

Casting light on organic/solid interfaces

Computational spectroscopy at molecule/solid-interfaces: converting spectral fingerprints into molecular structure

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In Short

- Identify the adsorption geometries of organic molecules on quasi-1D nanowires on Si(hhk)-Au
- Selectively control the adsorption using hydrogen co-doping
- Identify optical and electronic fingerprints of molecular adsorption

Organic functionalization of semiconductors is an important route towards the development of novel semiconductor-based devices in optoelectronics and sensor technology. The self-organization of organic molecules is a promising bottom-up approach in contrast to further downscaling lithographic techniques for device manufacturing. The critical issue is, however, to control the chemical interaction of the molecules with the surface which governs the structure formation. In contrast to metal surfaces where a weak molecule-substrate interaction allows molecules to diffuse and arrange according to molecular interaction, on semiconductors a strong molecule-substrate interaction arises from covalent bonding. Thus, the formation of molecular structures has to be controlled by the local surface reactivity with the impinging molecules.

Silicon, being a covalent semiconductor, provides various adsorption paths for organic molecules. The interaction of organic molecules with metal surfaces appears much simpler. A very well known example concerns molecules with thiol -SH end groups on gold surfaces, where it is well established that S-Au bonds underpin the molecule-substrate interaction. This explains, for example, the formation of self-assembled monolayers (SAMs) of thiol-modified alkanes on gold.

For generating a well-defined and ordered molecule-Si-interface a promising approach could be the use of metal-adsorbate-modified Si surfaces as a template, such as the Au atomic nanostructures formed on Si surfaces. One-dimensional atomic gold chains are known to form by self-assembly on vicinal Si(111) surfaces and act to stabilize their geometry over long distances [1]. These metallic chains constitute possible templates for the interaction with

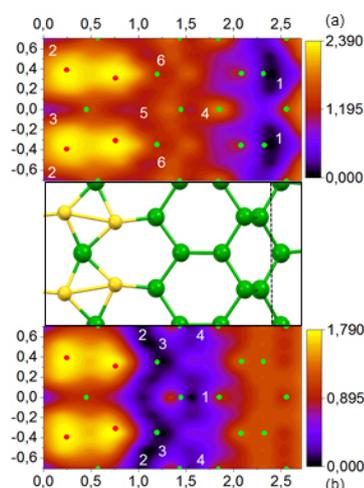


Figure 1: Potential energy surface for a thiolate group on Si(553)-Au. The step edge appears on the right, and Au chains are on the left. The top figure refers to the clean surface, while in the bottom figure, the step edge dangling bonds have been co-doped (passivated) with hydrogen.

organic molecules aimed at the formation of regular, ordered patterns of organic-metal hybrid nanostructures [2]. The Au chain structure can be easily tuned by varying the vicinal angle (single, double, and triple atomic chains have been prepared [3]). Such one-dimensional (1D) Au₁Si nanostructures as a template for organic SAM growth represent a quite attractive substrate choice, as they may even yield unique chemical and physical properties due to the hybridization of the 1D metallic states with the organic π -conjugated molecules.

The first step is to understand the mechanisms of adsorption itself. We started by exploring the mechanisms by which a typical organic molecule can adsorb to the Si(553)-Au surface (Figs.1 and 2), which has a double Au chain on the terrace and silicon dangling bonds at the edge. We consider a small molecule, toluene-3,4-dithiol (TDT). Will it bind to gold, like thiol ligands commonly do? To understand this, we first computed the potential energy surface (PES) for a small thiol molecule (methanethiolate). This is shown in the top part of Fig.1. Interestingly, we find that the thiolate strongly tends to bind to the Si edge, while adsorption on the gold is relatively unfavoured. These results suggest that we can use the step edge directly as a template for growing a 1D SAM. What if we switch off the step edge? Hydrogen is well known to passivate Si dangling bonds. Starting from such a configuration, we recomputed the PES as shown in the bottom panel. Now the

favoured adsorption sites move to the terraces instead, and Au remains unreactive. So the problem is: can we find a molecule or ligand that prefers to bind to Au than to Si? This is the focus of ongoing work.

One complicated aspect not mentioned before now is the role of hydrogen in the thiol (-SH) group. We looked at various different mechanisms for adsorption, and found that dissociation of the thiol group was strongly favoured, as shown in Fig.2. Any hydrogen released in this way also tends to bind to the step edge. Hence, it may act as a limiting factor in the formation of SAMs. These results have been recently published [7].

Thanks to their 1D nature, the family of Si(hhk)-Au surfaces are suitable for probing with reflectance anisotropy spectroscopy (RAS). RAS is very sensitive to the local structural motifs such as metal chains, Si dangling bonds and adatoms, and graphene-like silicon honeycombs on the step edges [4–6]. Thus one of our aims is to identify unique spectral fingerprints by means of ab initio calculations and interpret experimental results. For instance, thanks to calculations carried out at HLRN, the structure of two distinct phases of Si(775)-Au was identified using density functional theory (DFT) calculations of the optical properties and comparing the results with experiment [6]. Future work will be to compute the optical spectra and STM images of the molecule/surface interfaces in order to compare with new experimental measurements being carried out by our colleagues in Berlin.

More Information

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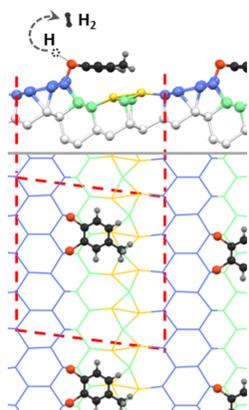


Figure 2: A possible adsorption process for toluene-3,4-dithiol on a Si(553)-Au step edge. The thiol ligand dissociates and molecular hydrogen is formed and released.

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