**Introduction**

*There is plenty room at the bottom.*

-Richard Feynmann

Nanoscience and nanotechnology has influenced almost every human made object in this century. Advances in the field of nanoscience has empowered human being with new tools with the possible smallest scale. Hence the study of nano-sized specimens has received a lot of interest recently. Nanosized structures are defined as the structures with at least one dimension in the range of nanometers ($10^{-9}$ meters). The nanosized specimens are of interest as a result of their peculiar and very fascinating properties, and applications different to their respective bulk counterparts.[1, 2]

Reducing the 1, 2, or 3 dimensions (D) of bulk material to the nanometer scale leads to nanometer thick 2D surface (or layer), 1-D nanowire (Nw) or 0-D nanoclusters (or nanodots), respectively. These structures can also be modified into nanorods, nanobelts, nanotubes, etc.

A nanowire has the cross sectional dimension in nanometer range and one dimension unconfined. The nanowires are usually classified as metallic (e.g. Ni, Pt, Au, Ag) or semiconducting (e.g. Si, InP, GaN). Typical nanowires (as shown in Fig. 1.1) have high aspect ratio i.e., length to width ratio of 1000 or more. The diameter dependent band gap, enhanced surface scattering of electrons and phonons, increased excitation binding energy, high surface to volume ratio of metal and semiconductor nanowires lead to unique electrical, optical, thermoelectric and chemical properties.[3] The nanowires show many interesting properties in comparison with that of bulk due to quantum confinement of electrons in lateral direction and hence in nanowires, the electrons occupy the energy levels which are different than continuum of energy bands in the bulk materials. This is illustrated schematically in Fig. 1.2. A system with different dimension (viz., 1D, 2D, 3D) can be distinguished by its density of states $\rho(E)$, which is calculated as the number of states per unit volume $L^D$, within the energy range of $E$ and $E + \delta E$. Here, $L$ is the linear size and $D$ is the number of the dimensions of the system. The dispersion energy is given by $E \propto k^2$, and is the number of states contained in a $D$ dimensional sphere in the $k$ momentum space and is proportional to $(L/2\pi)^D k^D$. The number per unit volume is proportional to $k^D$ or $E^{D/2}$. Therefore, the density of...
states becomes $\rho(E) \propto E^{D-1}$. The density of states of electrons in 3, 2 and 1 dimensional systems are proportional to $E^{3}$, $E^{2}$ and $E^{1/2}$, respectively, for bulk, quantum wells or layers quantum wires and quantum wires (Fig. 1.2(a)-(c)). In case of quantum dots, the density of states are just a series of delta functions ($\rho(E) \propto \delta(E - E_{n_x,n_y,n_z})$), where, $E_{n_x,n_y,n_z}$ are the confined energies with the quantum numbers $n_x, n_y$ and $n_z$, as the carriers are confined in all three dimensions (Fig. 1.2(d)). This confinement of the charged particles in different directions results in discrete bound states. This phenomenon of having bound states in quantum systems is the quantum confinement effect.[4] This effect makes nanostructured materials very interesting for electronic applications.

1.1 Overview

The focus in the present thesis is on metal nanowires. Metallic nanowires represents nature’s ultimate limit of conductors in one dimension and can be reduced to single atom thickness. The previous investigations show that, the term nanowire is reserved for the conductive structures. Non-conducting structures or lines are usually referred as nanolines, and the term nanowire includes the family of conducting structures viz., nanotubes, nanorods, nanobelts, nanosprings, nanofilms.[6, 7] All wires essentially are applicable for the main purpose of conduction. In comparison with the zero dimensional structures, viz., quantum-dots, nanoparticles, one dimensional structures provide a better platform for investigating the dependence of electronic transport, optical and mechanical properties on size confinement and dimensionality. The geometrical properties like structure and dimension strongly determine the mode of electron conduction i.e., with scattering or ballistic conductance. When the size of the conductor shrinks to one dimension, the electron transport is better described with quantum mechanics than classical physics.

In terms of conductance, the nanowires are characterized by two threshold values viz., material dependent mean free path (MFP) and material dependent Fermi wave-
Figure 1.2 – Schematic representation of the density of states for (a) bulk, (b) quantum well or layers, (c) quantum wires and (d) quantum dots, respectively. Ref.: V.V.R. Kishore, PhD thesis,(2013)[4].

length¹ (electron wavelength). For classical like conductance, material should possess cross sectional dimensions (height and width or diameter) larger than the MFP. The nanowires with dimensions between the MFP and approaching the Fermi wavelength exhibit semi-classical nature of conductance. However, nanowires with dimensions near and below the Fermi wavelength exhibit quantized conductance and such conductance is also referred as ballistic conductance (Fig. 1.3). For example, in gold the MFP is \( \sim 38 \text{ nm} [8, 9] \) and the Fermi wavelength is \( \sim 5.2 \text{ Å} \), which is approximately double than that of diameter of the gold atom (2.88 Å).[10] It indicates that, the conductance in gold nanowires exhibit ballistic behavior. Hence, the quantum mechanical models of wave-like electron transport are essential to understand the conductance behavior of nanowires.

The phenomenon of quantum conductance was observed initially in semiconductor devices. The MFP is on the scale of nanometers for silicon and the Fermi wavelength is about 40 nm, hence for semiconductors, the device can not have atomic dimensions. However, due to low density of states and small energy difference between the quantum nodes, the quantum conductance is observed at very low temperature. The noble metal gold on the other hand has high electron density and due to its small Fermi wavelength, quantized (ballistic) conductance is observed even at room temperature if the nanowire has thickness of a single atom.[11] Hence gold nanowires having atomic scale have always been an interesting topic of research for conductance properties. This is one of important motivations of this thesis work to investigate the conducting properties in gold nanowires.

¹Fermi wavelength is the de Broglie wavelength of electrons near the Fermi energy. Most of the properties of solids, involving electron transport can be described by the dynamics of electrons near the Fermi energy.
The mesoscopic transport is influenced significantly by the spin phenomenon and this has been the focus of attention in recent times in the area of spintronics. The interplay between the quantum coherence with the quantum confinement gives rise to numerous unexpected spin phenomenon in ballistic conductors, which allows to control the spin of the charge carriers. For instance, with the increasing interest in the spin dependent transport, the interplay of electron spin and charge degree of freedom has been used in many spin interference devices.[13] The charge as well as spin transport through conductors at mesoscopic scales can lead to new type of materials. This is often applicable in spin valves, spin filters and detectors and also in spin switches.[13] The mechanism of spin transport may strengthen the world of spin electronics. Hence, in the present thesis we have exploited the spin dependent transport and magnetic phenomenon in the atomic scale nanowires.

In comparison with the quantum dots or clusters, the advancement of nanowires has been little slow recently, due to difficulties associated with the fabrication of nanowires with well controlled size, morphology, phase purity\(^2\) and chemical composition. In the next section, the fabrication of nanowires is discussed in short.

### 1.2 Synthesis of Nanowires

An interesting question to answer is how can atoms be rationally assembled into a structure with nanometer size diameter and having a longer length. Answering this question is central idea to the preparation of 1D nanowires, and various techniques

\(^2\)Without impurities or defects in the desired composition
have been used to synthesize nanowires. The synthesis mechanism is mainly divided into two approaches, viz., (i) bottom-up approach and (ii) top down approach.

1.2.1 Bottom up approach

The bottom up approach is achieved by putting atoms together one by one, through various physical or chemical processes. The vapor-liquid-solid (VLS) technique is now a popular one to synthesize semiconductor nanowires. There are other methods viz., physical vapor deposition (PVD), chemical vapor deposition (CVD) and metallorganic chemical vapor deposition (MOCVD). Among these methods, VLS technique is most successful for generating nanowires with single crystal structures and in abundant quantities.

1.2.1.1 Vapor Liquid Solid (VLS) Method

A typical VLS process begins with the dissolution of gaseous reactants into nanosized liquid droplets of a catalyst metal, followed by nucleation and growth of single crystalline rods which turn later into the wires. The 1-dimensional growth is mainly induced and dictated by the liquid droplets, whose size remain unchanged during the entire process of growth of the wire. In this method, every liquid droplet represents a soft template to strictly limit the lateral growth of individual wire. All major steps involved in a VLS process are schematically shown in fig. 1.4, where growth of Ge nanorods is shown as an example. It is based on Ge-Au alloy binary phase diagram (Fig. 1.4(b)), Ge and Au form liquid alloys when the temperature is raised above 361°. After supersaturation of liquid droplet takes place, the growth of the nanowire will start to occur at the solid-liquid surface. Yang et al. have used this mechanism by observing in situ growth of Ge nanorods within the chamber of TEM equipped with a temperature controllable stage.[14] In addition to the nanowires with a circular or square cross section, the formation of nanobelts (or nanoribbons) with a rectangular cross sections was also observed by evaporating commercial metal oxide powders at elevated temperatures.[15]

In addition to the CVD, there is a physical vapor deposition method, in which the source is evaporated and condensed directly onto the substrate without any catalyst. In the method of thermal annealing, the vaporization and transportation of the source material is done by a carrier gas to the substrate surface with the deposition of the catalyst material. This vapor is condensed to the molten catalyst and source alloy. After saturated equilibrium condition, nanowire is observed to grow to maintain the equilibrium in the liquid phase.[16]

1.2.2 Top down approach

In this approach, one starts from the bulk material and subsequently reduces the size using methods such as, lithography or etching till the desired size is achieved. This is a cost effective method for fabricating certain types of 1D nanowires which are difficult to generate at the nanometer scale. Here we mention three of the most promising methods for size reduction viz., (i) use of isotropic deformation of a poly-crystalline or amorphous material, (ii) anisotropic etching of a single crystal and (iii) near-field optical lithography with a phase shift mask.[1] These techniques can reduce the size of the nanowire up to $1 \sim 10 \mu m$ to $< 100 \text{ nm}$.

The size reduction of a material in two directions can be achieved by an uni-axial elongation of a solid. The size reduction is thus obtained at the expense of dimensional increase in the third direction. An elastomer is used to reverse such a deformation. This

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Figure 1.4 – (a) Schematic picture showing the growth of nanowire through vapor-liquid-solid technique. (b) The binary phase diagram between Au and Ge with an indication of the composition zones responsible for alloying, nucleation and growth is shown. Ref.: Y. Xia et al., Advanced Materials, 15, 353, (2003)\[1].

adds another interesting feature that the lateral dimension of 1D nanostructure can be continuously reduced and iteratively adjusted by controlling the extent of mechanical deformation. The efficiency of this method depends on the uniform deformation of a solid material.

In the anisotropic etching of a single crystalline substrate, the surface has been patterned with an array of trenches, and the width of the trenches decreases in a controlled manner as the etching proceeds, due to different etching rates along various crystallographic directions. This method can reduce the size of the material continuously from several micrometers to less than 100 nm by controlling the etching time.\[17] This technique provides a simple and convenient approach to the fabrication of supported 1D nanowires. For example, tungsten nanowire of 20 nm width have been fabricated by sputtering.\[18]\[18]

Third method of size reduction i.e., near field optical lithography uses masks constructed from an elastomeric polymer such as poly(dimethylsiloxane) (PDMS).\[19, 20] Such soft mask can now come into conformal contact with photo-resist layer for an area about several hundreds square centimeters without any need of external force. As light passes though such phase-shift mask, its intensity can be modulated in the near field, so that, an array of nulls or peaks in the intensity are observed at the edges of the PDMS mask. This results in the transformation of patterned photoresist film into underlying...
Other Potentially important approaches

Figure 1.5 – Schematic picture showing the procedure that generates 1D nanostructures by (A) shadow evaporation,[22, 23] (B) reconstruction at the bottom of V-grooves,[24] (C) cleaved-edge overgrowth on the multilayer film cross section[25] and (D) templating on step edges on the surface of solid substrate.[26] Ref.: Xia et al., Adv. Mater. 15, 353, (2003).[1]

substrate using reactive-ion etching or wet-etching mechanism. Previously, Whitesides et al., used polychromatic, incoherent source of light and conventional photoresist to produce parallel lines of ~90 nm in width for large area of flat surface.[21]

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1.3.1 Template directed synthesis

Template directed synthesis is a straightforward way to synthesize 1D nanostructures. The template serves as a material which shapes the sample into a nanostructures with its morphology complementary to that of template. If the chemical method is involved for harvesting the final nanostructure, it becomes necessary to remove the template from the nanostructure using post-synthesis process.[1] Usually the template is consumed as the reaction proceeds however, it is possible to get the nanostructure in the pure form. The template directed synthesis provides a simple and cost effective procedure for synthesis of nanowires in a single step. There are different techniques of template directed synthesis such as, templating against features on solid substrates, filling channels in porous materials, templates against self assembled molecular structure and existing nanostructures. In this thesis, we discuss two methods which are widely used for nanowire synthesis.

1.3.1.1 Templates of solid surfaces

The micro-structures that could be conveniently patterned on the surface of a solid substrate using lithography and etching could be exploited as templates to synthesize nanowires of different elements.[27] Decorating these templates with different materials provides a powerful tool for the formation of nanowires from various metals and
semiconductors. For example, Jorritsma et al., prepared a metal nanowire as thin as 15 nm by shadow sputtering (Fig. 1.5(A)), a metal source on array of V-grooves etched on the surface of Si (100) wafer. In the other procedure, metal or semiconductor was applied at normal incidence using the technique based on vapor-phase deposition or solution-phase electrochemical plating. It is then reconstructed to form 1 D nanostructures at the bottom of each V-groove (Fig. 1.5-(B)). With this approach, nanowires with lengths up to hundreds of micrometers and thickness in nanometers can be continuously prepared as parallel arrays on solid surface. These nanowires can be released in free standing form or can be transferred onto surface of other substrates.

The cross-sections of multilayer films prepared through molecular beam epitaxy (MBE) have been used as templates to grow simple patterns of structures consisting of metal and semiconductors (Fig. 1.5-(C)). This technique is also known as cleaved-edge overgrowth (CEO), and is based on high accuracy of MBE in controlling the layer thickness of superlattice. A superlattice made of alternating layers (e.g. AlGaAs and GaAs) is prepared through MBE and then cleaved in situ through the thickness of the multilayer structure producing to an atomically clean surface. In the next step, MBE/electrochemical deposition is used to grow the epitaxial layers on selected regions of the exposed surface.

The growth of metal nanowires by templating against the step present on a precisely oriented, pyrolytic graphite was carried out by Penner and co-workers using electrodeposition (Fig. 1.5-D). They employed two different type of materials in their investigations viz., noble metals (e.g., Pd, Cu, Ag and Au) and electronically conductive metal oxides (e.g., MoOx,MnO2,Cu2O and Fe2O3 that could be reduced subsequently to the corresponding metals (Mo, Mn, Cu and Fe) at elevated temperature by the hydrogen gas.

1.3.1.2 Templates of porous material with channels

Another class of templates for the synthesis of 1D nanostructures (developed by Martin et al.) are the channels in porous materials (Fig. 1.6). There are two types of membranes for such types of synthesis, viz., polymer film containing track-
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etched channels and alumina film containing anodically etched pores.[1] For track-etching, a polymer film of 6 – 20µm thickness is irradiated with heavy ions to generate damaged spots on the film surface. These spots are amplified using chemical etching to generate uniform, cylindrical pores penetrating the membrane film.[34] A large variety of materials have been examined with the use of such templates like metals,[35] semiconductors,[36, 37] ceramics,[38] etc. With this method, single crystal nanowires have been obtained under carefully controlled conditions. [39]

1.3.2 Formation of atomic sized metallic point contacts

A wide variety of techniques have been developed in last decade to prepare metal nanowires with the thickness of atomic size. At this point, it is important to stress the difference between the room temperature and low temperature experiments. At low temperature, atomic sized contacts can be held stable for any length of time, and hence allow detailed investigation for its physical properties. Whereas, at room temperature, the thermal diffusion of the atoms prevents long term stability of the structure and this needs ultra high vacuum (UHV) conditions for a clean metal structure. In this subsection, we discuss few popular techniques to get atomic sized nanowires or point contacts for metals.

1.3.2.1 Spear-anvil technique

This is very early technique for fabrication of ballistic metallic point contacts.[40] The technique consists of bringing a needle of a metal gently into contact with the metal surface, also called as spear-anvil technique. A differential-screw mechanism is used to adjust the point contact manually. Using this technique, the stable points contacts are formed having resistances in the range from ~ 0.1 to ~ 10Ω, and contact diameters in the range of 10 – 100 nm. The elastic and inelastic mean free path of the charge carriers can be much longer than this length, when clean metals at low temperatures are used. This technique is useful for study of electron-phonon interaction in metals.[41] However contacts of spear-avil type are not much suitable for the investigation in the quantum regime, which needs contact diameters in the range of the Fermi wavelength, i.e. contacts of the size of the atoms. The experiments in the quantum regime need fine control over the contact size of the metal, which can be met by using the scanning tunneling microscope (STM) or mechanically controllable break junction technique (MCBJ).

1.3.2.2 The use of scanning tunneling microscopes

The scanning tunneling microscope (STM) is a ideal tool for studying and modifying the atomic sized contacts. The basic requirement for STM experiment is that, the sample must be conducting and for operation of STM, the control of the relative position of the tip and sample with subnanometer accuracy is essential, which is possible through piezoelectric ceramics. Using piezo ceramic devices, high accuracy in the position and movement is easily achieved through the voltage control. Since these ceramic devices are incorporated into STM’s, these are very commonly used in research. The first report of formation and investigation of a metallic contact using a STM was from Gimzewski and Möller.[44] Different groups have performed STM experiments on the conductance of atomic sized contacts under different experimental conditions: at cryogenic temperatures,[45, 46]; at room temperature with ambient conditions[47, 48]

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[4] The STM is a tool which allow studying the topography and electronic properties of a metal or semiconductor surface with atomic resolution. For detailed overview, Ref.[43]
and also under high vacuum.[49, 50]

The direct observation of metallic nanocontacts is possible through high-resolution transmission electron microscopy (HRTEM). For this type of experiment, the STM is constructed with the tip apex at the focal point. Kizuka et al., have observed the atomic contact formation process in gold using a piezo driven specimen holder.[42, 51] In this experimental set-up as shown in Fig. 1.7, piezodriving specimen holder for a transmission electron was developed for subnanometer scale mechanical movement. The mobile side is connected with a pipe-type piezoelectric device for precise displacement. The specimen on the mobile side is mounted on the tip of a lever and is connected with the piezoelectric device. The x-direction of the mobile side can be moved from 0 to 1 mm with the help of motor. Besides this, the fine displacement along the x-direction is controlled through piezo-device by elongation and shrinkage.

In a typical STM experiment for producing atomic contacts, a small tip is crashed into a sample and then it is withdrawn producing a nanowire at the last stage until it breaks apart. Using this technique, Takayanagi[53] and Ohnishi et al.[52] have investigated the structure of gold nanowires just before breaking. Kondo and Takayanagi formed gold nanowires by electron-beam irradiation on gold film in an ultrahigh vacuum transmission electron microscope (UHV-TEM).5

They observed the thinnest nanobridge with four atomic rows by irradiating the bridge by electron-beam as shown in Fig. 1.8. Further reduction in the thickness of

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5The UHV-TEM was equipped with a field emission gun operated at 200kV. Operating the UHV-TEM for high resolution at $10^{-8}$ Pa enabled the clean fabrication of the gold tips which eliminated any effect of contamination on the structure.
Figure 1.8 – Transmission electron microscope showing the formation of nanowire: The dark dots represent the gold atoms. From top to bottom, the diameter of the nanowire decreases as: 1.3 nm, 1.1 nm, 0.8 nm and 0.6 nm, respectively. (Ref.: Takayanagi et al.,) JSAP International, 3, (2001).[12].

Figure 1.9 – The electron microscope picture of gold atoms (four colored dots) forming a linear strand between the gold tips. The spacing between gold atoms are 0.35 – 0.40nm. The strand is oriented along the (001) direction of the gold (110) film. (Ref.: H. Ohnishi et al., “Quantized conductance through individual rows of suspended gold atoms.” Nature 395, 780 (1998))[52].
1.3 Other Potentially important approaches

1.3.2.3 The mechanically controllable break junction technique

In conjunction with the scanning tunneling microscopy, in which the tip is driven into contact with the metal surface and conductance is measured during subsequent retraction, the other technique used is mechanically controllable break junction.[55]

In this case, one starts with a macroscopic notched wire[56] which is mounted on a flexible surface, which is insulating and elastic. The substrate is mounted in a three point bending configuration between the piezo-device and two fixed counter support. This set up is mounted in the vacuum can and cooled down to liquid helium temperature. The wire or bridge is broken at low temperature in the vacuum by bending the substrate through the piezo element and the contact is re-established between the fracture surfaces of the substrate bending controlled by piezo-device.[55] The schematic picture of the mechanically controllable break junction is shown in Fig. 1.10. The substrate is bent by moving the piezo-element forward using mechanical arrangement. The bending causes the top surface to expand and elongate the nanowire and finally to break at the notch. The broken ends can be brought into contact by relaxing the force on elastic substrate.[41] The advantages of this method is obtaining a clean surface and the stability of two electrodes with respect to each other. Yanson et al.,[55] observed breaking of gold nanowires of atomic scale, which leads to the formation of gold chain of one atom thickness and at least four atom long.

Figure 1.10 – The schematic picture showing the mounting of mechanically controllable break junction. (Ref: R. J. Nichols et al., Phys. Chem. Chem. Phys. 12, 2801-2815, (2010)[57]).

gold nanowires in terms of atomic rows was carried out by Ohnishi and coworkers. They fabricated sharpened gold tips mechanically and was dipped into gold islands. This was slowly withdrawn at a constant speed under computer control. They observed structural changes continuously during the withdrawal of tips by means of video monitor. During the withdrawal of tips, the conductance was measured corresponding to the thickness of the gold bridge. Figure 1.9 shows observed electron microscope image of linear strand of gold atoms as a bridge between the STM tips when was pulled from the gold island. The advantage of this method is that, the structure is very stable and process can be followed with a video frame time resolution. This type of feature have also been reported for STM experiments by other researchers.[45, 48, 54]
One dimensional nanostructures exhibit distinct electronic, optical, chemical and thermal properties with respect to their bulk counterparts due to large surface area and possible quantum confinement effects. In many cases, the one dimensional nanowires show surprising physical properties than their bulk counterparts, e.g., gold nanoelectrodes (of 10 nm diameter) show cyclic voltammetric detection limits for electroactive species with three orders of magnitude less than those observed for a conventional disk microelectrode of bulk gold.[58] The magnetic 1-D structures; such as Ni nanowires of 30 nm diameter show enhanced coercivities as large as 680 Oersteds, whereas bulk Ni shows upto tens of Oersteds. In addition, such Ni nanowires show up to 90% remnant magnetization.[59] The nanowires with controlled dimensions, composition and crystal structure represent new class of materials for investigating relationship between structure dependent properties and related applications. In the present section, such important properties of nanowires are highlighted in short.

1.4.1 Thermal properties

The thermal stability of nanowires are of critical importance because of their importance in order to implement them as building block in electronic and photonic devices.[1] Previous investigations show that, melting point of a solid material is significantly reduced with the reduction in the dimensions.[60] El-Sayed et al. investigated photothermal melting and shape transformation for gold nanorods using spectroscopic methods.[61] They observed that, gold nanorods were melted and transformed into particles with spherical shape upon exposure to femtosecond laser pulses at sufficient energies. For higher energies, these nanorods fragmented and transformed into smaller spherical particles. Their investigations showed that, an average energy of $\sim 60 \text{ fJ}$ was enough to melt a single gold nanorod.

Wang et al. observed that various morphologies were formed for different temperatures for Si nanostructures when Si/SiO$_2$ composition in an alumina tube was thermally evaporated.[62] It was observed that, the Si nanostructures evolve through spheroidization. Their investigations showed that, the annealing and formation temperature plays crucial role in determining the relative ratios of the Si nanostructures in the products, viz., octopus, pin, tadpole or linear chain. This indicates that, one can have controlled synthesis of nanostructures, with the knowledge of their thermal stability.

The significant reduction in the melting point of materials with the dimension has remarkable implications. The annealing temperature necessary for the synthesis of defect free nanowire might be small by fractions than that of bulk material. This makes possible to perform zone refining in order to purify nanowires at modest temperatures.[1] In addition, a reduction in melting point helps to cut, interconnect and weld the nanowires at relative low temperatures which may provide a tool to integrate such one dimensional nanostructures into functional devices and circuitry. Another implication is that, with the reduction in the thickness in the nanowires, their stability can become highly sensitive to the environmental changes like temperature fluctuation and residual stress variation.[1] For instance, according to Rayleigh instability,[63]...
nanowires can spontaneously undergo a spheroidization to reduce the relative free energy associated with 1 dimensional system.

1.4.2 Mechanical properties

In order to manipulate and modify the nanostructures at atomic scale, it is essential to understand their mechanical properties. It was observed that, the hardness and yield stress of a polycrystalline material increases with the decrease in the size of the material on the micrometer scale. This is also known as Hall-Petch effect[64, 65] and is due to pilling up dislocations at the grain boundaries during shearing of the crystal planes in an individual grain. With the decrease in the grain size, the area of the boundaries increases, making the material tougher by blocking the dislocations. The computational investigations showed contrast result at the nanoscale. The samples of copper and palladium became softer with the decrease in the grain size.[66] This happened due to sliding motions at the boundaries. Hence the strength of the polycrystalline material initially increases and then decreases with the decrease in the grain size.

The mechanical strength of the single-crystalline 1-dimensional materials are supposed to be stronger than their bulk counterparts, due to reduction in the number of defects per unit length. The defects can cause the mechanical failure in the material. Whiskers have been extensively studied for the fabrication of rough composites for testing the toughness.[67] By using the atomic force microscopy (AFM), the mechanical properties such as elasticity, strength and toughness was determined for individual SiC nanorods that were pinned at one end to the surface of a solid substrate.[68] The bending force was measured with respect to the displacement along the pinned length. It was observed that, continued bending of these nanorods led to fracture.

Fernandez et al. used AFM to measure the length of Au nanowires during the elongation compression cycles.[69] The Au nanowires were formed by pushing the AFM tips into the physical contact. It was observed that, the Au nanowires elongated under stretching in quantized steps up to 3 integer multiples of 0.176 nm that they spontaneously shorten in the steps of 0.152 nm when they were relaxed. It was explained by assuming that the sliding of the crystal planes within Au nanowires created the stacking faults and that changed the local structure from cubic close packed (ccp) to hcp. These provide the direct evidence for the mechanism responsible for the plastic deformation of nanowire during stretching or compression.[1] This approach can also be used to examine the atomic events occurring during the plastic failure of different metals and respective alloys. The mechanical properties of freely suspended Au chain of single atoms was investigated with a force sensor in STM experiment.[70] The bond strength of the nanowire was observed twice than that of the bulk metallic bond.

1.4.3 Optical properties

The investigations by Leiber et al., have shown that, the light emitted from nanowires is highly polarized along their longitudinal axis.[71] They showed that, there exists a striking anisotropy in the photoluminiscence (PL) intensities recorded in the direction parallel and perpendicular to the long axis of individual, isolated InP nanowires. The

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8 The defects are reduced because the lateral dimensions are reduced.
9 Photoluminiscence is the phenomenon of the light emission from any form of the matter after the absorption of photons.
use of this large polarization response was demonstrated to be useful to fabricate polarization sensitive nanoscale photodetectors which can be used in integrated photonic circuits, optical switches and interconnects and high resolution detection applications. Krenn et al. demonstrated that, the metal nanowires sustaining collective electron oscillations can be used as optical wave-guides.[72] Their experimental investigation showed that, gold nanowires can be used to guide the light via surface plasmon polarization excitation. The gold nanowires can be used for non-diffraction limited light transport.

For nanorods made of noble metals viz., Au and Ag, their surface plasmon resonance properties have been extensively studied by El-Sayed et al.[73] The one dimensional structures exhibit two excitation modes, viz., longitudinal and transverse. If the wavelength of transverse mode is fixed around 520 nm for Au and 410 nm for Ag, their longitudinal modes can be easily tuned to span across the spectral region from visible to near-infrared with the control on their aspect ratios. It was also demonstrated that, the gold nanorods with an aspect ratio of 2.0 – 5.4 could fluoresce with quantum yield more than one million times that of the metal in the bulk form.[74] These properties when coupled with biological inertness, can make Au and Ag nanowire/nanorods ideal candidates for use of colorimetric markers or sensors, and contrast enhancing reagents for optical imaging.[75]

1.4.4 Sensing properties

Another important application for nanowires is related to sensing of molecules, either for medical, environmental or security-checking purposes. The extremely high surface-to-volume ratios of nanowires make their electrical properties extremely sensitive to the things adsorbed on their surfaces. For instance, Tao et al. generated an automated electrochemical process using the arrays of Cu nanowires.[76] The quantized conductance was reduced when organic molecule was adsorbed onto Cu nanowires, due to scattering of electrons by the adsorbing material. Penner et al. fabricated the hydrogen sensors with Pd nanowires when supported it on the polymeric thin film surface.[77, 78] Each nanowire contained many break junctions and this was observed to reduce when the hydrogen gas was adsorbed on the crystal lattice. The resistance of the nanowires exhibited a dependence on the concentration of a hydrogen gas, with the response as small as 75 ms. Cherevko et al. have investigated that, the partial oxidation of glucose takes place on Au Nw array electrode at more negative potential than that on Au film electrode. The gold nanowire array electrodes thus were used to detect non-enzymatic voltametric and amperometric glucose. The nanosized gold are also used in the detection of sugars.[79] Chae et al. have demonstrated that, helix-coiled gold nanowires exhibit distinctly enhanced molecule sensing efficiency than that for simple smooth gold nanowires. It was showed that the gold nanowires bearing the narrower lateral width exhibit enhanced molecule sensing efficiency with respect to those of thicker width helix nanowires.[80] Very recently, Jamal et al. investigated that, Pt coated Ni nanowire electrodes remarkably enhanced electrocatalytic activity towards glutamate and also showed higher catalytic activity when compared with other metallic nanostructure electrodes.[81] The sensitivity observed for Ni nanowire array was 6 to 9 times higher than the state of art glutamate sensor. Their experiments showed that the vertically aligned ordered nickel nanowire array electrode can be used to fabricate cost effective, sensitive, enzyme-less, stable and selective sensors.[81]

In addition to pure metal nanowires, the bi-metallic alloy nanowires also exhibit specific sensing properties. Jo et al. have synthesized Pd-Au nanowires with a good
resistance of a few hundred Ω showing hydrogen detection in the range from 100–2500 ppm.[82] Zhu et al. also investigated the bimetallic alloy nanowire of Pd with Au and Pt which showed direct alcohol fuel cells sensing and electrochemical sensing properties.[83] It was shown that, these nanowires exhibit enhanced stability and activity towards ethanol and methanol electro-oxidation in alkaline medium, indicating potential as effective electrocatalysis for direct ethanol alkaline fuel cells.

1.4.5 Magnetic properties

Magnetic nanowire arrays have been of considerable interest from viewpoint of perpendicular magnetic recording. When the magnetic field is applied parallel to long axis of the magnetic nanowire, it exhibits coercive field, which is inversely dependent to the wire diameter.[84, 85] It was reported that, the squareness of the hysteresis loops can be increased from 30% to nearly 100% by decreasing the wire diameter. Skomski et al. demonstrated that, the coercivity can be increased gradually with an increase in the aspect ratio (length(l)/diameter(d)), however the change is very little for l/d > 10.[86] It was shown by Liu et al. that, different sites on the surface lead to variation in the magnetic moment due to different coordination number.[87] Similarly, as the diameter of the nanowire increases, the differences in the surface free energy between the crystallographic plane becomes more significant. The change in the morphology is expected to cause the change in the magnetization characteristic of the nanowire.[3]

Hexagonally arranged Ni nanowires in alumina templates exhibit a strong enhancement in their magneto-optical response. [88] The magnetic nanowires like Fe, Co, Ni exhibit enhanced magnetic coercivity with respect to bulk materials.[88] Investigations based on magnetoresistance property of nanowire give a lot of information on the quantization effect, wire boundary scattering of electrons as well as the effect of doping and annealing on scattering.[89] The magnetoresistance of Bi nanowire was investigated in detail by Zhang et al.[90] The longitudinal magnetoresistance, where the applied magnetic field is along the wire axis, the peak maxima for magnetoresistance varies linearly with reciprocal of the wire diameter.[89–92]

These properties of nanowires have potential applications in the magnetic storage medium. The periodic arrays of magnetic nanowires have shown to possess the capability of storing about $10^{12}$ bits/in$^2$ of information. The single domain of fabricated Ni, Co nanowires with small diameter have been found to be most suitable for storing information.[85] The high aspect ratio of nanowires leads to enhanced coercivity, and is considered to be essential for preventing loss of magnetically recorded data between the nanowires.[3] A suitable separation between the nanowires is used to avoid the inter-wire interaction and coupling between magnetic dipoles. It has been investigated that, the stable magnetic medium consists of nanowire with density of $10^{11}$ wires/cm$^2$.[3]

1.4.6 Transport properties

As the size of the individual device achieves smaller and smaller dimension, the electron transport properties of their intrinsic components become a critical issue. It is investigated that, upon miniaturization the transport properties of several materials are changed significantly. Few metal nanowires, showed a transition to become semiconducting as their diameters are reduced below a particular value. Dresselhaus et al. showed that, single crystal Bi nanowire array underwent a metal-semiconductor transition at a diameter of ~ 52 nm.[93] Due to quantum confinement, it was explained
that, the external sub-band and valence sub-band of the system moved in an opposite direction in order to open up a band gap. For Bi metal, the carrier charge mobility is also suppressed because of the carrier confinement along the long axis of the wire.

Another phenomenon that makes the transport in nanowires very interesting is the quantum conductance behavior. The noble metals like Au, Ag represent electron transport properties in the form of short nanowires with linear chain of atoms. The conductance in this linear chain of atoms was observed in the quantized pattern, as was initially investigated by Yanson et al.\[55\] and Ohnishi et al.\[52\]. The first observation of conductance in the step size of $G_0$ was in quantum point contacts (QPCs) fabricated in semiconductor heterostructures.\[94\] It is an universal phenomenon in metallic nanowires.\[95–99\] This feature was also observed in liquid metal contact.\[54\] Bürki et al. have demonstrated that, the precision of the conductance quantization (especially for multivalent atoms) is poorer than that in semiconductor nanowires because of inherently rough structure on the scale of Fermi wavelength ($\lambda_F$), which leads to back-scattering.\[100, 101\] This is due to imperfect hybridization of atomic orbitals at the contact area, especially when there are multivalent atom involved.\[102\] In gold nanowires, the quantum properties are observed by breaking a metallic contact between two electrodes. Just before the break, the abrupt transition to tunneling occurs, the electrical conduction through a monovalent metal contact is always equals to $2e^2/h$ ($\approx 12.9$ kΩ$^{-1}$), where $e$ is the charge on the electron and $h$ is the Planck’s constant and it is shown in Fig. 1.11. This quantity is often referred as $G_0$, as a quantum or one unit of transmission, thus indicating that the neck diameter of a single atom. From Fig.
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1.11, it can be inferred that, the conductance curve reflects some structural evolution of particular atomic configuration, during which the conductance reduces in sharp steps. The curve for successive rupture sequences does not repeat in detail, as it might depend on exact atomic position in the contact.[55]

Ohnishi et al., have also investigated the quantized form of the conductance in gold nanowires with fine control on number of strand of Au atoms between the STM tips. They observed that, the conductance of a single strand of gold atom is $2e^2/h$ and that the conductance of a double strand is twice as large for single strand, indicating equipartition holding even for electron transport.[52] Hence one or two atom defect (either by addition or removal of one or two atoms), may change the number of transport channels and hence may cause variation in the conductance behavior. The dependence of number of conductance channels on certain physical parameters is discussed in Sec. 1.5, which is the primary motivation for this thesis work. The conductance quantization in gold nanowires was confirmed by many researchers experimentally[99, 103–110] and was also discussed theoretically.[110–115] The phenomenon of quantized conductance was observed to be independent of the material.[116] For semiconductors, recent measurement indicated that, GaN nanowires with thickness of 17.6 nm could still function as properly as semiconductor.[117] However, Si nanowires with a thickness of ∼15 nm show insulating nature.[117, 118]

These conducting 1-D nanostructures are applicable in many electronic devices. For example, Mallouk et al., have synthesized nanorods containing diode junction, and assembled into arrayed systems.[119, 120] Lieber et al., have assembled semiconductor nanowires into cross bar p-n junctions, which are further used to create integrated FET arrays, with nanowires as both conducting channel and gate electrode. In addition to these devices, OR, AND and NOT logic gate structures with significant gain have been configured using nanowires for basic computation. The doped silicon nanowires have been applied in fabrication of passive diodes, bipolar transistors, and complementary inverters with the help of self assembly. There are few appealing features in nanoelectronics. The size of the nanowire building blocks can be readily tuned to 10–100 nm, which can lead to high density of devices on a chip. Another, the material systems for the nanowires are essentially large enough, that gives flexibility to choose the right materials for desired device functionality. For instance, Leiber et al., have demonstrated GaN nanowire based device which are of high-power/high-temperature electrical applications.[6]

1.5 Motivation for the thesis work

As discussed in the previous subsection (Sec. 1.4.6), the transport properties of metal nanowires are of major interest not only from applicatory value but also from its basic physics studies. The ultimate limits of metal conductors, i.e., nanowires of single atom thickness show significantly different behavior than those having larger diameter. The experimental techniques to measure the conductance in atomic sized metallic contacts have been explained in brief in Sec. 1.3.2.2 and Fig. 1.10, which involve usually mechanical driven breaking and making cycles between two metal electrodes. A typical example of the conductance curve measured on a gold sample at room temperature is shown in Fig. 1.12. The curves shown in the figure are recorded while breaking the contact and we recognize the series of plateaus in the conductance, which are approximately horizontal for lowest value of conductance. However for larger contact size, the curve is no more horizontal and have negative slope. In addition, at the end of the
plateau, a sharp jump is observed, for which conductance usually varies by an amount of order of the quantum unit of $G_0$. Although the coincidence of the plateaus with the multiples of $G_0$ is not perfect and for some cases it is nearly absent, a marked exception is the position of the last conductance plateau just before the contact is lost. For gold metal, this plateau is reproduced consistently very near to $1G_0$. This property is generally observed for monovalent metals such as Cu, Ag and Au and alkali metals like Li, Na and K.[1] This plateau is however, less regularly spaced for sp and sd- metals and also the last plateau before tunneling is a factor of two or more away from $1G_0$. Similar anomalous slopes are also observed for other metals. For gold, being a monovalent metal, is highly tensile and ductile noble metal, is comparatively easy for conducting the experiments at atomic scale and hence large variety of experimental results are also available. Surprisingly, gold seems to be favorable candidate for wire/chain formation while, Ag or Cu do not have this property to that extent. Smit et al.,[121] and Bahn et al.[122] demonstrated that, gold is distinct from other noble metals in another surface property: Clean gold surfaces reconstruct in remarkable ways. The (110) surface shows a missing row reconstruction, where every second row along the [001] direction is removed. The (001) surface has a herringbone reconstruction that is slightly more density packed than that of the bulk. It turns out that three of 5d elements viz., Ir, Pt and Au have similar surface reconstructions, which are absent in the related 4d elements like, Rh, Pd and Ag, suggesting that the explanation for the reconstructions cannot lie in any particular detail of the $d$ band electronic structure. There appears to be a growing consensus that it can be explained using a stronger bonding of low-coordination atoms of 5d metals with respect to 4d metals as a result of relativistic effects in the electronic structure.[123, 124] Hence as a metal atomic conductor, we choose gold as the first elemental composition in one dimensional nanowires for characterization in this thesis.

The interpretation of sharp steps that are observed in the conductance (Sec. 1.4.6) has very important significance. Early investigations[125, 126] have pointed out that, the dynamics of the conductance of point contact around the steps strongly favors an interpretation in terms of atomic arrangement, which is due to step-wise variation of contact diameter during elongation. This has been investigated by certain experiments.
and classical molecular dynamics simulations to visualize the atomic rearrangement. The conductance curve for gold contacts shows that, the steps are distinctly steep and slopes are not easy to resolve on the time scale of 1 ms. It implies that, the jumps in the conductance are very fast. In addition, the conductance traces are different in each measurement, since it is difficult to have control over the structural rearrangement of the atoms in the breaking region. However, at the low temperature, the series of the structures that evolve during elongation can be obtained when the contact is made again over limited range. All these observations clearly do not show any coincidence of smoothly varying contact radius of nanowire and step resulting directly from the quantization of conductance. An interpretation, rather is formed by model investigations that describe the contact of the nanowire have a stable atomic geometry over a plateau in the conductance, where the total energy finds itself in a local minimum. During the jumps in the conductance, the local energy in the conductance for a new structure drops below that of the present state as a result of the stress applied to the contact.

From the above discussion, it is clear that, the nanowire contacts fabricated by experimental methods show a wide variety of behavior, where the atomic structure plays a significant role. The methods used, with a few exceptions do not permit detailed understanding over atomic scale behavior of the one dimensional structure. Hence it is very important to investigate the possible quantization effects in the conductance. It is very difficult to separate the step-wise conductance behavior as a function of contact size resulting from atomic structure and the step-wise pattern due to quantization of the conductance. However, researchers performed experiments in order to get the atomic structure in the quantum conductance of gold nanowires.
1.5 Motivation for the thesis work

![Figure 1.14](image)

Figure 1.14 – Top and side view for (a) parallelopiped (b) planer zigzag with 3 rows, (c) planer zigzag with 2 rows and (d) planer zigzag with 1 row. The circle size shows the height difference from the horizontal plane. (Ref.: Kurui et al., Phys Rev. B 77, 161403(R), (2008). [104]).

For instance, Rodrigues et al. have demonstrated that, just before rupture, the contacts adopt only three possible atomic configuration, whose occurrence probability can be estimated.[103] Kurui et al. have investigated the relationship between the structure and conductance quantization in gold nanowires. They observed that, during thinning, quadruple, triple, double strands and a single strand are formed successively. These wires have atomic configuration of (111) or (100) atomic sheets.[106] Figure 1.13(a) shows the conductance histogram reproducing the peaks and relative heights of peak as discussed in previous section. Figure 1.13(b) shows the conductance curve during the thinning of (110) nanowire. The labels A-D, which represent flat plateaus, appear in the vicinity of 4, 3, 2 and 1 $G_0$. Among all these structures, the ultimate thin nanowire i.e. linear nanowire was investigated for its stability in finite as well as infinite length form.[113, 130–132] Theoretically, first systematic investigation for relative stability of linear nanowire with two row nanowire was performed by Sánchez-Portal et al.[131, 133] They demonstrated that zigzag shaped nanowire was more stable over linear shaped nanowire.

More recently, Tavazza et al. have performed relatively more detailed theoretical investigation of gold nanowires under tensile stress and strain.[134] They observed that, gold nanowires elongate to form single atom chains just before fracture via series of intermediate structural transformations. However, they investigated seven structures as a starting point and investigated evolution of these into a single atom chain under tensile strain. It is an interesting observation that, 2-D structures were energetically more stable over 3-D structures. However, the study was limited only to the stability of...
structures under stress and strain. This fact formed the basis of motivation to this work in order to study the electronic origin of the quantum conductance of wires different than linear chain.

Most of the experimental and theoretical investigations so far are limited largely to structural stability and the measurement of the conductance in gold nanowires pulled from atomic tips.\[103, 105, 108, 110, 113, 135, 136\] In addition, most of the investigations are related to single or double rows of gold nanowires. The short chains with 4–5 atoms as well as single and double row have limited applications in comparison with somewhat longer atomic chains. Structural stability of longer nanowires under device operating conditions and with respect to the likely atomic processes happening at these temperatures, however will play an important role in the integration of nanowires in many technologies.

Hence in the present thesis, we investigate the stability of infinitely long gold nanowires and concomitant quantized conductance in the wires from a detailed theoretical perspective. The work in the thesis consists of the stability of 2-D ribbon-like gold nanowires of different shapes with the increasing number of atomic rows. The electronic structure has been analyzed to understand the correlation between the structure, stability and quantized form of the conductance in these nanowires. The investigations based on the electronic structure show that, the atomic structure plays a crucial role in determining the stability and conductivity of the nanowires. Gold being rich in valence d electrons, also involve contribution from p electron. The work on atomic nanowires of gold is limited to measuring the conductance. However, the electronic origin of the conductance has not been investigated in detail. Hence initial part of this thesis, we address our work on pure gold nanowires. The electronic structure calculations were performed to find out the relationship between the atomic configuration, stability and the conductance.

1.5.1 Magnetic phenomenon in 1-D nanostructures

We discussed in previous sub-section that, electron transport in metallic nanowires has attracted much attention. The investigations show that, in metal nanowires, the conductance decreases step-wise following atomic rearrangement. For noble metals, such as Cu, Au, Ag and alkali metals like, Li, Na and K, the last conductance step before breaking takes value very close to \(G_0 = 2e^2/h\), which corresponds to propagation of one conduction electron, per spin. Recently, there have been experimental investigations of ballistic transport in atomic sized contacts of ferromagnetic metals, using STM,[54, 137] break junctions[138] or contact between microscopic nanowires.[139, 140] The transition metal contacts (e.g., Ni, Co and Fe) exhibit partially occupied d shell, and also display conductance steps.[97, 141] Some experimental results for Ni[138, 139] and Fe[142] nanocontacts show well defined peak near \(1G_0\), whereas some other show a fractional peak at \(0.5G_0\) in Ni[138] and Co.[143] In comparison with the noble metals, the transport properties in ferromagnetic metals are less understood, due to incorporation of the spin phenomenon. Hence, from basic understanding point of view, it is essential to investigate the spin dependent transport in ferromagnetic nanowires. The transport properties of ferromagnetic nanowires open a new opportunities to get deeper understanding of spin dynamics or spin control in nanostructures and can have important implications for the development of spintronics devices in future. Although the atomic sized nanowires are little difficult to implement in devices, the study of atomic structure of such nanowires provide a good insight for designing and
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In order to use the magnetic nanowires in spintronic devices, it is essential to have knowledge of magnetic properties in addition to that of the transport properties. For example, the applications of magnetic materials are mostly determined by the softness or hardness of the magnet. The soft magnets are used for flux guidance in permanent magnets and in transformer cores for high frequency and microwave applications.[144, 145] In hard magnets, knowledge of the easy direction of magnetization and magnetic anisotropy energy is necessary for high density recording devices such as memories and magnetic tapes in audio-visual technology.[144, 145] The magnetic properties of materials in the nanoscale region are quite interesting as they show enhanced magnetic moments due to reduced coordination, and exhibit magnetic anisotropy due to symmetry breaking. In the present thesis, we investigate nickel as a magnetic material for nanowire characterization, because of its magnetic properties and potential applicability in material science. The magnetic properties of Ni has been investigated in detail for bulk,[146–151] surfaces[152–158] and layers.[154, 159–163] Experimentally, it was first noticed that ferromagnetic Ni shows a magnetic transition to paramagnetic state when the number of atomic layers in the Ni slabs are reduced below 2 or 3.[164] The calculation of Ni (111) monolayer on Cu substrate by Pourovskii et al.[165] confirmed the experimentally observed paramagnetic behavior. This dependence of the magnetic behavior on the thickness of the surface under investigation raises an interesting question. If the material is reduced further, from a 2D monolayer to two dimensional nanostrips/nanoribbons, what would happen to its magnetic behavior? In the present thesis, the fundamental understanding of the magnetic behavior of Ni at reduced dimensions is discussed.

Single atom linear chains and zigzag nanowires of Ni have been studied earlier for their stability.[144, 166–173] The investigations by Tung et al., on the magnetic properties of all 3d transition elements have found that in Ni the linear and zigzag wires are ferromagnetic. In a recent work, Zelený et al.,[166] have investigated systematically the variation in structural and magnetic properties of one dimensional nanowires, two dimensional strips and three dimensional rods, under compression. The compressed two dimensional (2D) Ni nanowires have a ferromagnetic ground state, because of magnetic shape anisotropy[144, 166]. This result contradicts the work of Mermin-Wagner[174], which showed that, one and two dimensional structures cannot exhibit ferromagnetic or antiferromagnetic behavior, under the isotropic Heisenberg model; nevertheless, Gambardella et al.[175] have recently revealed magnetic ordering in chains of Co atoms deposited on Pt and spin blocks consisting of 15 atoms at 45 K were reported. Certainly, Pt substrate must play a non-negligible role, but this result indicates that, ferromagnetism can be expected in the short freely suspended chains. Clearly, the magnetic anisotropy plays a crucial role which needs to be understood and investigated for a fundamental understanding of the magnetic behavior and its dependence on the structure. This kind of an investigation is not available either theoretically or experimentally for 2D nanostrips.

The electronic properties of magnetic linear nanowires like Ni, Co, Fe have been investigated in detail previously.[176–181] In the case of nickel, zigzag shaped nanowire has been studied by Zelený et al.[166] and Tung et al.[144] Most of the calculations in literature on Ni nanowires are restricted to single and double row structures, which do not give a complete qualitative understanding of the effect of the increasing width of nanowires on their magnetic properties. Such unsupported, free standing nanowires form an important bridge between one dimensional chains and monolayered atomic
films. Hence in this thesis, the magnetic and electronic properties of nickel nanowires are investigated as their structure varies from a linear chain to two dimensional nanostrips of increasing widths. Besides their stability, the effect of the geometrical structure on their magnetic properties have also been investigated. The present calculations demonstrate the existence of a so far unreported transition from the ferromagnetic state to the paramagnetic state for (111) oriented nanowires under the Stoner criterion. In the case of (100) oriented nanostrips, such a transition is not observed. Our calculations demonstrate that, magnetic anisotropy has a crucial role in affecting the magnetic behavior of these different structures.

1.5.2 Effect of alloying

Motivated by the fact that, the heat of formation of the alloy clusters can be larger than that of the bulk alloy, due to charge transfer induced electrostatic interaction between different elements in the alloy,[186] we turn to modulate the charge transfer in gold alloy nanowires. An interesting geometry to consider is noble metal (5d) nanowire with a transition magnetic metal (3d) for alloying. Due to reduced coordination, the 3d element will develop a magnetic moment. This will induce a magnetic moment on noble metal atoms, which can change the electronic and magnetic properties of the nanowires. Such bimetallic nanowires that are compositionally modulated along the axis of the nanowire can be useful for nanowire based devices including diodes,[187] spin valves,[188] and optical tables.[189] The large magnetic anisotropy and high remnant magnetization arising from reduced dimension makes the suspended bimetallic nanowires highly orientable. These nanowires can be easily manipulated by small external fields, enabling control of the nanowire dipolar forces to obtain ordered structures.[190] Experimentally, Wanekaya et al. have assembled segmented Ni/Au/Ni arrays of nanowires and investigated the effect of magnetic field on the directionality of nanowires.[191] Miura et al., have investigated theoretically, the effect of magnetic Ni impurity on monatomic gold nanowire.[192] However, to the best of our knowledge, there are no theoretical studies on the structural, magnetic and electronic properties of Au/Ni nanowires with respect to their elemental composition. In the present thesis, the physical properties of Au/Ni bimetallic nanowires have been discussed based on ab initio calculations.

1.5.3 Non-collinear magnetism

In addition to Au/Ni bimetallic nanowires, we have also investigated other bimetallic nanowires which consist of non-magnetic 5d element along with magnetic 3d element, viz., 3d – 5d (with 3d ≡ Fe, Ir; 5d ≡ Ir, Au, Pt) for investigation of their magnetic properties. The 5d atom having high atomic number exhibits strong spin orbit coupling, which play an important role in particular magnetic phenomenon such as spin spiral ground state. Such materials, which exhibit spin spiral state are of great interest, due to their potential applications in magnetism based technologies.[193–195] For example, non collinear magnetic structures could play a significant role in future memory and spin electronics devices.[196] The occurrence of spin spiral ground state can only be explained by considering the Dzyaloshinskii-Moriya interaction (DMI).[197, 198] It arises due to electron propagation in inversion asymmetric environment. The DMI favors spiraling magnetic structure of unique rotational sense, in contrast to other interactions like the Heisenberg exchange\(^{10}\) or the magnetocrystalline anisotropy en-

\(^{10}\)Heisenberg exchange usually prefer the collinear magnetic structure or spirals without being sensitive to the rotational direction.
ergy. The competition between the magneto-crystalline anisotropy energy and DMI lead to a variety of possible magnetic ground states due to frustration.

There is lot of experimental evidence for systems showing spin spiral ground states in various types of systems, e.g., in semiconductors, in ferromagnetic bulk systems, or oxides. In addition to the experimental observations, theoretical and numerical calculations confirm the importance of spin spirals in one dimensional systems. Recently, the magnetic properties of various bimetallic 3d–5d nanowires of linear and zigzag shape have been investigated. However, the effect of DMI on such nanowires has not been studied so far, although it is expected to be present in the system. In the present thesis, the effect of DMI on the magnetic properties in 3d–5d nanowires is discussed in detail. Due to need of an inversion symmetry broken environment for non-vanishing DMI, we concentrate on zigzag chains only, and choose a combination of strong magnetic 3d element (Fe or Co), and heavy non-magnetic 5d element (Ir, Pt or Au) as a source of strong DMI.

1.6 Plan of the thesis

The thesis is organized as follows:

Chapter 2 discusses the essential theoretical background required for first principle calculations. This includes the density functional theory formalism to calculate the ground state energy eigenvalue using many body wave function. The thesis reveals the involvement of spin phenomenon in the density functional theory. The relativistic corrections are demonstrated within the Kohn-Sham formalism. For practical calculations, supercell approximations like Fourier representation, Bloch theorem, k-point sampling and pseudopotential approximations are discussed in brief for plane wave approach. Full potential plane wave is also introduced for non-collinear magnetic calculations. The chapter considers the transport phenomenon for ballistic conductors within Landauer-Büttiker’s method. The chapter is concluded by computational parameters used in the thesis for nanowire calculations.

Chapter 3 discusses our results on the geometrical structure of pure gold, pure nickel nanowires of increasing width and wires of Au/Ni alloy for one and two row rows of atoms. The stability of pure and bimetallic nanowires is discussed based on their binding energy calculations. The stability of the systems is explained based on the electronic band structure.

Chapter 4 reports our work on the transport properties of pure gold and nickel nanowires. Nickel being a magnetic system, the magnetic properties of nickel nanowires are discussed in detail as a function of number of rows in the system, viz., magnetic moment, magnetic anisotropy energy, magnetization dependent conductance. The magnetic ordering transition in nickel nanowire as a function of width of the nanowire is discussed based on Stoner’s criterion. The chapter also includes the general magnetic properties of Au/Ni nanowires as a function of their elemental composition.

Chapter 5 is based on the non-collinear magnetic properties in zigzag shaped 3d–5d nanowire alloys. The chapter begins with the structural parameters for the 3d–5d nanowires and their magnetic moments. The isotropic exchange in the ab-
sence of spin orbit interaction is investigated for all nanowires. The effect of spin orbit interaction on the magnetism in these systems is also discussed. The magnetic ground state of the system is determined based on the competition between the magnetocrystalline anisotropy energy and Dzyaloshinskii-Moriya interaction energy. The thesis also discusses about the minimal tight binding model of DMI in the zigzag trimer to understand the effect of hybridization on strength and sign of the DMI, which are observed analogous to the first principle results of the infinite length $3d \rightarrow 5d$ chains.

Chapter 6 concludes the important findings discussed in the thesis. The possible implications, applications of the finding are addressed in brief. The chapter is closed by future implications, as well as the possible extensions to this work.