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Adsorbate-induced de-reconstruction in the interaction of H₂S with Ge(001) 2 × 1

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Abstract. The room temperature adsorption of H₂S on Ge(001) 2 × 1 has been studied using surface-extended x-ray-absorption fine structure, low-energy electron diffraction and Auger electron spectroscopy. The Ge(001) 2 × 1–S system formed by a saturation dose followed by an anneal to remove H has a S–Ge bond length of 2.36 ± 0.05 Å, with S sitting in twofold bridge sites, consistent with breaking of the Ge–Ge dimer reconstruction. Further adsorption of H₂S at low or elevated temperatures is kinetically unfavourable, and it is proposed that this is consistent with the surface Ge atoms sitting in non-ideal rather than bulk-terminated positions.

1. Introduction

Adsorbate–semiconductor systems where the adsorbate provides a bulk termination to the semiconductor, removing the clean surface reconstruction, are of interest as model systems for testing new experimental and calculational techniques. For this reason there has been recent interest in the adsorption of S and H₂S on dimer-reconstructed Ge(001) 2 × 1. Three overlayer systems have been identified, as listed below:

(i) Ge(001) 1 × 1–S: Weser and co-workers used photoemission core-level spectroscopy [1] and ultraviolet photoemission spectroscopy (UPS) [2] to infer that molecules of S₂ adsorbing on this surface dissociate with S breaking the dimer bonds and adsorbing in bridge sites. An ideally terminated Ge(001) surface is formed with a 1 monolayer (ML) coverage and 1 × 1 periodicity. A core-level shift of the Ge 3d of 0.33 eV to higher binding energy results. These results are supported by the calculations of Krüger and Pollmann [3], their band structure for the bridge site being in good agreement with the experimental determination. They suggest a bond length of 2.36 Å for this system [3].

(ii) Ge(001) 2 × 1–HS: H₂S adsorption on Ge(001) 2 × 1 was characterized by Ranke and co-workers [4, 5] using Auger electron spectroscopy (AES), core-level UPS and valence band UPS. It was shown that at room temperature the H₂S dissociates to

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H and HS, the coverage of S is 0.5 ML and the adsorption is on the terrace sites. A core-level shift for Ge 3d of 0.43 eV to higher binding energy results for this system: the surface retains 2×1 periodicity, and both H and HS are present.

(iii) Ge(001) 2×1–S: Shirley and co-workers [6] have used low-energy electron diffraction (LEED) and electron energy loss spectroscopy (EELS) in showing that H can be removed by annealing to 300 °C leaving a Ge(001) 2×1–S overlayer. The bond length was determined by angle-resolved photoemission fine structure (ARPEFS) to be 2.36 ± 0.05 Å and the adsorption site favoured is the bridge site.

These results for these three closely related overlayer systems pose a number of questions. Firstly, the Ge–S bond length of 2.36 Å as calculated for Ge(001) 1×1–S [3] and as measured for Ge(001) 2×1–S [6] is long compared to the sum of the covalent bond radii of S and Ge (2.26 Å); a second experimental determination of this system is therefore desirable. Secondly, the Ge core-level shift to higher binding energy on Ge(001) 1×1–S (0.33 eV) and on Ge(001) 2×1–HS (0.43 eV) suggests that the adsorption site is similar while the ARPEFS results suggest a similar site for Ge(001) 2×1–S; because of this close interrelation it is puzzling that the periodicity remains 2×1 and the coverage 0.5 ML when dosing with H_2S at room temperature. It is of interest therefore to determine whether there are any conditions under which the coverage can be increased and the periodicity changed from 2×1 to 1×1 by further adsorption of H_2S.

In an attempt to address these questions we have used surface extended x-ray absorption fine structure (SEXAFS), LEED and AES measurements to characterize H_2S adsorption on Ge(001) 2×1. Our results confirm the bond-length for Ge(001) 2×1–S to be 2.36 ± 0.05 Å, and the bridge site is found to be the favoured one. No dosing method was found of transforming the Ge(001) 2×1–S overlayer to the Ge(001) 1×1–S overlayer and it is suggested that this may be because H_2S does not completely remove the clean surface reconstruction, leaving a kinetic barrier to further adsorption.

2. Experimental and analysis details

The SEXAFS experiments were performed on Surface Science beamline 6.3 at the Daresbury Laboratory [7]. This beamline provides monochromatic radiation of high intensity in the region of the S K-edge (2468 eV). The data were collected with a Physical Electronics double-pass cylindrical mirror analyser (CMA) using the yield of S KLL Auger electrons as a measure of the absorption cross section. Normalization was accomplished using an Al foil. SEXAFS experiments were done in both normal and grazing incidence. All measurements were performed at room temperature.

The sample was cleaned by cycles of sputtering with 1 keV Ar$^+$ ions and annealing to 1000 K. Several cycles were needed to produce a sharp 2×1 LEED pattern. The sample was then dosed with H_2S; a saturation dose of 5 L produced the Ge(001) 2×1–HS surface. The coverage was taken to be 0.5 ML by comparison with previously published work [4, 5].

The procedure developed by Shirley and co-worker [6] for removal of H was followed to produce an atomic 2×1 S overlayer; the S AES intensity remained unchanged, indicating a 0.5 ± 0.05 ML coverage of atomic S. This overlayer was found to be stable against contamination, remaining clean for periods of days in the vacuum

of $\leqslant 2 \times 10^{-10}$ Torr. The overlayer could be removed by annealing to 650 K leaving a clean Ge(001) 2 × 1 surface, again consistent with previous results [6].

Data reduction and analysis were done using the program library at Daresbury Laboratory. After normalization to the edge height and subtraction of a smoothly varying polynomial background the normalized oscillatory part of the fine structure $\chi(k)$ was analysed using the EXCURVE fitting program [8]. To evaluate an unknown bond length using EXAFS it is necessary to know the phase shift $\phi(k)$ which is the sum of the shifts experienced by the electron on encountering the central atom potential (twice) and the phase shift introduced by the backscattering atom. $\phi(k)$ can be assessed by calculation or by measuring a compound with the same absorber–backscatterer pair whose structure is known. Several systems were considered in choosing a model compound. Sulphides of Ge lack a well-defined first shell and may exist in several phases at room temperature [9]. ZnS which has a zincblende structure, and CoS$_2$, which has the pyrite structure [9] are suitable, provided the change in backscattering phase from Zn and Co to Ge can be accurately assessed. The calculated phase shifts of Teo and Lee [10] were used to make this estimate, yielding a value of -0.004 Å per element with decreasing atomic number. When this correction is applied, the phase functions of ZnS and CoS$_2$ are found to be consistent to within 0.005 Å. Accordingly for Ge–S bond length estimation the ZnS phase shift was used applying a correction of $+0.008$ Å.

The effective coordination number ratio was extracted from the data by comparing the amplitudes in grazing and normal incidence. Experimentally determined effective coordination numbers N_j^* were compared with calculated values for the different structural geometries. N_j^* can be calculated for any system from the expression

$$N_j^* = 3 \sum_{i=1}^{N_j} \cos^2 \theta_{ij}$$

where θ_{ij} is the angle between the polarization vector of the radiation and r_{ij}, and N_j is the total number of atoms in the jth shell.

3. Results

The edge jump (10%) in the SEXAFS data is small compared to more favourable cases (e.g. $\sim 100\%$ for 0.22 ML of S on a Cu(001) surface using fluorescence detection [11]). The background subtracted and edge-step normalized EXAFS $\chi(k)$ weighted by k for normal and grazing incidence are shown in figure 1 (left side). The modulus of the resulting Fourier transforms are shown in figure 1 (right side). In order to extract structural parameters of interest, the first-shell contribution was extracted by Fourier filtering; the back-transformed contribution from this component is shown as the smooth solid line superimposed on $\chi(k)$. A sulphur central atom with Ge backscattering atoms was assumed. The component at the unphysical distance of 1.6 Å in the grazing incidence data arises from the difficulty in performing a background subtraction when the SEXAFS oscillations are weak. It does not affect the distance determination, and its effect on the amplitude determination is reflected in the error bar in the coordination number ratio which was estimated to be $\pm 20\%$. The only amplitude parameters varied were the effective coordination numbers. Error bars in

the distance determinations were estimated by studying changes introduced by varying the threshold energy E_0 and by taking different k-space ranges for the data.

Distances of 2.34 ± 0.05 Å and 2.38 ± 0.05 Å were found for the first shell in normal and grazing incidence giving an average value of 2.36 ± 0.05 Å. The ratio of amplitudes for normal to grazing incidence was found to be 1.1 ± 0.2. The possibility that these results represent a disordered overlayer can be discounted because of the sharp 2×1 LEED pattern. To identify the adsorption side, calculations of the expected coordination number ratio were performed for (a) an atop site, (b) a bridge site, where the S atom sits between two Ge atoms with a fourth-layer Ge atom below (c) an anti-bridge site, where the S atom sits between two Ge atoms with a second-layer atom below, (d) a four-fold hollow site and (e) where S sits on a Ge dimer atom. These sites are shown in figure 2. The results are shown in table 1, together with the experimental data.
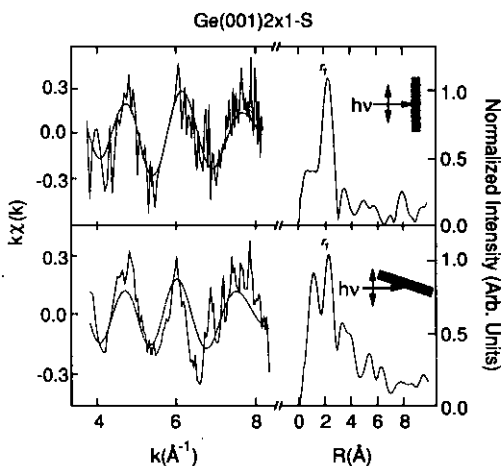
Figure 1. S KLL Auger yield SEXAFS data $\chi(k)$ and corresponding Fourier transforms for Ge(001) 2×1-S. Top panel: normal incidence SEXAFS after background subtraction and normalization to the edge jump. The SEXAFS function $\chi(k)$ is shown weighted by k. The solid line is the filtered and back-transformed first-neighbour shell r_1. Bottom panel: as above for grazing incidence.
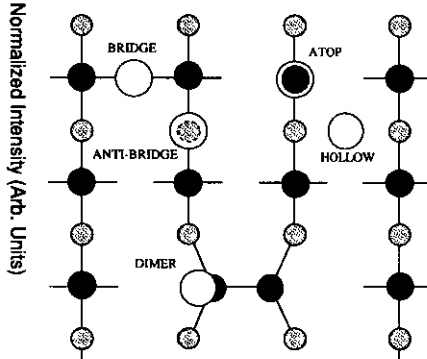
Figure 2. Plan view of the surface structures for S adsorption on Ge(001) considered in the calculations of effective coordination number. The solid lines indicate bond directions. White circles denote S atoms, filled circles denote top-layer Ge atoms and dotted smaller circles denote second-layer Ge atoms.

Table 1. Calculated first-shell normal/grazing amplitude ratios for the five possible adsorption sites shown in figure 2.

Site	Ratio
Atop	0.0
Bridge	1.2
Anti-bridge	1.2
Hollow	1.4
Dimer	0.1
Experiment	1.1 ± 0.2

Only the bridge and anti-bridge sites are consistent with the data. A higher shell at ~ 2.7 Å should be present in the grazing incidence data for the anti-bridge site but not for the bridge site (see figure 2); however, the data quality is not sufficient to clarify this point. A strong argument against the anti-bridge site is that the dangling bonds for the neighbouring Ge atoms point perpendicular to the Ge–S–Ge bond direction for this site (as indicated in figure 2). This site was discounted by the calculations of Krüger and Pollmann [3] for Ge(001) 1×1–S. As the 2×1 periodicity is maintained, and the coverage is 0.5 ML, there are a number of possibilities for the medium-range-order arrangement of the atoms in the bridge sites [6]. As SEXAFS is a short-range-order probe, these cannot be distinguished in this study.

A series of dosing experiments were performed to establish the conditions under which the 2×1 overlayer is obtained, and whether the 1×1 overlayer (coverage 1 ML) can subsequently be formed. These attempts followed a methodology developed previously in a study of H₂S adsorption on Cu(001) [11]. The Ge(001) 2×1–S surface formed after annealing for removal of H was re-dosed with H₂S. This did not lead to any increase in H₂S adsorption or change in the LEED pattern. The 0.5 ML Ge(001) 2×1–S surface was cooled to 150 K and re-dosed, then warmed to room temperature. Again this did not result in additional S coverage. Finally, the clean surface was dosed at 575 K; this again produced the Ge(001) 2×1–S 0.5 ML overlayer. These results all point to a strong kinetic barrier to further H₂S adsorption and dissociation.

4. Discussion

The SEXAFS results presented here for Ge(001) 2×1–S confirm the results of Leung *et al* [6] that the S–Ge bond length in this system is 2.36 Å. This is longer than the sum of the covalent radii (2.26 Å) and the S–Ge bond length of 2.23 ± 0.05 Å in Ge(111) 1×1–S [13]; this is a reflection on the different adsorption sites in these two systems.

It is the same bond-length and adsorption site as determined for the Ge(001) 1×1–S system [1–3]. It is clear therefore that there are major similarities in the structures of both the 1 ML Ge(001) 1×1–S system formed by dosing with atomic S and the 0.5 ML Ge(001) 2×1–S system formed by annealing the Ge(001) 2×1–HS system. The bond length and the adsorption site in both cases are the same. The similarities in core-level results from Ge(001) 1×1–S [1] and Ge(001) 2×1–HS [5] provide indirect evidence that the site is similar also for these systems.

The question remains as to why the 1×1 1 ML surface cannot be formed by H₂S dosing. A possible explanation comes from studies of the adsorption of H₂S on Cu(001). Here a kinetic barrier to room temperature H₂S dissociative adsorption is found after the adsorption of 0.22 ML of H₂S [11]. In a separate study using grazing incidence x-ray diffraction a reconstruction of the Cu surface was found [12] involving a small (0.03 Å) outward lateral relaxation of the four Cu atoms to which an S atom was bonded; this was proposed to make the adjacent sites unfavourable to further H₂S adsorption. A similar mechanism may obtain in the present study, whereby upon H₂S dosing, the Ge(001) surface does not obtain its ideal termination (as it does with S₂ dosing), a small remaining reconstruction providing a barrier to further H₂S adsorption despite the breaking of the Ge dimers.

5. Conclusions

The adsorption of H_2S on Ge(001) 2×1 has been studied using SEXAFS, LEED and AES. The Ge(001) 2×1–S overlayer formed after H desorption has the S atoms in bridge sites with a bond length of 2.36 ± 0.04 Å which is consistent with previous work. No further adsorption of H_2S takes place on this surface suggesting a kinetic barrier to dissociative adsorption which could be caused by small disturbances of the Ge atoms from their bulk-terminated position. It is planned to test this proposal using scanning tunnelling microscopy (STM) which would provide information about the medium-range order of the Ge(001) 2×1–S overlayer.

Acknowledgments

References

[1]   Weser T, Bogen A, Konrad B, Schnell R D, Schug C A and Steinmann W 1987 *Phys. Rev.* B **35** 8184
[2]   Weser T, Bogen A, Konrad B, Schnell R D, Schug C A, Moritz W and Steinmann W 1988 *Surf. Sci.* **201** 245
[3]   Krüger P and Pollmann J 1990 *Phys. Rev. Lett.* **64** 1808
[4]   Kuhr H J, Ranke W and Finster J 1986 *Surf. Sci* **178** 171
[5]   Kuhr H J and Ranke W 1987 *Surf. Sci* **189/190** 420
[6]   Leung K T, Terminello L J, Hussain I, Zhang X S, Hayashi T and Shirley D A 1988 *Phys. Rev.* B **38** 8241
[7]   MacDowell A A, Norman D and West J B 1986 *Rev. Sci. Instrum.* **57** 2667
[8]   Gurman S J, Binsted N and Ross I 1984 *J. Phys. C: Solid State Phys.* **17** 143
[9]   Wyckoff R W G 1982 *Crystal Structure* 2nd edn (Malabar, FL: Krieger)
[10] Teo B K and Lee P A 1989 *J. Am. Chem. Soc.* **101** 2815
[11] McGrath R, MacDowell A A, Hashizume T, Sette F and Citrin P H 1990 *Phys. Rev. Lett.* **64** 575
[12] Vlieg E, Robinson I K and McGrath R 1990 *Phys. Rev.* B **41** 7896
[13] Robey S W, Bahr C C, Hussain Z, Barton J J, Leung K T, Lou J R, Schach-von Wittenau A and Shirley D A 1987 *Phys. Rev.* B **35** 5657