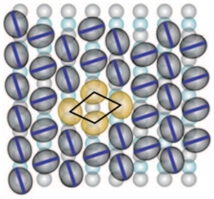
Size Matters in SAM Organization

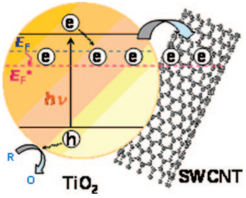
Self-assembled monolayers (SAMs) can change the surface properties of metals. Understanding these changing properties could lead to new applications in corrosion resistance, molecular electronic devices, nanolithography, and other areas. The most studied SAMs are alkanethiols, which have been structurally characterized on metals such as Au, Ag, and Cu. However, very few systematic structural analyses of alkanethiol SAMs on semiconductor substrates have been performed, despite the importance of these materials. McGuiness *et al.* (p 30) characterize SAM patterns of alkanethiol chains of various lengths on GaAs, a semiconductor widely used in electronic and optoelectronic devices.



Using grazing incidence X-ray diffraction, infrared spectroscopy, and ancillary probes, they found changing patterns based on alkanethiol chain length. For chains longer than ∼16 carbons, the team found that the monolayers form a mosaic structure with domains of ≤10 nm. However, as chain length decreases, the researchers found that translational ordering decreases as well, completely disappearing at ∼14 carbons. The researchers explained the loss of ordering as a balance between intermolecular packing forces, substrate–molecule bond strengths, molecular and substrate lattice matching, and substrate surface lattice forces. The long alkyl chains' strong molecular–substrate bonds and intermolecular interactions appear to force atoms in the intrinsic square symmetry surface of GaAs to adjust and to restructure to form an incommensurate pseudo hexagonal adsorbate lattice over short distances. However, in the shorter chains, intermolecular forces seem to be insufficient to drive substrate restructuring, which leads to lower coverages of the surface and disordered structure. McGuiness *et al.* note that the effects of changing chain length need to be thoroughly studied to predict SAM behavior on a variety of surfaces.

Sun Shines on Carbon Nanotubes

Single wall carbon nanotubes (SWCNTs) have established a place for themselves as conduits for transporting electrons in solar cells. SWCNT networks appear to boost solar cell photocurrent and photoconductivity in semiconductor–SCWNT composites. Until now, the electron storage capacity of this nanomaterial has not been measured quantitatively. Researchers also do not have a firm grasp on what factors control the electron-accepting property of SWCNTs and how this capacity influences the overall energetics of semiconductor–SWCNT composites.

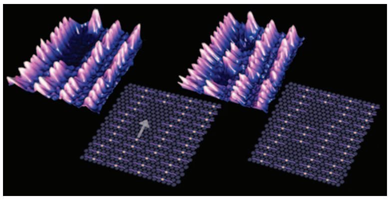


To answer these questions, Kongkanand and Kamat (p 13) examined the charge equilibration processes between photoirradiated TiO_2 nanoparticles and SWCNTs as well as TiO_2–SWCNT composite and a redox couple. When in contact with TiO_2 nanoparticles, SWCNTs effectively accept and store electrons. Measuring the Fermi level equilibration with these photoirradiated particles, the researchers found that the SWCNTs appear to store up to 1 electron per 32 carbon atoms. When Kongkanand and Kamat exposed TiO_2–SWCNT composites to electron acceptors, they found that SWCNTs readily discharge these stored electrons, a fact seen in the changing colors of these dyes. Understanding SWCNTs' electron-charging and electron-discharging properties could eventually play a role in optimizing light harvesting in solar cells.

A Dibutyl Sulfide Molecular Abacus

Researchers have good reason to concentrate their efforts on investigating self-assembled monolayers (SAMs). These structures have applications in sensing, lubrication, and device self-assembly. About half of the literature in this area focuses on thiol-based SAMs. These have the advantage of allowing excellent control over assembly in one dimension perpendicular to the surface. However, they have several disadvantages: less control over lateral assembly, inhomogeneity in the form of etch pits and domain boundaries, and susceptibility to oxidation. To solve these problems, Jensen *et al.* (p 22) investigated the characteristics of a SAM made of a simple thioether on a Cu surface.

Using scanning tunneling microscopy, the researchers examined dibutyl sulfide monolayer assembly at low temperature (78 K) and in ultrahigh vacuum (*i.e.,* free of contaminants). They observed that the thioether first formed small, highly ordered islands that continually changed in length but not in orientation to each other, hinting that individual molecules desorbed from each island and reattached to others. The islands themselves remained stable, however, from molecule–surface and van der Waals interactions. After coverage grew to a complete monolayer, the researchers briefly annealed the sample at room temperature, which led to a striking transformation. The warmer temperature created an ordered surface layer consisting of a single rotational domain.



They found that the dibutyl sulfide molecules, which formed neat rows of seven or eight molecules with a space between each, could be manipulated with the microscope tip to function like a molecular abacus. Up to three dibutyl sulfide molecules could be moved at once across a row into the vacancy. The authors suggest that the ordered assembly and easy manipulation of this thioether show promise for new applications.

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