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Comparative study of water adsorption on Ge(100)-(2×1) and Ge_xSi_{1-x}(100)-(2×1) by high-resolution electron-energy-loss spectroscopy

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The identification of vibrational modes of OH in the electron-energy-loss spectrum of water-exposed Ge(100)-(2×1) allows us to give an alternative interpretation of high-resolution electron-energy-loss spectroscopy data of water on Ge_xSi_{1-x}(100)-(2×1) given in a recent publication. We show that the use of adsorbed species as markers to determine the surface composition as proposed by Broughton *et al.* is misleading, and that the evolution of electron-energy-loss spectra as a function of temperature can be explained in terms of mobility of adsorbed species rather than of changes in surface composition.

The study of adsorption and dissociation of small molecules on semiconductor surfaces is one of the most important topics in current surface physics research. In particular, the single-crystal surfaces of silicon[1–7] and germanium[7–13] have been the subject of many adsorption studies in recent years. One of the most suited techniques for such kinds of studies has been the high-resolution electron-energy-loss spectroscopy (HREELS), which, in most cases, permits a direct identification of the atomic or molecular species adsorbed on a surface. In fact, by this technique the vibrational spectra of water, oxygen, and hydrogen chemisorbed on Si (Refs. 1 and 4–7) and Ge (Refs. 7 and 11–13) surfaces have been obtained.

We have studied the interaction of water with the Ge(100)-(2×1) surface by HREELS, and details about the experimental procedure can be found in Refs. 12 and 13. We found no water adsorption at 300 K, while at liquid-nitrogen temperature (LNT) the HREEL spectrum clearly indicates the presence of H, OH, and undissociated water; the latter completely dissociates if the sample is warmed at 300 K.[12] Figure 1(a) shows the HREEL spectrum of the Ge(100)-(2×1) surface after 1 L (1 Langmuir$=1.33\times10^{-6}$ mbar sec) water exposure at LNT and subsequent annealing at 345 K.

To identify the origin of the 83- and 115-meV losses in Fig. 1(a), we have exposed the same surface to 5 L D_2O at LNT.[13] The HREEL spectrum after annealing at 345 K is shown in Fig. 1(b). The OH and OD stretching modes, with oxygen bonded to Ge atoms, should occur at nearly the same energy, while the mass factor should be important in the bending case. Comparison of the spectra in Figs. 1(a) and 1(b) allowed us to conclude that the 83- and 115-meV peaks in Fig. 1(a) are due to the OH stretching and bending modes, respectively.

Quite recently, Ge_xSi_{1-x}(100) surfaces, obtained by molecular-beam epitaxy on Si(100), have been exposed to hydrogen and water and studied by HREELS.[14–16] Both monohydride and dihydride forms have been obtained in hydrogen exposure experiments,[14] and the relative intensities of Si-H and Ge-H stretching modes have been used to determine the composition of the topmost layer of a $Ge_{0.2}Si_{0.8}$(100)-(2×1) surface.

It has been shown that very different surface concentrations of Ge and Si can be obtained by slightly chang-

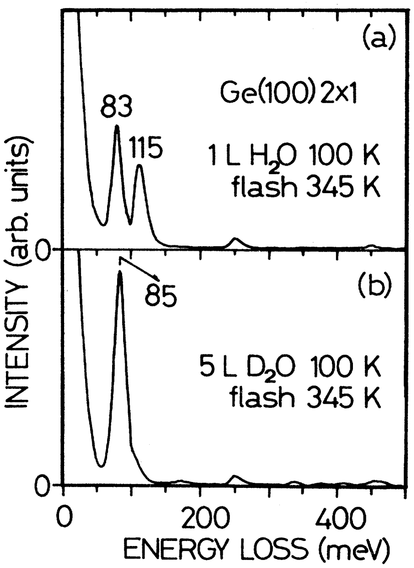

FIG. 1. HREEL spectra of the Ge(100) surface after exposure to (a) 1 L H_2O at LNT, (b) 5 L D_2O at LNT. Both spectra have been obtained after annealing the surface at 345 K. Peaks at 243 and 450 meV in (b) are due to dissociation of water contaminant.

ing the annealing procedure of these ordered alloys.[14] In the case of a "nominal" 1:2 Ge-to-Si surface composition, Schaefer *et al.*[14] obtain, by analysis of the Si-H and Ge-H stretching mode intensities, and assuming an equal oscillator strength for both species, 33 at. % of Ge in the outermost layer. The same authors also performed a water adsorption study on the same surface.[15,16] The HREEL spectrum obtained after 1 L water exposure at room temperature (RT) is shown in Fig. 2. By analysis of the hydride stretching modes, the authors conclude that the $Ge_{0.2}Si_{0.8}(100)$ surface, annealed for 5 min at about 670 K, is approximately 75 at. % Ge. For what concerns the assignment of the various peaks present in the spectrum in Fig. 2, Broughton *et al.*[16] assume that the OH bending mode and the O-H stretching mode occur at 98 and 460 meV, respectively, and that their positions are independent of the surface atom to which they are attached. In view of our results, the above conclusions must be taken with caution.

Contrary to the assumption of Ref. 16, the bending and stretching frequencies of the hydroxyl are *dependent* on the substrate atom to which they are attached. Supposing the vibrational frequencies to remain unchanged passing from pure Ge and Si to $Ge_{0.2}Si_{0.8}$ surfaces, as nearly exactly verified for hydride stretching modes, the HREEL spectrum in Fig. 2 should contain 83- and 115-meV losses in the case of OH bonded to Ge atoms, while, in the case of bonding to Si atoms, the OH stretching and bending modes should both occur around 100 meV, as already found, for instance, by Ibach *et al.*[1] The presence of only an intense peak at 98 meV clearly indicates that the OH radicals are predominantly attached to Si atoms. If quantitative calculations, similar to that performed using hydride stretching modes (which give 75 at. % Ge in the topmost layer) were done using OH bending and stretching modes, one should conclude that the $Ge_{0.2}Si_{0.8}(100)$ surface annealed at 670 K contains only silicon atoms. This contradiction is indicative of the fact that, at least in the case of the $Ge_{0.2}Si_{0.8}(100)$ surface, the H and OH chemisorbed species *cannot* be used in a simple way to determine the surface composition.

The reactivity with respect to water seems to be very similar for Si(100) and $Ge_{0.2}Si_{0.8}(100)$ surfaces, which promptly dissociate the water molecule at RT. In comparison, at RT the Ge(100) surface is nearly inert.[9,12,13] As also hypothesized by Broughton *et al.*,[16] an identical water dissociation mechanism should operate on both Si(100) and $Ge_{0.2}Si_{0.8}(100)$ surfaces. A realistic hypothesis about the water dissociation process on the latter surface can be made: the water molecule dissociates on a Si surface atom, leaving an OH group attached to it; the disposable hydrogen is captured by a neighboring dangling bond, which can belong to a Ge surface atom. This picture is consistent with the HREEL spectrum in Fig. 2, from which it may be concluded that, at the saturation, the OH radicals are attached to Si atoms only, while hydrogens are predominantly bonded to Ge atoms, although some amount of them are Si bonded.

Annealing the preexposed $Ge_{0.2}Si_{0.8}(100)$ surface at different temperatures produces marked changes in the HREEL spectrum (Fig. 3). Between 423 and 573 K the Si-H stretching mode intensity increases with respect to the Ge-H stretching mode, while the other structures remain almost unchanged. At 623 K, the Ge-H stretching mode becomes not clearly visible, the structures at 98 and 460 meV decrease, and two new peaks appear at 80 and 115 meV, assigned by Broughton *et al.*[16] to the Si-H bending mode and to a "surface oxide or suboxide mode," respectively; these findings are explained as due to an inversion in the surface concentration of surface atoms. The main conclusion of Ref. 16 is that chemisorbed species can be used as markers for determining the surface composition of heterogeneous substrates.

The evolution of HREEL spectra as a function of temperature in Fig. 3 can be also explained in view of our results. In fact, the 80- and 115-meV peaks in the spectrum in Fig. 3(d) are located at almost the same energies as those present in Fig. 1(a). Furthermore, the hypothesis made by Broughton *et al.*,[16] which explains the peak at 115 meV as due to a surface oxide mode, is unlikely. In fact, oxidation experiments performed by heating Si (Ref.

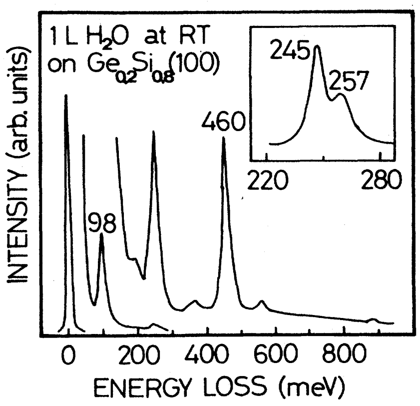

FIG. 2. HREEL spectrum of the $Ge_{0.2}Si_{0.8}(100)$-(2×1) surface after exposure to 1 L water at RT.

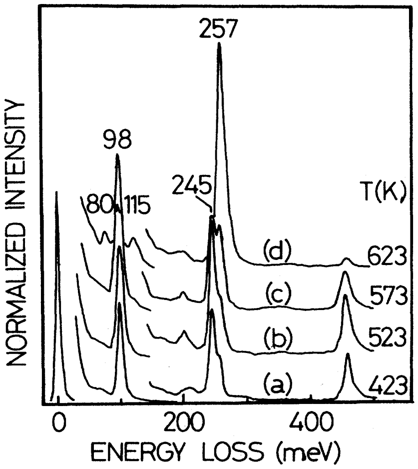

FIG. 3. HREEL spectra after heating the $Ge_{0.2}Si_{0.8}(100)$ surface, preexposed to 1 L water at RT, at (a) 423 K, (b) 523 K, (c) 573 K, and (d) 623 K.

5) and Ge (Ref. 13) surfaces preexposed to water, give, in the first case, a strong mode at 130 meV, while in the Ge case we obtain structures at 60 and 100 meV.[13]

If the 80- and 115-meV peaks in Fig. 3(d) are interpreted as due to Ge-bonded OH, the evolution of HREEL spectra in Fig. 3 can be explained by considering mobility of adsorbed species. The Si-bonded OH radicals begin to dissociate at about 420 K, but around 600 K, before the complete disappearance of all hydroxyls, some of them can transfer onto Ge atoms. The increase of the Si-H stretching peak with respect to the Ge-H one is also due, for temperatures around 600 K, to the availability of Si dangling bonds caused by the OH transfer mechanism. In the temperature range 520–570 K, the above change in relative intensities without the appearance of the 80- and 115-meV modes indicates that, at "saturation," not all the silicon dangling bonds are passivated by OH groups.

It should be noted that in our water adsorption experiment on Ge(100),[13] at 510 K we observe no presence of OH radicals, while Broughton *et al.*[16] still observe such radicals at 623 K on $Ge_{0.2}Si_{0.8}(100)$ [Fig. 3(d)]. This fact can be due to a different reactivity of the Ge atoms in the two surfaces, or to different temperature measurement modalities. However, this observation does not have influence on our main conclusions, which can be summarized as follows.

(i) The stretching and bending modes of hydroxyl bonded to Ge atoms are located at 83 and 115 meV, respectively.

(ii) The chemisorbed species cannot be used in a simple way to determine the surface composition, at least in the case of water adsorption on $Ge_{0.2}Si_{0.8}(100)$.

(iii) With increasing temperature, the mobility of adsorbed species can explain the evolution of HREEL spectra; the fact that OH species, for increasing temperature, preferentially stick to Ge is consistent with the Lewis model of acid and base, in which OH behaves as an acceptor and H_2O behaves as a donor. So OH tends to bound to Ge because this is more electronegative with respect to Si. The opposite way around happens for water which preferentially bonds to Si atoms.

[1] H. Ibach, H. Wagner, and D. Bruchmann, Solid State Commun. **42**, 457 (1982).
[2] Y. J. Chabal, Surf. Sci. **168**, 594 (1986).
[3] S. Katircioglu, Surf. Sci. **187**, 569 (1987).
[4] H. Froitzheim, H. Lammering, and H. L. Gunter, Phys. Rev. B **27**, 2278 (1983).
[5] H. Ibach, H. D. Bruchmann, and H. Wagner, Appl. Phys. A **29**, 113 (1982).
[6] J. A. Schaefer, J. Anderson, and G. J. Lapeyre, J. Vac. Sci. Technol. A **3**, 1443 (1986).
[7] P. A. Thiel and E. Madey, Surf. Sci. Rep. **7**, 354 (1987).
[8] S. Sinharoy and M. Henzler, Surf. Sci. **47**, 525 (1975).
[9] H. J. Kuhr and W. Ranke, Surf. Sci. **187**, 98 (1987).
[10] H. J. Kuhr and W. Ranke, Surf. Sci. **189/190**, 420 (1987).
[11] L. Papagno, X. Y. Shen, J. Anderson, G. Schirripa, and G. J. Lapeyre, Phys. Rev. B **34**, 7188 (1986).
[12] L. Papagno, L. S. Caputi, D. Frankel, Y. Chen, and G. J. Lapeyre, Surf. Sci. **189-190**, 199 (1987).
[13] L. Papagno, D. Frankel, Y. Chen, L. S. Caputi, and G. J. Lapeyre (unpublished).
[14] J. A. Schaefer, J. Q. Broughton, J. C. Bean, and H. H. Farrel, Phys. Rev. B **33**, 2999 (1986).
[15] J. A. Schaefer, J. Q. Broughton, J. C. Bean, and H. H. Farrell, J. Electron Spectrosc. Relat. Phenom. **39**, 127 (1986).
[16] J. Q. Broughton, J. A. Schaefer, J. C. Bean, and H. H. Farrell, Phys. Rev. B **33**, 6841 (1986).