Synopsis

The constant trend of device miniaturization along with ever-growing list of unusual behavior of nanoscale materials has fueled the recent research in fabrication and applications of ultrathin (∼2 nm diameter) nanowires. Although semiconductor nanowires of this dimension is well-researched, molecular-scale single-crystalline metal nanowires have not been addressed in details. Such single crystalline Au nanowires are formed by oriented attachment of Au nanoparticles along [111] direction. A very low concentration of extended defects in these wires result in a high electrical conductivity, making them ideal for nanoscale interconnects. Some of them, e.g. Ag and Cu, have very low absorption co-efficient useful for fabrication of transparent conducting films. On the other hand, because of the reduced dimensions, there exists a tantalizing possibilty of dominating quantum effects leading to application in sensing and actuation. Also, speaking in terms of atomic structure, these systems suffer from intense surface stress, and the atomistic picture can be drastically different from bulk. Thus, although a myriad of applications are possible with ultrathin metal nanowires, a rigorous systematic knowledge of atomic and electronic structure of the [111]-oriented {110} bound metal nanowires is not yet available. This thesis is the first one to model such computationally demanding systems with emphasis on their possible applications.

In this thesis, we have explored various structural and electronic aspects of one-dimensional ultrathin (∼2 nm diameter) nanowires with *ab initio* density functional theory coupled with experiments. The merit of Au nanowires has been tested as nanoscale interconnects. From atomistic point of view, these FCC Au nanowires exhibit an intriguing relaxation mechanism, which has been explored by both theory and experiment. The primary factor governing the relaxation mechanism was found to be the anisotropic surface stress of the bounding facets, and it is extended to explain the relaxation of other metallic nanowires. Our studies suggest that AuNWs of this dimension show semiconductor-like sensitivity towards small chemical analytes and can be used as nanoscale sensors. Also, we have found that further reducing the diameter of the Au-nanowires leads to opening of a band gap.

The thesis has been organized as follows:

Chapter 1 provides a general introduction to the one-dimensional materials, their importance and potential applications. An overview of the synthetic methodology of these nanowires is also presented across the scale from ∼2 nm diameter to few-atom systems such as single atomic chains (SAC). The motivation of the current research work has also been highlighted in this chapter.

Chapter 2 describes the theoretical methodology adopted in this work. It gives brief understanding on first principles based Density Functional Theory (DFT) and various exchange and correlation energy functionals used here to obtain electronic, structural, vibrational and magnetic properties of the concerned materials. A brief description of non- equilibrium electronic transport calculations has been also included.

Chapter 3 discusses the merit of the nanowires as nanoscale interconnects. Two aspects, namely the diameter dependent mechanical stability and electronic conductivity of the nanowires are addressed in detail. We find that these wires are comparable to bulk Au in terms of mechanical stability. Also, they have high enough electrical conductivity to serve as nanoscale interconnects. Our computed conductivity is in excellent agreement with experiments. On a further note, these nanowires show a systematic d-band confinement with decreasing diameter, which opens up a possibility to use them as sensors.

Chapter 4 is concerned with an intriguing relaxation phenomenon influencing the atomic structure of the Au nanowires. This relaxation warps the closed-pack planes of the nanowire into saddle-like surfaces. This observation was captured by our DFT- based simulations and was corroborated with atomic-resolution aberration-corrected electron microscopy of the nanowires. The planar wrinkling was confirmed as a crystallographic effect, and it was found to render an influence on the electronic properties of the nanowires.

Chapter 5 generalizes the phenomenon of planar wrinkling in [111]-oriented FCC Au nanowires to other FCC metal nanowires such as Cu, Ag, Au and Pt. The anisotropic surface stress of the {110} bounding facets being responsible for such planar wrinkling, it has been shown that the systematic out-of-plane atomic displacements for different nanowires can be predicted from the surface-stress based analysis. The effect of the planar wrinkling on the electronic structure of different nanowire has also been studied.

Chapter 6 explores the possibility of using the ultrathin Au nanowires as nanoscale sensors. We have shown that nanowire bind different analytes more strongly compared to surfaces. Also, such adsorption leads to a strong electronic interaction in-between the wire and analyte, leading to a change in the electrical conductivity of the system. Surprisingly, these ultrathin Au nanowires show semiconductor nanowire equivalent sensitivity towards different analytes. Most importantly, based on the electron affinity of the analyte, we propose an empirical relationship

by which the sensitivity can be predicted, giving a guideline for the experiments.

Chapter 7 investigates the structural and electronic aspects of experimentally achievable two types of thin zigzag atomic-scale wires of Au, Ag and Pt. One of the structures exhibits reconstruction for Au and Ag. Owing to this structural reconstruction, we observe a band gap opening in the nanowires. The energetics of the structures shows that the band gap opening depends strongly on the reconstruction.

Chapter 8 summarizes and concludes the work presented in this thesis.