# Chapter 1

# Thesis Overview

Surface atoms/molecules of a material act as an interface to its surrounding environment; their properties are often complicated by external adsorbates/species on the surface and are often poorly understood because of a lack of accurate description of surface adsorbates/species. Surface modification often dramatically changes the surface chemical and physical properties (e.g., reactivity and surface electronic structure). As the size of objects enters into the nanometer scale, surface properties gradually dominate owing to the increasing surface-area-to-volume ratio. It is therefore important not only to thoroughly understand the surface structure but also to engineer the surface in a controllable way. In this thesis, the modifying surface chemical and physical processes will be carried out in a controllable way and characterized at the nanometer and atomic scales through both conventional and novel scanning probe microscopy methods. Other spectroscopic characterization techniques, such as infrared and X-ray photoelectron spectroscopy, are also employed in our studies. Four major research areas are discussed in this thesis and are outlined here.

### Functionalization of silicon

Traditional semiconductor silicon devices are often covered by a high-quality, thick silicon dioxide layer, which acts as both a dielectric and a protection layer. This strategy prevents the devices from the external ambient environment and inhibits deleterious chemical reactions. However, surface states induced by the oxide layer increase the electron-hole recombination rate, and this problem worsens as the devices shrink in lateral size to nanometer scale. Replacement of oxides with a chemical (molecular) passivation layer has increasingly drawn a large amount of research interest. It is expected that with a well-defined chemical passivation layer, it is possible to understand and control the introduction of electronic states on Si surfaces.[1, 2]

In Chapter 2 and 3, a novel two-step chlorination/azidation functionalization protocol is developed and systematically investigated through various surface characterization techniques in order to understand the chemistry occurring on surfaces. Our scanning tunneling microscopy (STM) studies on chlorinated Si(111) surfaces show an unreconstructed 1×1 structure.[3] Tuning of surface etch pit density is demonstrated experimentally, which may enable the tailoring of the surface chemical reactivity toward subsequent alkylation and other functionalization processes. Tunneling spectroscopy reveals a non-zero density of states near zero applied bias, in contrast to analogous measurements on H/Si(111), methyl/Si(111), and ethyl/Si(111) surfaces. Subsequent grafting of azide group to replace chlorine demonstrates an example of non-oxidative passivation of silicon surfaces with new functionalities. For example, the Cu(I)-catalyzed Huisgen 1,3-dipolar cycloaddition ("click" chemistry) may be employed to introduce bio-functionalities onto the surface. By varying the solvent used in the azidation process, different azidation kinetic rates, final azide coverages, and surface-area distributions have been achieved.[4]

## Graphene wrinkles and nanoribbons

Graphene refers to a monolayer of carbon atoms tightly packed into a two-dimensional (2D) honeycomb lattice. The linear dispersion spectrum of graphene causes its charge carriers to behave like massless Dirac fermions, leading to various novel electrical properties that are of fundamental interest. Small ripples (<1 nm) existing in both $SiO_2$-supported and free-standing graphene have been observed via transmission electron microscopy and STM. Attempts to correlate local electrical properties with these corrugations, however, have achieved only limited success.

Chapter 4 describes the STM study of a new class of corrugations in monolayer graphene sheets that have been largely neglected in previous studies, i.e., wrinkles ~10 nm in width and ~3 nm in height. We found such corrugations to be ubiquitous in graphene, and have distinctly different properties in comparison to other regions of graphene that only contain small ripples. In particular, a “three-for-six” triangular pattern of atoms is exclusively and consistently observed on wrinkles, suggesting the local curvature of the wrinkle is a perturbation that breaks the six-fold symmetry of the graphene lattice. Through scanning tunneling spectroscopy (STS), we further demonstrate that the wrinkles have lower electrical conductance when compared to other regions of graphene, and are characterized by the presence of midgap states, which is in agreement with recent theoretical predictions. Our results suggest that, in addition to the previously investigated, low-amplitude ripples, these larger wrinkles likely also play an important role in determining the electrical properties of graphene sheets.[5]

While graphene has drawn tremendous attention for studies of its fundamental structural and electronic properties in recent years, the absence of an energy gap in graphene poses a challenge for conventional semiconductor field-effect transistor (FET) device operations. Previous studies have shown that an energy gap can be opened up by patterning graphene into ribbons of nanometers in width. This is explained in terms of a quantum size effect, where the originally 2D carriers are confined into a 1D system. Most of these studies have been focused on *individual* graphene nanoribbons (GNRs). The measurement results often vary from sample to sample due to the disorders introduced along the GNR edges during the lithography process. The origin of the energy gap is therefore complicated in this situation.

Chapter 4 also describes our fabrication of ultrahigh-density parallel GNR arrays. Measurements on these GNRs show consistent results, as variations previously observed on individual GNR devices are averaged out across multiple GNRs in our studies. We found that the electron transport in all of our GNR devices exhibits thermally activated behavior (regardless of number of layers): conductance decreases with decreasing temperature. This contrasts with the behavior of “bulk” graphene films, the conductance of which generally increases as temperature decreases. More importantly, we have also for the first time clearly observed how the properties of GNRs evolve as a function of number of graphene layers. The band gap (and so the on-off ratio) diminishes as the number of layers increases. These results suggest that, in addition to single layer graphene, properties of GNRs of different thicknesses can also be harnessed for engineering the GNRs as different building blocks for FET applications.

## Graphene-templated imaging

As mentioned above, surface chemical and physical properties are often closely correlated to the surface microscopic structures. Direct imaging of the microscopic structures of adsorbed water and other weakly-bound small molecules on solid surfaces at ambient conditions has been a long-time dream for surface scientists. Due to the dynamic nature of these weakly bound adsorbates, the structures of these surface species are often strongly perturbed during imaging by scanning probe microscopy because of tip-sample interactions.

Chapter 5 describes our discovery of a novel imaging technique through graphene templating. We report on the use of monolayer graphene sheets as ultrathin coatings for enabling atomic force microscopy (AFM) studies of the first water (and small organic molecules) adlayers on mica. Sputtered carbon is commonly used to coat biological systems, such as cells, for electron microscopy imaging. The carbon enables the imaging experiments by providing a protective (and conductive) coating. The graphene coating used here plays a somewhat similar role; we find graphene can tightly seal what are otherwise elusive adlayers, and stably "fix" the water adlayer structures, thus permitting the detection of the structure of the first water adlayers under ambient conditions.[6]

We found that under ambient conditions, water adlayers grow epitaxially on the mica substrate in a layer-by-layer fashion. Submonolayers form atomically flat, faceted islands of height 0.37±0.02 nm, in agreement with the height of a monolayer of ice. The second adlayers, observed at higher relative humidity, also appear ice-like, and thicker layers appear liquid-like. Our results also indicate nanometer-scale surface defects serve as nucleation centers for the formation of both the first and second adlayers.[6]

For studies of tetrahydrofuran (THF) and cyclohexane on mica, we found that the first two adlayers of both molecules adsorb in a layer-by-layer fashion, and atomically flat two-dimensional islands are observed for both the first and the second adlayers. THF adlayers form initially as rounded islands, but over a time period of weeks evolve into faceted islands, suggesting that the adlayers possess both liquid and solid properties at room temperature. Cyclohexane adlayers form crystal-like faceted islands, and are immobile under the graphene template. Precise adlayer height measurements further permitted the identification of the crystal structures of the adlayers. The heights of the second adlayers of THF and cyclohexane are measured to be 0.44±0.02 and 0.50±0.02 nm, respectively, in good agreement with the layer thicknesses in the monoclinic crystal structure of THF and the Phase I “plastic crystal” structure of cyclohexane. The first adlayers appear slightly thinner for both molecules, indicative of interactions of the molecules with the mica substrate.[7]

## Quartz-tuning-fork-based low temperature atomic force microscopy

In Chapter 6, we describe the design of a quartz-tuning-fork-based force sensor and related electronics for applications in low-temperature atomic force microscopy. Noise performance of three types of pre-amplifier electronics has been compared. Results show that the force-sensor-global-feedback circuit detector system induces the lowest noise floor. The high detection sensitivity of this system demonstrates its ability to be used in frequency-modulated AFM at cryogenic temperatures. The quality factor of the tuning-fork-tip ensemble has also been examined. We found that a high Q of ~9000 in vacuum at ~77K is obtained for a q-Plus type of tuning-fork-tip system. This facilitates accurate detection of frequency in AFM. Surface topographic imaging from H-terminated Si(111) has been achieved, which verifies our design of quartz tuning fork-based force sensor and pre-amplifier.

## References

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