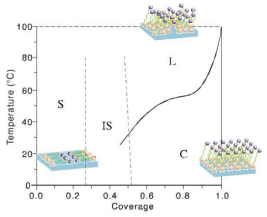
Self-assembled monolayers

Self-assembled monolayers: from 'simple' model systems to biofunctionalized interfaces
Frank Schreiber
J. Phys.: Condens. Matter 16 R881-R900



Schematic phase diagram of decanethiol on Au(111) in temperature and coverage space. The different regions and phases are denoted as S (stripes), IS (intermediate structures), C (c(4 × 2)), and L (liquid). The broken lines indicate phase boundaries of the IS, which are not yet fully established. The solid curve between C and L (melting transition) exhibits a sharp rise near full coverage. Note that this is similar to the behaviour found for much simpler systems such as nitrogen on graphite

Frank Schreiber (Oxford) reviews recent developments in the area of self-assembled monolayers (SAMs) and their applications. There is increasing interest in soft condensed matter, and in thin films additional issues related to the reduced dimensionality come into play.

The term 'self-assembly' may be defined as the spontaneous formation of complex hierarchical structures from pre-designed building blocks, typically involving multiple energy scales and multiple degrees of freedom. Specifically, self-assembled monolayers are ordered molecular assemblies that are formed spontaneously by the adsorption of a surfactant with a specific affinity of its headgroup to a substrate. They are usually prepared from solution, although some systems can be prepared from the vapour as well.

The discovery of SAMs has transformed surface chemistry and also led to new physics. It has brought together the study of well defined inorganic surfaces and organic species, which from a physics perspective were previously often considered rather undefined. The great flexibility of the concept of SAMs brought about by the wide choice of endgroups which can be anchored to the substrate has led to a broad range of applications of SAMs including important developments in the area of biotechnology.

Schreiber first discusses issues related to the structure, the phase transitions, the phase diagram, and the growth dynamics. He explains how the internal degrees of freedom and the multiple interactions involved can lead to fairly rich phase behaviour even for systems which are commonly considered 'simple' model systems. Then he discusses selected problems for more complex SAM-based systems, including SAMs as substrates for growth, SAMs and molecular electronics, electrochemical applications, and 'switchable' SAMs, as well as the use of SAMs for biofunctionalized surfaces and lateral structuring.

The fundamental questions of adsorption, structure, phases, and phase transitions have been thoroughly studied in the past, but several issues remain unresolved, probably reflecting the complex competition of multiple interactions and degrees of freedom, giving rise to various structures which are energetically similar. Much present and future work is related to utilizing the various ways to modify and functionalize surfaces by SAMs, with biorelated applications being the most dynamic area. Since SAMs are not so much a specific class of compounds, but rather a very flexible concept with virtually unlimited potential for applications, we expect that the area of SAMs will continue to thrive.

Quantum cascade structures

Coherent charge transport in semiconductor quantum cascade structures
Michael Woerner, Klaus Reimann and Thomas Elsaesser
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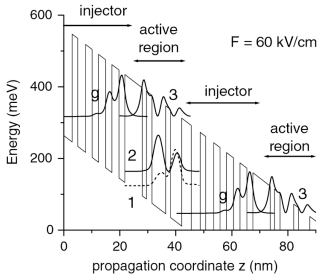

A conduction band diagram of the GaAs/$Al_{0.33}Ga_{0.67}As$ quantum cascade laser structure (sample A). Probability densities $|\psi(z)|^2$ are shown for the wavefunctions relevant for the QCL dynamics: $|g\rangle$ (ground state in the injector), $|3\rangle$ (upper laser state), $|2\rangle$ (lower laser state) and $|1\rangle$ are eigenstates of the electronic Hamiltonian without the tunnel coupling through the injection barrier (the wide barrier to the left of the active region).

Quantum cascade structures have wide application in electrically driven semiconductor lasers working in the mid- to far-infrared spectral range. Optical amplification in such unipolar devices is based on a population inversion between quasi-two-dimensional conduction subbands in coupled quantum wells. The population inversion in the active region is generated by electrons tunnelling from an injector region through a barrier into the upper laser subband and by ultrafast extraction of these electrons out of the lower laser subband through a barrier into the next injector region. Such transport processes on ultrafast timescales have been the subject of extensive experimental and theoretical work without reaching a clear physical picture of the microscopic electron dynamics.

Thomas Elsaesser of the Max Born Institut and colleagues review a comprehensive experimental study of electron transport in electrically driven quantum cascade structures. They investigated ultrafast quantum transport from the injector into the upper laser subband by mid-infrared pump-probe experiments directly monitoring the femtosecond saturation and subsequent recovery of electrically induced optical gain. For low current densities, low lattice temperatures and low pump pulse intensities, the charge transport is dominantly coherent, leading to pronounced gain oscillations due to the coherent motion of electron wavepackets. For higher current densities, lattice temperatures, or pump intensities, the gain recovery shows an additional incoherent component, which essentially follows the pump-induced heating and subsequent cooling of the carrier gas in the injector.

Even at the high electron densities present in a quantum cascade laser the coherence properties of the electron wavefunction play an important role for the microscopic injection process. This process is crucial for generating gain in quantum cascade lasers and represents a key step in the overall charge transport through the device. These results strongly support the empirical finding that the design of the wavefunction overlap between the injector subbands and the upper laser subband is essential for the performance of a quantum cascade laser. Theoretical calculations that include both the quantum character of transport and the decoherence caused by electron-electron scattering are still lacking and pose a challenge for the future.

Slow and fast light in solids

Ultra-slow and superluminal light propagation in solids at room temperature
M S Bigelow, N N Lepeshkin and RW Boyd
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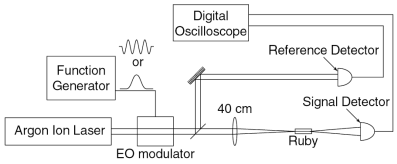

The experimental setup used to observe slow light in ruby.

Recent interest in the old problem of how a wave travels through a dispersive material has been sparked by the discovery of systems that have high dispersion, yet allow a pulse to propagate relatively undistorted. In addition, these new systems have relatively low loss so the pulse dynamics are easy to observe. However, until now, all of the systems developed to generate slow or fast light have been difficult to implement.

In this review, R W Boyd and colleagues at Rochester University explore ways to produce slow and fast light in a room-temperature solid-state material. First they describe the concept of coherent population oscillations—the primary physical mechanism used to generate large dispersion. They show that when the beat frequency between the pump and probe beams is slow enough, it will cause the population in a two-level atom to oscillate. This time-varying population will cause energy to be scattered out of the pump beam and into the probe, so the probe will see less absorption over a narrow frequency range. Correspondingly, the group velocity for the probe can be very large within the same frequency range.

They describe their experimental demonstration of ultra-slow light propagation in ruby using coherent population oscillations. They observed a group velocity as low as 58 m s^{-1}. Their results included the observation of a delay of both amplitude modulations and pulses.

They showed how it is possible to observe both ultra-slow and superluminal group velocities in another material, alexandrite. Since alexandrite is an inverse saturable absorber at certain wavelengths, the sign of the group velocity is changed. In alexandrite the chromium ions can occupy either mirror sites (having mirror symmetry) or inversion sites (having inversion symmetry). As a result of the energy level structure at each site, ions at mirror sites experience inverse-saturable absorption (fast light), whereas ions at inversion sites experience saturable absorption (slow light). The competing effects from ions at either site can be easily distinguished because they have markedly different population relaxation times.

Finally, the authors discuss the significance of ultra-slow light propagation. While much work remains to be done, they conclude that these slow light techniques could be very important in developing all-optical control of communication and storage applications.