

# First-Principles Study Of Ethanol Adsorption On Hydrogen-Terminated Si(111)

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The interaction of small organic molecules with semiconductor surfaces, namely hydrogen-terminated Si(111), is a topic of great recent interest. This recent surge is not only due to the understanding of the fundamental aspects of the interaction, but also to their importance in various technological applications, such as insulator films, resistance of nanolithography, chemical and biological sensors, and molecular electronics. Each of these requires the development of a well defined organic layer on the semiconductor surface. As these organic layers are basically formed by exposing the semiconductor surface to organic compounds, the understanding of the first stages of the interaction between the surface and the organic structure is crucial in order to improve their quality.

Structural and electronic properties of ethanol adsorbed on hydrogen-terminated Si(111)-(2x2) surface are investigated using *ab initio* density functional theory. Equilibrium atomic geometries of single ethanol molecules adsorbed on silicon and the potential energy surface are obtained. The calculated surface band structures, charge densities and differential optical absorption spectra for different configuration are discussed in comparison with the electronic properties of the clean Si(111):H surface.

Adsorption mechanisms of acetylene and ethylene adsorption on Si(001)-(2x1) have been investigated thoroughly in the past,<sup>1-3</sup> on the other hand, preferred adsorption geometries of ethanol adsorbed on Si(111), and the effects on the electronic structure of the surface, have received far less attention.<sup>4</sup> Equilibrium atomic geometries of single ethanol molecules adsorbed on silicon obtained by total energy minimization method are shown in Fig. 1. The adsorption energy per molecule is calculated as the

difference between total energies of the entire system Si-ethanol and the energies of the isolated components divided by the number of adsorbed molecules  $N$  per unit cell. Note that the adsorption energy is positive by definition when the adsorbates bind to the substrate. The predicted preferred ethanol monomer configuration exhibits the OH group directed down to the surface as presented in Fig. 1. The second shown predicted configuration has a smaller adsorption energy.

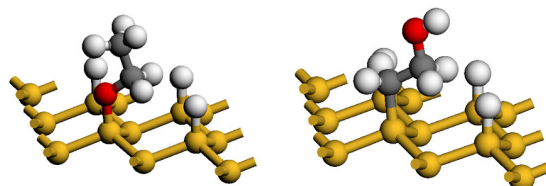


FIG. 1. Equilibrium geometries of ethanol molecules in a 2x2 surface cell. The white, grey, red, yellow atoms denote H, C, O, Si atoms, respectively.

Calculated differential optical absorption spectrum allows to eliminate the signal from bulk Si and to focus only on the surface contribution. It is defined as the normalized difference between optical absorption of the bare surface and the surface with adsorbate. Predicted optical gap depends substantially on the orientation of ethanol molecule on the surface. These results could be used for optical characterization of molecular adsorption on Si surface.

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