

In this study three-dimensional (3D) force (frequency shift: df) mapping method has been applied to the investigations of molecular-scale hydration structures at solid-liquid interfaces as well as those around biomolecules such as proteins and DNA molecules. The 3D visualization of the hydration structures allows us to make a precise comparison of the experimental data with theoretical calculations of water structures, which can provide a molecular scale understanding of the hydration structure. However, there have been several difficulties in the 3D force mapping in liquids because of a large, linear and nonlinear thermal drift of the tip position relative to the surface in an unstable liquid environment. We have developed a low-thermal-drift FM-AFM working in liquids based on a commercial AFM instrument. A sufficiently low, lateral thermal drift rate of less than 1 nm/min was achieved in liquids by an accurate temperature control of the environment and by a large reduction of the liquid evaporation. We obtained 3D frequency shift (df) data on a muscovite mica surface in a 1M KCl solution [3]. The result was compared with water density distributions calculated using the 3D reference interaction site model (3D-RISM) theory. In addition, we also discuss a latest result of 3D visualization of hydration structures around biomolecules such as DNA molecules.

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Step flow and interface structure during the growth of semiconductor nanowires

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Silicon, germanium and III-V semiconductor nanowires, formed via the vapour-liquid-solid and vapour-solid-solid mechanisms, can be grown *in situ* in an ultra high vacuum transmission electron microscope [1]. This enables structural and kinetic observations to be made during growth under different conditions and for a range of catalyst materials. Since growth takes place at the catalyst/nanowire interface, measurements at this interface provide insights into the surprisingly complex nanowire growth mechanism.

Observations of Si nanowires growing *in situ* from liquid catalysts, such as AuSi, and solid catalysts, such as Cu₃Si, show that growth is by the flow of steps across the catalyst/nanowire interface [2]. However, the kinetics of step flow are strikingly different for solid versus liquid catalysts, in terms of the speed of step flow and the time interval between step flow events [3]. Furthermore, an unexpected interface morphology is visible *in situ*: rather than having a planar catalyst/nanowire interface, the nanowire is truncated around its edges, and the size of this edge truncation oscillates in synchronization with the flow of steps [4]. A similar edge oscillation is also visible during the growth of Ge nanowires [5] and GaP nanowires from AuGa liquid catalysts [4].

In this presentation, we will describe a kinetic model that can explain both the step flow kinetics and the interface structure and edge oscillation. From the step flow kinetics, this model allows us to identify the key parameters that control growth, and evaluate changes in the catalyst composition and supersaturation during growth. We can also understand the conditions under which we expect to form abrupt heterojunctions in nanowires, as required for fabricating electronic nanowire devices.

The edge oscillations are also related to the catalyst supersaturation, and provide a direct visualization of the supersaturation as it varies during the step flow cycle. Because edge oscillations are present in at least one III-V nanowire system, they force us to re-examine our understanding of polytypism in III-V nanowires, which is thought to be determined by the nucleation process of each new layer of semiconductor at the periphery of the growth interface. Both step flow and the changing interface structure therefore provide a window into the nanowire growth process, helping to relate structure to growth mechanism and suggesting how to optimise nanowires for advanced applications.

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Transient phases and prenucleation clusters in biomimetic calcium phosphate mineralization

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The often astonishing materials properties of crystalline biominerals are generally related to the hierarchical assembly of specifically interacting organic and inorganic components. A yet unfulfilled dream of many scientists is to synthesize new materials with similar advanced properties applying Nature's biomimetalization strategies.[1] An absolute prerequisite for the design of such hybrid materials with predetermined structure and properties is to unravel the mechanisms of biologically and biomimetically controlled mineral formation.

The *in situ* study of the development of mineral formation can make an important contribution to the understanding of the processes involved in biomineralization.[2] CryoTEM has been demonstrated as a method to investigate the early stages of mineral formation without removing the developing particles from their aqueous environment. [3,4] For calcium phosphate these investigations revealed that the formation of apatite is preceded by an amorphous phase, which itself is formed through the assembly and aggregation of what we have called "prenucleation clusters" [5,6]. Here we will discuss the precise structure of these "clusters" and their role in the formation of the subsequent amorphous and crystalline phases. It will be demonstrated that these recent insights re-unite classical and non-classical theories about mineral formation.

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