

Adsorption and Self-Assembly of Alkanethiols on GaAs (001) Surface*

O. Voznyy and J. J. Dubowski

Department of Electrical and Computer Engineering
Université de Sherbrooke, Sherbrooke, Québec J1K 2R1, Canada
E-Mail: jan.j.dubowski@usherbrooke.ca

Abstract - Adsorption of alkanethiols on GaAs (001) surface under low coverage and high-coverage conditions was studied using density functional calculations in a periodic supercell approach. The thiolate adsorption site and tilt angle are dictated by the high directionality and covalent character of S-As bond. Calculated sulfur-surface binding energies are found to be significantly different for Ga-rich and As-rich surfaces and stronger than that of thiols on gold and copper surfaces. However the desorption of thiol requires much less energy in the presence of hydrogen on the surface.

I. INTRODUCTION

Self-assembled monolayers (SAMs) of organosulfur compounds on solid surfaces attract a lot of interest both from a fundamental perspective and due to their potential applications, among which are the development of precursors for the growth of II-VI materials, creation of transition layers for ohmic contacts and Schottky diodes, surface passivation, nanolithography, electrochemical applications and biosensing [1-3].

Theoretical modeling of the semiconductor-thiol interface can provide valuable information about the bonding nature in such a material system and, ultimately, it would help to design and optimize a semiconductor-thiol interface addressing specific applications. In contrast to alkanethiols on gold, which are considered a prototype example of SAMs, theoretical studies of thiols on GaAs appear to be missing in literature. The adsorption of a thiol is strongly influenced by the surface chemical reactivity, lattice constant, crystallographic orientation, etc. Therefore a little information available from the well-studied SAMs of thiols on noble metals [4-6] can be applied to GaAs.

II. CALCULATION DETAILS

The calculations have been performed using a density functional theory (DFT) in a periodic supercell approach, based on pseudopotentials and numerical localized atomic orbitals as basis sets, as implemented in the SIESTA code [7].

The structure of a chemisorbed monolayer film of thiol is determined by the sulphur-surface chemical bond and the intermolecular van der Waals forces between the hydrocarbon chains. Generalized gradients approximation (GGA) is considered to better describe organic molecules but weak intermolecular interactions are known to be better reproduced in local density approximation (LDA). Thus, we performed tests of different exchange-correlation functionals, including

CA, BLYP, PBE and revised PBE for adsorption of thiols on GaAs(001) as there are no other theoretical studies of this system for the moment. GGA was found to accurately reproduce chemisorption binding energies while unable to reproduce van der Waals attraction between thiols in self-assembled monolayer (SAM). Although the energetics of chemisorption was found to be strongly overestimated in LDA, it didn't affect the obtained geometries and physisorption energies were correctly reproduced.

III. RESULTS

A. Adsorption geometries and bonding nature

The equilibrium geometries obtained from molecular dynamics simulations and subsequent conjugate gradients geometry optimization starting from a thiolate lying parallel to the surface and from a thiolate standing upright are shown in Fig. 1. The sulfur atom is situated almost on top of arsenic, while structures with sulfur in bridge or hollow site positions were found to be 1 eV higher in energy. As-S bond lies along the arsenic dangling bond and the As-S-C angle is close to the value of H-S-C angle in free thiol. Geometries with As, S and C lying in one line are found to be up to 0.5 eV higher in energy than the optimal configurations - similar to reported values for thiols on gold [4]. Such a preference for bond

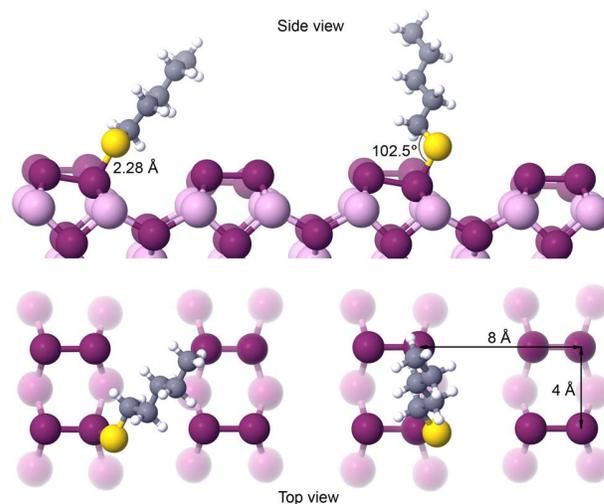


Fig. 1. Optimized geometries of pentanethiol on As-rich GaAs (001) surface obtained from relaxation of thiolate (a) lying flat to the surface and (b) standing upright.

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directionality from both surface and thiol indicates a high covalency and thus the high strength of the bond. The length of the As-S bond is 2.28 Å which is shorter than 2.5 Å for Au-S [4, 5] and 2.35 Å for Cu-S [6] suggesting stronger binding of thiol to GaAs than to gold and copper surfaces. The high-lying molecular orbital on sulfur has a pronounced p_x character, similar to that in free thiol, thus, the bonds to carbon and to arsenic (or hydrogen) which are formed by the remaining p_y and p_z orbitals should tend to be at right angle. The deviation to higher angle values is explained by steric repulsion between hydrogen atoms in the first CH₂ unit and arsenic in adjacent dimers.

Mulliken population analysis shows transfer of 0.05 electrons from thiolate to surface, which is very small in comparison to an accumulation of 0.4 and 0.6 electrons on thiolate on gold [5] and copper [6] surfaces, respectively. This indicates low ionicity and high covalency of the bond, consistent with our previous conclusions from energy dependence on As-S-C angle and suggesting strong binding of thiolate to GaAs surface.

B. Adsorption energetics

Calculated S-As and S-Ga binding energies of 2.1 eV and 2.8 eV respectively are bigger than 1.7 eV for thiols on gold [4, 5] and 2.03 eV for thiols on copper [4, 6]. Available temperature programmed desorption (TPD) data for Ga-rich (001) [8] and (110) [9] surfaces show the absence of thiolate desorption peaks showing instead the recombinative desorption of thiol, alkane and molecular hydrogen with energies around 1.45 eV. Calculations of different adsorption configurations with hydrogen, which stays on the surface upon S-H bond cleavage, have shown that desorption of thiol requires much less energy in qualitative agreement with available experimental results.

C. Formation of self-assembled monolayers

Calculations of the high surface coverage regime have shown that thiols can cover only every second surface arsenic atom, since the distance of 4 Å between adjacent As atoms is too small to accommodate two thiols with the optimal distance between them equal to 4.5 Å. Moreover, the surface reconstruction should change from that shown in Fig.1 at low coverage to a reconstruction with As dimers placed in a checkerboard configuration.

The geometries of dense-packing of long-chain thiols in the presence and without the surface were studied using LDA. Calculations have shown that the chains 62° tilt angle of the optimally packed free monolayer is about 5° higher than that calculated in the presence of surface and that observed experimentally. This suggests that alkanethiols cannot pack

densely on the GaAs surface due to the high directionality of the As-S bond and steric repulsion of the first CH₂ unit from surface.

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