

Heads or Tails: Which Is More Important in Molecular Self-Assembly?

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ABSTRACT Self-assembled monolayers can modify the functionality of the surfaces on which they assemble. Because they alter the surface properties, self-assembled monolayers can be used for a multitude of applications. Understanding the forces that drive the formation of a self-assembled monolayer on a given surface remains an important area of investigation. A new paper discusses some of the considerations for self-assembly on semiconductors. The results highlight the tradeoffs between achieving crystalline packing of the tail groups and forming commensurate bonding between the head groups and the underlying surface. Where the emphasis should be placed depends on the application, but obtaining both interfacial and intermolecular ordering may be possible.

At their best, self-assembled monolayers provide a dense, nearly crystalline organic skin on an underlying solid surface. In this ordered state, they may passivate the surface or afford new functionality to the substrate. Because they can impart many new properties, self-assembled monolayers have come under scrutiny for use in a broad range of applications, from biosensing and cell patterning to corrosion resistance and molecular electronics. For many applications, especially those in which surface passivation is needed, the requirements on the bonding and packing in the assembled monolayer are stringent. Consequently, understanding the forces that drive the packing of a self-assembled monolayer is important in the design of systems that bestow desired interfacial properties to a variety of substrates.

In their Article this issue, McGuinness *et al.* address some of these key considerations for self-assembly on bare semiconductor surfaces.¹ They show that long-chain alkanethiols form monolayers on GaAs with translational and orientational order, generating small domains (~75 Å) of pseudo-hexagonal close-packed molecules with a herringbone packing, similar to the packing that is observed for the well-studied alkanethiolate self-assembled monolayers on Au(111). This high degree of order on GaAs gradually decreases with decreasing chain length of the alkanethiol. The chain length dependence can be understood as a competition between intermolecular and interfacial forces. Each additional methylene group in the alkyl chain increases the intermolecular forces, which favor crystalline-like packing. Eventually these intermolecular forces overcome the molecule–substrate and lattice forces that promote molecule separations that are incompatible with a crystalline organic layer. For long-chain alkanethiols on GaAs(001), the intermolecular interactions of the thiols are sufficiently

strong to cause a crystalline-like hydrocarbon layer to form.

The results further show that the intermolecular driving force is powerful enough to induce short-range restructuring of the underlying GaAs(001) surface lattice, causing the As atoms (to which the thiols preferentially bond) to be displaced and generating an incommensurate adlayer.^{1,2} Thus, this system provides a valuable illustration of the tradeoffs that can occur in the formation of self-assembled monolayers. Although the highly ordered thiolate monolayer imparts good chemical resistance (for example, the thiolate monolayer inhibits oxidation of the underlying GaAs), it fails to provide good electrical passivation.³ The poor electrical passivation is attributed to generation of surface defects caused by the restructuring of the GaAs surface lattice. As McGuinness *et al.* illustrate, the modified interfacial structure introduces a variety of possible surface traps, which reverses the benefits of the surface passivation. In contrast, simple commensurate structures that can be formed at the GaAs surface by adsorption of elemental S are much more effective in the prevention of electrical surface traps.³ The surface restructuring for the organosulfur case is a result of the lattice mismatch, including mismatched symmetries (hexagonal *versus* square), between the crystalline alkanethiolate layer and the underlying GaAs(001) surface.

The behavior of the alkanethiolate layer on GaAs can be contrasted with its behavior on gold. Long-chain alkanethiols are well known to form monolayers on Au(111) with a high degree of conformational and translational order, which remain commensurate with the underlying gold surface.^{4–6} Nature seems to help with suitable spacings in the case of gold and related metals such as palladium and silver. But the sensitivity of the alkanethiols to the underlying lattice is acute. Even Ag(111), which has surface lat-

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tice spacing nearly identical to that of Au(111), forms a different ordered overlayer of thiolates with smaller crystalline domains.^{4,5} For semiconductors such as GaAs, Ge, and Si, which have significantly larger lattice spacings, can we hope to achieve both good organic packing and commensurate binding sites? The closest spacing between two neighboring surface atoms for these semiconductors is nearly 4 Å, versus 2.5–2.9 Å for the noble metals. Alkane chains require an intermolecular spacing of nearly 5 Å in the crystalline solid.¹ Significant mismatch must be relieved through either incommensurate molecule–surface bonding or disorder in the monolayer, or both (see Figure 1).

It is interesting that, with respect to alkanethiols on GaAs(001), the interchain forces appear to dominate over the interfacial forces. This fact leads to the well-ordered, but incommensurate, monolayers that McGuinness *et al.* observed. However, the stronger and more directional the molecule–surface bonds are, the more likely the lattice mismatch is to be mediated by disorder in the organic monolayer rather than by disorder in the head group bonding. This is the case for monolayers based on Si–C, Ge–C, or Ge–S bonds, which are strong and directional and for which neither

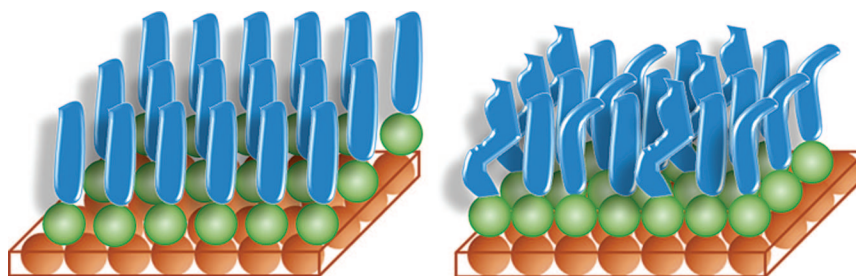


Figure 1. Competition between interfacial and intermolecular forces may result in incommensurate monolayers containing crystalline packing of the tails (left) or commensurate head–group–surface bonds with disordered tail groups (right).

the surface atoms nor the adsorbates are expected to be very mobile. Interfacial forces, combined with the mismatch between the semiconductor lattice and the molecule–molecule spacings, prevent formation of crystalline monolayers, according to recent studies.^{7,8} For example, for alkanethiolate self-assembled monolayers on Ge(111), the degree of packing and stability of the monolayers have not yet reached the quality of the self-assembled monolayers on gold.⁷ Likewise, grazing incidence X-ray diffraction of alkyl monolayers formed from alkenes on Si(111) surfaces revealed that the monolayers are all amorously structured, regardless of their alkyl chain length.⁸ In the silicon system, the molecule–surface bonds are commensurate with the underlying lattice, although crystalline monolayers do not form.

The results from McGuinness *et al.* suggest that scientists should question the goals of molecular assembly on semiconductors. Should we strive for systems in which the adsorbates form a commensurate structure and/or bond to every surface atom, or must the alkyl monolayer chains be crystalline? In other words, is the head or tail group more important? The answer depends on the application. For chemical passivation, formation of a dense monolayer, even if it introduces disorder at the underlying interface or leaves some surface atoms unbonded, may suffice. The densely packed hydrocarbon tail will act as a barrier against reactants, protecting the interface from

unwanted reaction. On the other hand, electrical passivation may be the desired goal. Electrical surface passivation is especially important for semiconductors such as GaAs and Ge, which have beneficial electronic properties when compared to silicon but face significant challenges in future device applications because of the lack of a good surface oxide. For electrical passivation, each surface atom will likely need to be functionalized to eliminate surface trap states, and consequently the adsorbate head–surface interaction will be critical.

Observations from alkyl-terminated silicon lend credence to the importance of the head group interactions (*i.e.*, adsorbate–surface bonding) in controlling interfacial electrical properties in semiconductors. Studies have shown that, although these monolayers do not form crystalline layers on silicon,⁸ they can provide good electrical passivation as well as good chemical protection.^{9,10} Of interest is that the best electrical passivation is provided by the shortest chain, *e.g.*, methyl-terminated Si(111). The largest surface coverage is obtained for this system, with a methyl group bonded to nearly every Si surface site in a commensurate 1×1 overlayer.¹¹ Longer alkyl chains have too much steric hindrance to pack this closely,⁸ but even with a lower surface density, scientists still observed chemical and electrical passivation. This protection may be assisted by the presence of hydrogen atoms bonded to Si sites that are not alkylated.¹⁰

Should we strive for systems in which the adsorbates form a commensurate structure and/or bond to every surface atom, or must the alkyl monolayer chains be crystalline?

The available examples highlight the challenges faced in achieving commensurate molecule–surface bonding concomitant with crystalline packing of the tail group. Whereas alkanethiolate monolayers on GaAs(001) are crystalline but incommensurate, alkyl monolayers on Si(111) form commensurate Si–C bonds but the tails are amorphous. We should not, however, abandon the goal of forming ordered monolayers on semiconductors that are also commensurate with the underlying lattice. A number of possible strategies are available for achieving this. One approach is to design molecules with sizes that better match the surface lattice spacing. For example, the studies of 4'-methyl-biphenyl-4-thiolate (MBT) monolayers on GaAs(001) give evidence for ordered structures that may be commensurate along one crystallographic direction.¹ The molecular spacing for the MBT monolayers along this direction is close to the next-nearest neighbor distance on the GaAs(001) surface. Another approach is to explore new head groups that rely on different types of bonding at the surface. One such example is dative bonding of Lewis base head groups at semiconductor surfaces. Yet another possibility is to intercalate small terminating groups like methyl or hydrogen into a monolayer formed by long-chain or aromatic molecules, thereby achieving both complete surface saturation and good packing of the tail groups.

As for the question of which matters more—heads or tails—in molecular assembly on semiconductors, the answer rests with the desired application. But achieving both, *i.e.*, both interfacial and intermolecular ordering, may lie within our grasp.

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