on.

The study presented here shows that the surfaces are similar in many respects, with the sticking coefficients at 300 K as the main difference. The sticking coefficient is close to one for H₂O adsorption on Si(100) at 300 K while it is several orders of magnitude lower for Ge(100). The Ge samples in this study were therefore always cooled to 160 K before H₂O dosing to increase the sticking coefficient.

2. Experimental

The core-level and valence band spectroscopy experiments described in this report were performed at the Toroidal Grating Monochromator (TGM) beamline[9] at the MAXLAB synchrotron light source, Lund, Sweden and at the wiggler/undulator beamline at the flipper monochromator[10], HASYLAB, Hamburg, FRG. These experimental chambers were equipped with Cylindrical Mirror Analyzers (CMA) for energy analysis of the photoelectrons emitted from the sample and for Auger spectroscopy. LEED optics were mounted on the uhv chambers to check the surface layer symmetry. The base pressure was better than $2 \cdot 10^{-10}$ torr at all times.

The samples were cut from polished wafers to ~1 cm² size and rinsed in ethanol before introduction to the vacuum system. The samples were Ar⁺–ion sputtered using 1 keV beam energy and 2 μA beam current for 30 min. The sputtering was followed by an anneal to ~600°C for Ge and to ~850°C for Si using resistive heating or heating from the back of the sample with a W-filament. This was repeated in cycles until the surfaces were clean. The clean surfaces had a distinct LEED pattern; from a two-domain 2 × 1 reconstructed surface with no evidence of

quarter order spots at 300 K. The clean surface valence band and the surface sensitive core-levels were also recorded to check the sample cleanliness.

3. Results

3.1. Si(100). Saturation coverage of H₂O was obtained by dosing the surface with 5 L H₂O at 300 K. This procedure is known to form only one chemisorbed layer, since the sticking coefficient after the first chemisorbed layer is very low at 300 K (ref 11). After the H₂O exposure the valence band spectrum of the surface recorded at 30 eV photon energy changes as shown in Figure 1. These results are in close agreement to the spectra recorded by Schmeisser *et al*[12], but our interpretation is different. The surface state emission at 0.5 eV binding energy relative to the valence band maximum (VBM)[13] disappears completely after the H₂O dosing. Adsorbate induced structures appear at higher binding energies in the valence band spectrum. Two peaks at 6.3 and
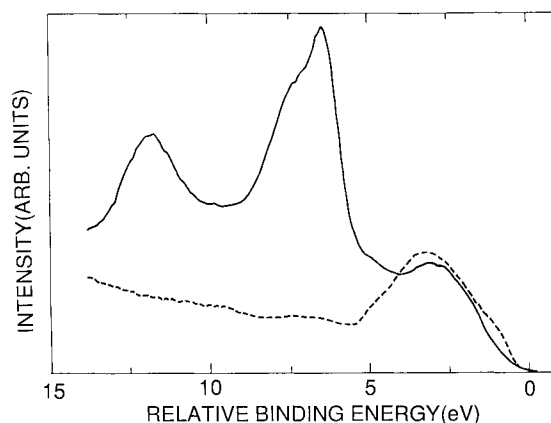
Figure 1. Normalized Si(100) valence band spectra recorded at 30 eV photon energy. The dashed line shows the clean surface spectrum and the full line the surface spectrum after dosing with 5 L H₂O. The H₂O exposures were done at 300 K. The binding energy is referred to the valence band maximum.
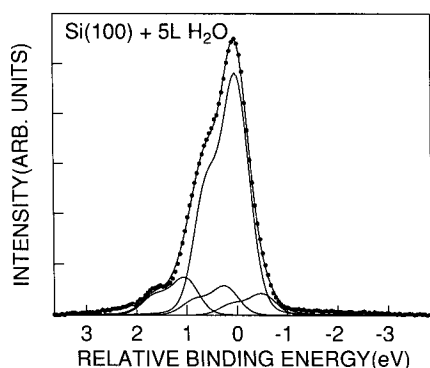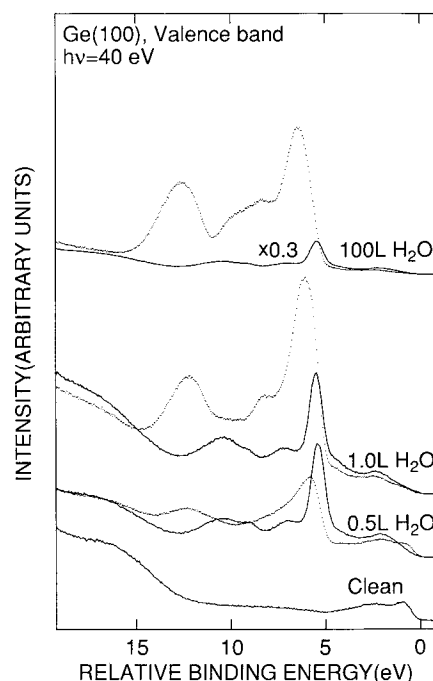
Figure 2. Si(100) 2p core level spectra recorded at 130 eV photon energy. The filled circles show the raw data after background subtraction and the full lines show the calculated fits to the data. The binding energy is referred to the bulk Si $2p_{3/2}$ component.

7.4 eV are poorly resolved. A third wide peak is found at 11.2 eV binding energy referred to the VBM.

In Figure 2 the Si 2p spectrum for the H₂O dosed Si(100)2 × 1 surface is presented. To achieve maximum surface sensitivity the incident photon energy was set to 130 eV yielding an electron kinetic energy, $E_K \approx 30$ eV close to the minimum in the electron mean free path[14]. We find a 0.08 eV Lorentzian width, a 0.53 eV Gaussian width, a 0.60 eV spin-orbit split and a 0.52 2p branching ratio. The surface sensitive 130 eV spectra were fit by adding bulk and surface 2p peaks having the same shapes and line widths as the bulk peak but different relative intensities and being separated in binding energy by $\Delta = E_S - E_B$. E_S and E_B are the binding energies for the surface and bulk peaks, respectively. The parameters obtained from our best fits to the Si 2p spectrum are summarized in Table 1. The spin-orbit split Si 2p bulk peak is the dominant feature in the spectrum; the clean Si 2p surface peak at $\Delta = -0.43$ eV has decreased to $R = 0.05$. The H₂O induced structure at higher binding energies can be deconvoluted into two surface peaks; one with $\Delta = +0.24$ eV and the other with $\Delta = +1.04$ eV energy.

3.2. Ge(100). The valence band emission from the clean Ge(100)2 × 1 surface is shown in Figure 3 together with spectra

Table 1. Core-levels

	Δ (eV)	R
Si(100)2 × 1		
+5 L H₂O, 300 K	−0.43	0.06
	+0.24	0.09
	+1.04	0.11
Ge(100)2 × 1		
Clean	−0.43	0.17
+1 L H₂O, 160 K	−0.43	0.04
	+0.43	0.12
	+0.75	0.06
+1 L H₂O, 300 K	+0.43	0.09
	+0.75	0.05

The positions and peak intensity to total intensity ratio R for the peaks in the core-level spectra shown in Figures 2 and 4.

Figure 3. Normalized Ge valence band spectra recorded at 40 eV photon energy. The clean surface spectrum was recorded at 300 K. All H₂O exposures were done at 160 K. The dotted lines show spectra recorded at 160 K sample temperature. The full lines show spectra recorded after heating to 300 K. Note that the spectra after 100 L H₂O dose are multiplied with a 0.3 factor. The binding energy is referred to the valence band maximum.

from a series of H₂O exposures. All the spectra were normalized to the clean valence band spectrum. The strong emission intensity in the clean valence band spectrum from 0.5 to 1.3 eV below the VBM is due to surface states that are characteristic for the clean Ge(100)2 × 1 surface[15,16] and these peaks disappear accordingly as the surface is exposed to H₂O. The broad emission shoulder at 16 eV below VBM is the Ge$_{MNN}$ Auger peak.

The sticking coefficient is high for H₂O adsorption on the Ge(100) surface at 160 K. The $c(4 \times 2)$ surface symmetry seen in LEED disappears after a 0.5 L H₂O dose and is replaced with a very weak 2 × 1 pattern. The surface state emission is reduced in intensity after a 0.5 L dose and new features develop in the valence band spectrum, peaks at 5.9 eV, 8.1 eV and 12.4 eV below VBM. These three peaks are present in all the 160 K H₂O dosed spectra, but they shift to higher binding energies with higher H₂O dose. with 1.0 L H₂O dose these peaks have shifted to 6.2 eV, 8.2 eV and 12.4 eV below VBM. There are not any new features in the 100 L H₂O spectrum with the three peaks at 6.5, 8.4 and 12.7 eV but the intensity has increased uniformly and the peak at 12.7 eV has become more dominant while the peak at 8.4 eV has widened.
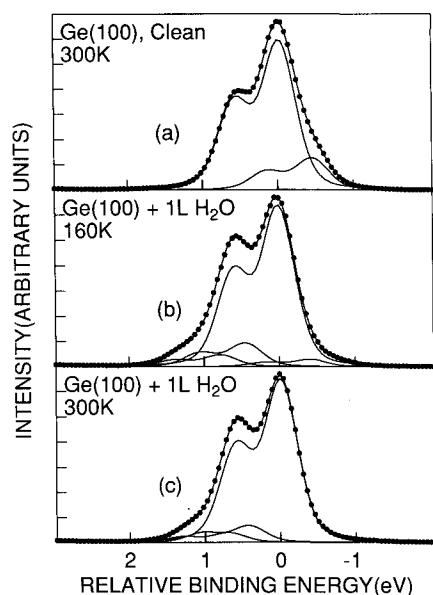
The valence band spectra recorded from the H₂O dosed samples after heating to 300 K are also shown in Figure 3. These spectra are all very similar with H₂O induced peaks at 5.5, 7.3, 9.3 and 10.4 eV below the VBM. The peak at 5.5 eV is very sharp with a full width half maximum (FWHM) of only 0.8 eV. The LEED changes into a sharp 2 × 1 pattern when the H₂O exposed sample is heated to 300 K.

The 3d surface sensitive core-level spectra from the clean surface and after 1.0 L H₂O exposure are shown in Figure 4. The 3d

Figure 4. Ge(100) 3d core level spectra recorded at 70 eV photon energy. The filled circles show the raw data after background subtraction and the full lines show the calculated fits to the data. (a) Shows the spectrum from the clean surface. (b) Shows the spectrum from the surface after a 1 L H₂O exposure at 160 K. (c) Shows the spectrum from the surface after a 1 L H₂O exposure at 160 K and heating to 300 K. The binding energy is referred to the bulk Ge $3d_{5/2}$ components.

doublet parameters are obtained from a fit to a surface sensitive core-level spectrum recorded with 70 eV photon energy from a clean surface. The clean surface raw data after background subtraction and the calculated fit are shown in Figure 4(a). We found a 0.15 eV Lorentzian width, a 0.42 eV Gaussian width, a 0.59 eV spin-orbit split and a 0.58 3d branching ratio. This deviation from the statistical value for the branching ratio, 0.67 is probably due to final state effects. These parameters are used for all the fits to the 3d core-level spectra in this paper.

The fit to the clean surface core level shown in Figure 4(a) has a surface peak that is shifted $\Delta = -0.43$ eV in binding energy. We interpret this peak as emission from the dimer pair atoms with dangling bonds. The position of this surface peak that is characteristic for the clean Ge(100)2 × 1 surface agrees well with previous measurements[17 19].

The Ge(100) sample was dosed at 160 K to increase the sticking coefficient to H₂O. This is shown in Figure 4(b). When the sample was heated to 300 K the peak at $\Delta = -0.43$ eV, typical for the clean surface, disappeared completely. This is shown in Figure 4(c).

4. Discussion

4.1. Si(100). We assign the peaks at 6.3 and 7.4 eV binding energy in the Si valence band to the OH π-orbital. This orbital is degenerate in the case of a free hydroxyl group. It is known from electron stimulated desorption ion angular distribution (ESDIAD)[3] that the OH group is tilted away from the surface normal. It is likely that the tilt removes the π-degeneracy resulting in a split peak in the spectrum. The peak at 11.2 eV is assigned to the OH σ-orbital.

The H₂O dosed Si 2p core-level spectra can be interpreted after comparison with H and O adsorption experiments on Si (refs 13,

20). The 0.24 eV shifted peak can be compared to the surface peak reported in ref 13 for the hydrogen terminated Si(111)1 × 1 surface. An atom in the first layer of unreconstructed Si(111) bonds to three Si atoms and has one dangling bond that after hydrogen termination, induces a shifted peak $\Delta = +0.26$ eV (ref 13). The bonding configuration when hydrogen atoms bond to the dimerized Si(100)2 × 1 surface without 'destroying' the 2 × 1 reconstruction should be similar. The agreement between the core-level shifts observed on the two different surfaces indicates that the $\Delta = 0.24$ eV peak should be assigned to Si top-layer atoms bonded to one H-atom each.

The $\Delta = +1.04$ eV surface peak in our H₂O dosed Si 2p core level spectrum can be compared with results reported by Hollinger and Himpsel[20] where this surface was dosed with O₂. They report four peaks with $\Delta = 1.0$, 1.8, 2.7 and 3.5 eV in the core-level spectrum after an anneal to 700°C. The shifts were assigned to Si[1+], Si[2+], Si[3+] and Si[4+], in that order[20]. We assign the $\Delta = +1.0$ eV peak in our H₂O dosed core level spectrum to Si atoms that bond to one OH each. The results presented in Table 1 show that Si–H and Si–OH bonds are found in approximately equal numbers on the H₂O dosed Si(100)2 × 1 surface.

4.2. Ge(100). The valence band spectra in Figure 4 from the H₂O dosed Ge(100)2 × 1 surface at 160 K show that H₂O adsorbs molecularly even for small doses and that ice forms. The peak shapes and separations are very similar to the valence band spectrum from ice[21]. We assign the three peaks, starting at low binding energy, to the $1b_1$, $3a_1$, and $1b_2$ molecular orbitals of H₂O. This does not exclude that there is dissociated H₂O on the surface at this temperature. Electron energy loss spectroscopy measurements[7] show that some H₂O dissociates even at low temperatures. That some dissociated H₂O is present is also evident from our Ge 3d core-level spectra.

When the sample is heated to 300 K the valence bands become almost identical for the different exposures. We interpret these 300 K spectra as OH and H groups adsorbed on the surface in the same manner as on the Si(100) surface, in on-top sites. The peaks at 5.5 and 7.3 eV below the VBM are assigned to the π-orbital. The peak at 10.4 eV below the VBM is assigned to the σ-orbital. The spectrum in ref 6 shows the same features but our interpretation is different. We assign the peak at 9.3 eV below the VBM and the broad emission on the low energy side of the 5.5 eV peak to atomic H bonded to the surface. Valence band spectra from hydrogenated Ge(100) surfaces[22,23] have emission intensities at these energies.

There are also differences between the Ge(100) and the Si(100) valence band spectra. The two peaks that we assign to the π-orbital are split 1.8 eV for Ge but are only split 1.1 eV in the Si case. Furthermore, the two peaks have approximately the same intensity in the Si case while this is not the case for Ge. In this context it is interesting to consider a different interpretation that has been suggested by Shao and Paul[24]. They base their interpretation on calculations on a Ge cluster with OH adsorbed at different sites. The peaks at 5.5 and 10.4 eV binding energy are assigned to the π- and σ-orbitals, respectively of OH groups adsorbed at an on-top site. The weak peaks at 7.3 and 9.3 eV binding energy are assigned to a minority OH species in a bridge site. The two models are illustrated in Figure 5.

The interpretation of the Ge core-level spectra is similar to that of the Si core-level spectra. We assign the shifted doublet peak in the surface sensitive core-level spectra at $\Delta = +0.75$ eV to OH radicals bonded to surface Ge atoms. That corresponds

299
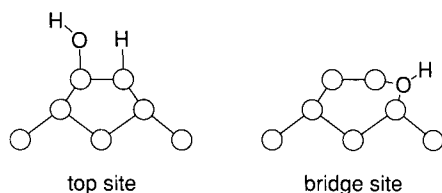
Figure 5. OH in a tilted on-top position and one possible OH bridge site position.

to the first oxidation state found in a study of O adsorption on the Ge(100) surface by Schmeisser *et al*[25]. In that study the first oxidation state was found at $\Delta = +0.8$ eV. The doublet at $\Delta = +0.43$ eV is assigned to H radicals bonded to the surface Ge atoms. A Ge(100) surface with adsorbed H has one H induced core-level shift at $\Delta = +0.41$ eV (ref 22). This is consistent with our interpretation of the valence band spectra.

Acknowledgements

References

[1] C U S Larsson, A S Flodström, R Nyholm, L Incoccia and F Senf, *J Vac Sci Technol*, **A5**, 3321 (1987).

[2] Y J Chabal and S B Christman, *Phys Rev*, **B29**, 6974 (1984).

[3] C U S Larsson, A L Johnson, A Flodström and T E Madey, *J Vac Sci Technol*, **A5**, 842 (1987).

[4] R McGrath, R Cimino, W Braun, G Thornton and I T McGovern, *Vacuum*, **38**, 251 (1988).

[5] K Fives, R McGrath, C Stephens, I T McGovern, R Cimino, D S-L Law, A L Johnson and G Thornton, *J Phys Condens Matt*, **1**, SB 105 (1989).

[6] H J Kuhr and W Ranke, *Surface Sci*, **187**, 98 (1987).

[7] L Papagno, L S Caputi, D Frankel, Y Chen and G F Lapeyre, *Surface Sci*, **189/190**, 199 (1987).

[8] C U S Larsson, A S Flodström, U O Karlsson and Y Yang, *J Vac Sci Technol*, **A7**, 2044 (1989).

[9] A Franks, B Gale, K Lindsey, M Steadman and W P Bailey, *Nucl Instrum Meth*, **208**, 233 (1983).

[10] F Senf, K Berens, V Rautenfeldt, S Cramm, C Kunz, J Lamp, V Saile, J Schmidt-May and J Voss, *Nucl Instrum Meth*, **A246**, 314 (1986).

[11] W Ranke and Y R Xing, *Surface Sci*, **157**, 339 (1985).

[12] D Schmeisser, F J Himpsel and G Hollinger, *Phys Rev*, **B27**, 7813 (1983).

[13] F Himpsel, P Heimann, T-C Chiang and D E Eastman, *Phys Rev Lett*, **45**, 1112 (1980).

[14] L Ley, M Cardona and R A Pollak, *Photoemission in Solids*, Vol *II* In *Springer Topics in Applied Physics* (Edited by L Ley and M Cardona). Springer, Berlin (1979).

[15] J G Nelson, W J Gignac, R S Williams, S W Robey, J G Tobin and D A Shirley, *Phys Rev*, **B27**, 3924 (1983).

[16] T C Hsieh, T Miller and T-C Chiang, *Phys Rev*, **B30**, 7005 (1984).

[17] R D Schnell, F J Himpsel, A Bogen, D Rieger and W Steinmann, *Phys Rev*, **B32**, 8052 (1985).

[18] D H Rich, T Miller and T-C Chiang, *Phys Rev Lett*, **60**, 357 (1988).

[19] T Miller, E Rosewinckel and T-C Chiang, *Solid State Commun*, **47**, 935 (1983).

[20] G Hollinger and F J Himpsel, *J Vac Sci Technol*, **A1**, 640 (1983).

[21] M J Campbell, J Liesegang, J D Riley, R C G Leckey, J G Jenkin and R T Poole, *J Electron Spectrosc Rel Phenom*, **15**, 83 (1979).

[22] C U S Larsson and A S Flodström, Unpublished.

[23] J A Appelbaum, G A Baraff, D R Hamann, H D Hagstrum and T Sakurai, *Surface Sci*, **70**, 654 (1978).

[24] Y Shao and J Paul, *Vacuum*, **42**, 313 (1991).

[25] D. Schmeisser, R D Schnell, A Bogen, F J Himpsel, D Rieger, G Landgren and J F Morar, *Surface Sci*, **172**, 455 (1986).