Applied Surface Science 329 (2015) 363–370

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Vibrational mode frequencies of H_2S and H_2O adsorbed on Ge(0 0 1)-(2 × 1) surfaces

M. Hartnett[a,b,*], S. Fahy[a,b]

[a] Tyndall National Institute, Lee Maltings, Cork, Ireland
[b] Physics Department, University College, Cork, Ireland

ARTICLE INFO

Article history:
Received 3 December 2014
Accepted 13 December 2014
Available online 19 December 2014

Keywords:
Germanium
Vibrational
Mode
Frequency
Stretch
Bending

ABSTRACT

The equilibrium geometry and vibrational modes of H_2S and H_2O-terminated Ge(0 0 1)–(2 × 1) surfaces are calculated in a supercell approach using first-principles density functional theory in the local density (LDA), generalized gradient (GGA) approximations and van der Waals (vdW) interactions. Mode frequencies are found using the frozen phonon method. For the H_2S-passivated surface, the calculated frequencies in LDA (GGA) are 2429 cm^{-1} (2490) for the H—S stretch mode, 712 cm^{-1} (706) for the H—S bond bending mode, 377 cm^{-1} (36) for the Ge—S stretch mode and 328 cm^{-1} (337) for H—S wag mode. Frequencies for the H_2O passivated surface are 3590 cm^{-1} (3600) for the H—O stretch mode, 921 cm^{-1} (947) for the bending mode, 609 cm^{-1} (559) for the Ge—O stretch, 1995 cm^{-1} (1991) for the Ge—H stretch mode, 498 cm^{-1} (478) for the Ge—H bending mode and 342 cm^{-1} (336) for the H—O wag mode. The differences between the functionals including vdW terms and the LDA or GGA are less than the differences between LDA and GGA for the vibrational mode frequencies.

1. Introduction

Clean and adsorbed Ge(0 0 1) surfaces have been studied both in theory and experiment [1,2]. The bare Ge(0 0 1) surface undergoes reconstruction, forming buckled dimers arranged in rows and reducing the number of dangling bonds from two to one. This germanium surface exhibits dangling-bond states in the fundamental energy gap [2], making it reactive and unsuitable for electronic applications. To reduce such surface states on the Ge(0 0 1) surface, a passivation process is required to saturate the dangling bonds.

Hydrogen, sulphur and water have been studied as absorbents on the Ge surface [2,3]. An absorbed monolayer of hydrogen completely passivates the Ge surface, with Ge—H bonding states lying far below the fundamental energy gap [2] in a (2 × 1) symmetric dimer structure. A monolayer of sulfur causes the bare (2 × 1) Ge surface to reconstruct, restoring the (1 × 1) bulk-like geometry but leaving surface electronic states in the fundamental gap [2].

To further passivate the sulfur-terminated surface, termination of the Ge(0 0 1) surface by H_2S has been studied [4], showing that the terminated surface forms a (2 × 1) reconstruction with (S—H)—(S—H) inter-Ge dimer bridges. The computed energy band gap of this configuration is free of surface states, which is of relevance to the future application of germanium in high performance integrated circuits.

Water, a contaminant in many growth and fabrication processes, also passivates the Ge(0 0 1) surface. Lee et al. [3] showed that terminating the Ge(0 0 1) surface with —OH and —H removes the surface states and thus proposed that H_2O might be used at low temperature for surface passivation. Besides the practical interest in passivation by both molecules in their own right, given the chemical similarities between H_2O and H_2S, it is of interest to compare their bonding with the Ge surface.

Infrared spectroscopy is often used to confirm or investigate proposed bonding geometries at surfaces, as pioneered in work of Chabal [5]. In this paper, having confirmed previously proposed bonding geometries of both H_2S [4], and H_2O [6], on the Ge(0 0 1) surface using density functional theory, we calculate and compare the vibrational mode frequencies for these structures for different exchange-correlation functionals, with and without van der Waals interactions, providing useful vibrational signatures of particular bonding geometries. Our results may be used in combination with infrared spectroscopy to confirm the surface geometries proposed in Refs. [4,6].

Van der Waals (vdW) interactions [7] or dispersive forces between two atoms or two molecules arise from the interaction of induced dipole moments, because the charge fluctuations in one part of the system that are electrodynamically correlated with

* Corresponding author at: Tyndall National Institute, Lee Maltings, Cork, Ireland. Tel.: +353 21 4904847.
E-mail address: mark.hartnett@tyndall.ie (M. Hartnett).

http://dx.doi.org/10.1016/j.apsusc.2014.12.096
0169-4332/

charge fluctuations of another. These dispersive forces at one point therefore depend on charge events at another. Thus, this quantum mechanical phenomenon is a nonlocal correlation effect.

2. Method of calculation

In our calculations the surfaces are represented in a supercell geometry [8]. Structural total energies and atomic forces are calculated using first-principles density functional theory [9] in both the local density (LDA) and generalized gradient (GGA) approximations [9]. Vibrational mode frequencies are obtained using the frozen phonon method [10], in which the dynamical matrix is calculated from the fitted restoring forces in the harmonic limit. Diagonalization of the dynamical matrix gives the vibrational mode frequencies and corresponding atomic motions for the H_2S and H_2O adsorbed on a Ge(0 0 1)–(2 × 1) surface. We also report the equilibrium bond lengths and angles at the surface and the energies required for breaking these surface bonds.

We use local density approximation (LDA) of Perdew-Wang [11] and the generalized gradient approximation (GGA) proposed by Perdew-Burke-Ernzerhof [12]. Both exchange-correlation functionals allow for an accurate analysis of the atomic structure by total energy minimisation. We calculate results with both to give an indication of the uncertainties arising from the specific form of the exchange-correlation functional used. We use the QUANTUM ESPRESSO [9] code to calculate the ground state energies and Hellmann–Feymann (HF) forces [13]. The *ab initio* separable psuedopotentials used by QUANTUM ESPRESSO have been computed in both LDA and GGA with the code of the Fritz–Haber–Institute (FHI) [14] implementing the scheme of Troullier-Martins [15], so that the *3d* states of Ge have been fully treated as valence states. The plane-wave cutoff energy was set at 10 Ha and 20 Ha for calculations involving sulfur and oxygen, respectively. The method of special k-point generation is based on the Monkhorst-Pack [16] scheme. We have used an 8 k-point mesh for all supercells considered.

The germanium surface is modelled using a nine-layer periodic slab of germanium atoms with a vacuum layer of 11 Å, as shown in Fig. 1(a). The bottom surface is terminated with hydrogen atoms to represent the underlying bulk. The lattice constant is held fixed at the calculated equilibrium value of 5.57 Å for bulk germanium, which is about 1% smaller than the experimental value of 5.65 Å. On relaxation, the Ge surface results in a Ge(0 0 1)–(2 × 1) reconstructed surface, with a Ge—Ge buckled dimer bond length of 2.43 Å and a buckling angle of 19°, in agreement with Ref. [2].

Two H_2S molecules are then positioned above the calculated equilibrium Ge(0 0 1)–(2 × 1) surface containing the Ge—Ge buckled dimers, as shown in Fig. 1(b) [4] and the structure is relaxed with atomic forces using the Broyden quasi-Newton algorithm [17]. One of the two H_2S molecules is adsorbed onto the surface, by bonding of the S atom to one of the Ge dimers (forming a Ge—S—H bond) while the other H atom is adsorbed onto one of the Ge dimers from the neighbouring dimer row, forming a Ge—H bond, as shown in Fig. 1(c). The Ge—H bond has been reported to break, with desorption of H from the surface at temperatures in the range of 200–250 °C [20], and since the temperature used for H_2S exposure is 330 °C [4], breaking of the Ge—H bond should occur. As we cannot simulate such a scenario directly with our molecular dynamics, we artificially cause the H desorption by breaking the Ge—H bond and moving the H atom away from the surface. With the Ge—H bond broken, another H_2S molecule adsorbs onto the surface. The equilibrium geometry after structural relaxation produces Ge—S—H bonds, which form (S—H)—(S—H) bridges between dimer rows on a (2 × 1) reconstructed surface, as shown in Fig. 1(d).

Weak van der Waals (vdW) interactions during the adsorption process might appear to be a concern when some species are neither entirely desorbed nor adsorbed. In order to investigate if such vdW interactions do occur, we complete an analysis with a larger unit cell (vacuum layer ≈30 Å) to ensure negligible interaction of the desorbed species with the surface, as is physically required. First-principles approaches for how vdW can be treated in DFT were proposed by Lee et al. [18], where they propose a second version of the vdW density functional of Dion et al. [19]. The structures of Fig. 1(c) and (d) are re-relaxed as before with this larger unit cell and the vdW density functional as described in Ref. [18]. In LDA, the H_2S molecule in Fig. 1(c) is located ≈0.4 Å above its initial position due to vdW, while in GGA the molecule is closer to the surface by ≈0.1 Å. The H_2 molecule in Fig. 1(d) for LDA is ≈2.1 Å further away due to vdW, while again GGA predicts the H_2 molecule closer to the surface by ≈0.3 Å.

However, it should be noted that in the initial and final physical geometries, all chemical species are considered to be either covalently bonded to the surface or are completely desorbed and far from the surface. Thus, we expect the weak vdW interactions will not be relevant to the final results presented. The differences between functionals including vdW terms and the LDA or GGA are expected to be substantially less than the differences between LDA and GGA.

The reduction of total energy using LDA (GGA) from structure Fig. 1(c) to (d) is 0.25 eV (0.25) per (2 × 1) supercell as reported in Table 1, confirming Fig. 1(d) as the most stable bonding geometry. Similarly the total energy using LDA with vdW (GGA with vdW) for structures Fig. 1(c) to (d) is 0.3 eV (0.31), also confirming Fig. 1(d) as the most stable structure. The calculated equilibrium lengths of the surface bonds are shown in Table 2 (this relaxed geometry is used as the initial atomic structure to calculate the GGA relaxed surface as shown also in Fig. 1(d))

3. Results and discussion

A comparison of the bond lengths for LDA, GGA, vdW, experimental values and calculated covalent radii are presented in Table 2. The LDA Ge—Ge dimer bond length of 2.49 Å is in excellent agreement with the experimental value of 2.45 Å measured using the grazing incidence X-ray diffraction from the clean Ge(0 0 1)–(2 × 1) surface [22]. The Ge—S bond lengths we calculated using LDA and LDA vdW and the H—S bond length using LDA provide better approximations when compared to the sum of their corresponding covalent radii [21].

The vibrational mode frequencies and atomic vibration amplitudes are determined upon diagonalization of the dynamical matrix. Within the harmonic approximation, the displacement $d_\beta(j)$ of atom j in the direction β creates a force on atom i in the direction α:

$$F_\alpha(i) = -\Phi_{\alpha\beta}(i,j)d_\beta(j). \quad (1)$$

Once the fully relaxed structure (Fig. 1(d)) has been obtained for the H_2S on the Ge(0 0 1)–(2 × 1) surface, we compute the force constant matrix $\Phi_{\alpha\beta}(i,j)$, calculating the Hellman–Feynman forces $F_\alpha(i)$ induced by making a displacement $d_\beta(j)$ of each surface atom in the three orthogonal directions. Displacements at intervals of 0.01 Å from equilibrium were used, up to a maximum of 0.04 Å. A good fit was obtained when the force on each atom i was fitted with a polynomial of order two in the displacement $d_\beta(j)$ and the corresponding element of the force constant matrix $\Phi(i,j)$ was taken as minus the derivative of the fitted force at zero displacement. Diagonalization of the dynamical matrix, $D(i,j) = \Phi(i,j)/\sqrt{m_i m_j}$, where m_i is the mass of atom i, results in the eigenvalues $\lambda_k = \omega_k^2$ and the eigenvectors $|u_k\rangle$, which give the relative direction and amplitude of the displacement (scaled by $\sqrt{m_i}$) of each atom i for each vibrational mode. Because we are concerned only with the calculation