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Defect formation on the GaSb (001) surface induced by hydrogen atom adsorption

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ABSTRACT

Density functional theory has been used to characterize the effects of adsorbed H on the electronic structure of the GaSb (001)-α(4 × 3) surface, which consists of a combination of Ga-Sb and Sb-Sb dimers. Adsorption of two H atoms at a Ga-Sb adatom dimer either has little effect on surface states above the bulk valence band maximum (VBM) or else eliminates them, depending on the mode of adsorption. However, adsorption at the Sb-Sb dimer in the terminating layer produces a state farther into the gap at ~0.10 eV above the clean-surface VBM. Relaxation accompanying the breaking of the Sb-Sb dimer bond leads to increased interactions involving three-fold-coordinated Sb sites in the terminating layer, which in turn raises the energies of the non-bonding lone-pair orbitals. This defect state, which appears to be unique to the reconstructed GaSb (001) surface, could potentially function as a hole trap on the surface of *p*-type GaSb.

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1. Introduction

There is growing interest in the GaSb (001) surface as a substrate in electronic devices for high-speed, low-power digital and analog applications [1,2]. Hence, the formation of electrically-active defects on surfaces and at interfaces is an important issue. Hydrogen occurs frequently as an adsorbate introduced either intentionally or inadvertently during processing. Although the effects of bulk H on GaSb electronic structure and properties have been studied intensively [3–12], less attention [10–12] has been devoted to the role of surface H, and such work has focused largely on the effects of H plasmas and the avoidance or mitigation of surface damage.

Fig. 1a shows the α-(4 × 3) reconstruction [13], which is the most stable GaSb (001) structure [14,15] except under Sb-rich conditions. This comprises 4 Ga-Sb adatom dimers per surface unit cell on the Sb terminating layer of the bulk lattice, which itself incorporates 1 Sb-Sb dimer. The surface is non-metallic [14] since all Ga (Sb) dangling bonds are empty (doubly occupied). The non-bonding lone-pair (NBLP) orbitals on the sp^3-hybridized Sb atoms form a band of surface states near the bulk valence band maximum (VBM), and the empty Ga sp^2 orbitals produce a band of states near the conduction band minimum (CBM). A frequently-observed variant is the pseudo-(1 × 3), resulting from disorder in the [$\bar{1}$10] direction [16], which occurs after cleaning the surface in an ultra-high-vacuum environment. Other structures include the c(2 × 6) that appears after desorption of an Sb capping layer from a sample grown by molecular beam epitaxy (MBE). All of the several possible GaSb (001) surface reconstructions [13-17] involve some combination of Ga-Sb and Sb-Sb dimers, and Sb-rich structures such as the β-(4 × 3) and c(2 × 6) consist mainly of the latter.

In contrast to other III-Vs [18,19], there has been little work on the adsorption of H on GaSb (001). A preliminary *ab initio* study [20] found that adsorption of 2H atoms to form a monohydride dimer (MD, Fig. 1b) is exothermic by 2.08 eV per H and involves a pronounced relaxation consisting mainly of a reversal in the up-down buckling of the dimer. However the corresponding dihydride, with adjacent GaH_2 and SbH_2 sites and a broken Ga-Sb dimer bond, is unstable towards desorption of H_2 and restoration of the MD. These results pertain to dimer #2, the shortest of the adatom dimers. The Ga-Sb distance is computed to be 2.67, 2.70 and 2.77 Å respectively for dimer #2, for the symmetrically-equivalent dimers #1 and #3 and for dimer #4.

The present work considers the effects of adsorbed H on the GaSb (001) surface electronic structure. While adsorption at a Ga-Sb dimer either has little effect on surface states just above the bulk VBM or else removes them, reaction with the Sb-Sb dimer will be seen to yield a defect state lying well above the clean-surface VBM. The focus here is on chemically-stable surfaces exhibiting electrically-active defects; hence, adsorption of a single H atom is not considered. Such a paramagnetic species, with a defect state at the Fermi level, is not expected to be stable on a practical surface exposed to room air.

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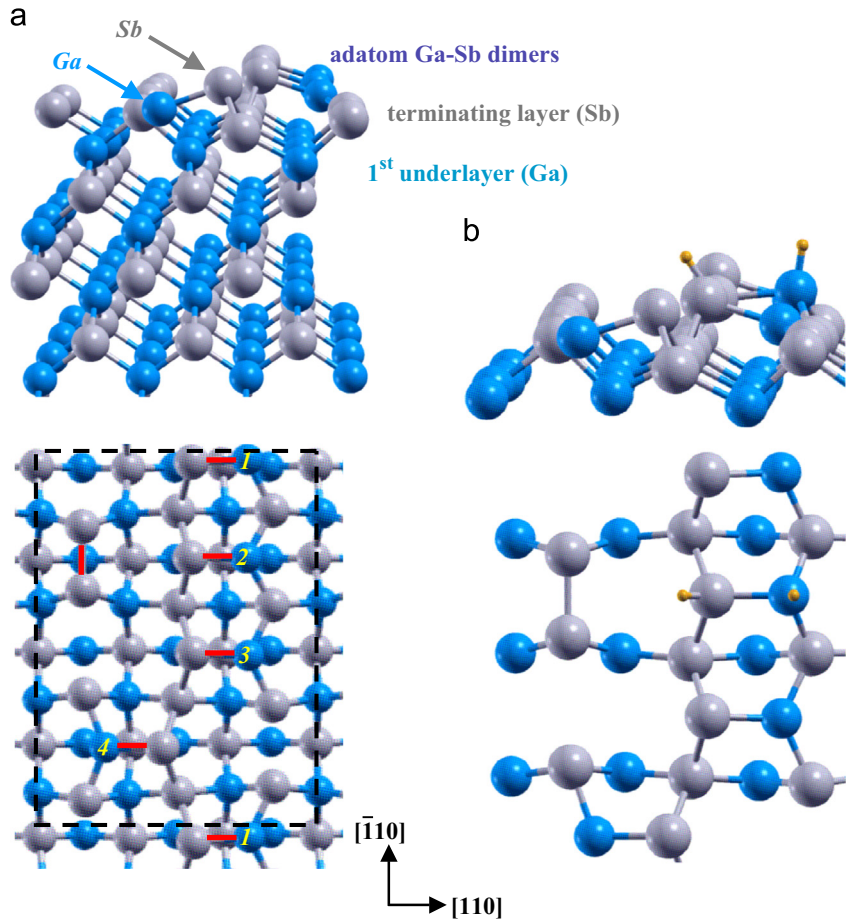

Fig. 1. (Color online) (a) The GaSb (001)-α(4 × 3) surface structure. The upper panel shows a view in approximately the $[\bar{1}10]$ direction, and the lower panel shows a view along the surface normal. Dimer bonds are emphasized in red, and Ga-Sb adatom dimers are numbered for reference. The dashed line shows the surface unit cell. (b) Same structure with a single MD at dimer #2 (Ref. [20]) with H atoms in yellow. For clarity, layers below the first Ga underlayer are omitted. Note the presence of three-fold-coordinated Sb atoms in the terminating layer (other than those in the Sb-Sb dimer). Two are bonded to the dimer #4 Ga and one each is bonded to the dimer #1 and #3 Ga.

2. Computational methods

All calculations were performed using density functional theory (DFT), including a semi-empirical treatment of dispersion, as described in detail previously [20,21]. Briefly, the model consists of a two-dimensionally-periodic (2DP) slab with 4 Ga-Sb bilayers. The bottom (Ga) layer is terminated with 2 pseudo-hydrogens (PHs) per Ga, each with a nuclear charge of 1.25 |e|. With the Ga-Sb adatom dimers bonded to the top (Sb) layer this gives a total of 5 Ga-Sb bilayers. The bottom bilayer and the PHs were fixed during relaxation, and a dipolar field was added to eliminate the spurious electric field in the vacuum space (30 Å wide). The Ga 3d and Sb 4d orbitals were included in the valence states, and scalar-relativistic effects were included in the PW91 pseudopotentials. The Sb spin–orbit coupling was neglected since a fully-relativistic treatment [9] of GaSb greatly reduces the band gap (in the local density approximation), which would complicate the task of identifying gap states. A (3 × 4 × 1) Monkhorst-Pack grid was used in geometry optimization and a (6 × 8 × 1) grid in computing the density of states (DOS). To facilitate comparison with possible future experimental results, a Gaussian broadening of 68 meV (5 milli-Rydberg (mRy)) was applied to the DOS in some cases in order to simulate the resolution attainable in synchrotron photoemission data. All results were obtained with identical computational parameters, which allows a reliable comparison between different modes of adsorption.

3. Results

The investigation begins with an extension of previous work (Fig. 1b) to other Ga-Sb dimers. Fig. 2 shows the structures that can form when 2H atoms react with dimer #4, in which the Ga is back-bonded to two three-fold-coordinated (TFC) Sb atoms. Bonding of H to a terminating-layer Sb is more exothermic (2.14 eV per H) than to the adatom Sb (1.94 eV per H). In the latter case the Ga-Sb dimer bond breaks, which may be facilitated by the fact that the terminating-layer Sb atoms bonded to the Ga are more free to relax than in the case of dimer #2. The Ga-Sb distance (2.99 Å) is only somewhat larger than before adsorption (2.77 Å), which suggests a possible weak residual bonding interaction. This site may also be favorable for dihydride formation, but this was not investigated. Similar results (not shown) were obtained for dimer #1, for which bonding of H to the TFC Sb in the terminating layer is more favorable (2.27 eV per H) than to the dimer Sb (2.03 eV per H). In the latter case the Ga-Sb dimer remains intact with a distance of 2.83 Å and a reversal of the buckling as for dimer #2.

Fig. 3 shows the structures that can form when 2H atoms react with the Sb-Sb dimer. Each is energetically favorable, with exothermic adsorption energies of 2.02–2.04 eV per H. Due to the large dissociation energy of H_2 the corresponding reaction with H_2 is endothermic by ~0.19 eV per H. In all cases the Sb-H bonds lie approximately in the surface plane. Using the HSb SbH structure (Fig. 3a) as an example, the Sb-H bond length is 1.74 Å,