Chapter 1

Introduction: An overview of nanostructures and Atomic chains

This chapter presents a short review on the important aspects of nanoscale structures and atomic chains. The purpose of this chapter is to provide the background to the atomic chains that have been investigated by us.

1.1 History, Present status and Futuristic applications

The current booming technological advancement touching almost all aspect of life has stemmed from the ability to manipulate matter in the atomic scale. In last three decades the continuing miniaturization of microelectronics have raised prospects of nano science and nano technology in multifolds. However, the onset of miniaturisation dates way back to 1960s when Richard Feynman in his famous lecture said, "There is plenty of room at the bottom". In an influential book, "Engines of creation" published in 1986, author Eric Drexler envisioned that if molecules and devices are manufactured by joining individual atoms under computer control, it will be possible to build structures stronger than steel, build computers smaller than a bacterium, and build assembler and mini factories of various size capable of making complex products and even duplicating themselves. The last four decades of 20th century witnessed a kind of technological revolution in electronic industry with the development of sophisticated experimental techniques and accurate theoretical models to understand, predict and manipulate the materials at reduced dimensions.

To get an idea of how the electronic industry is progressing and the future prospects we often refer International Roadmap for Devices and Systems (www.irds.com). A quick review of the progress in field of microchips is interesting.

In 1981 single chip processors produced by Hewlett-Packard contained approximately half million devices in its 1cm^2 area. This chip which had transistors having a nominal 1.25 mm gate length was considered a remarkable step forward in the race towards miniaturization. The semiconductor industry saw huge leaps in shirking of the gate size in integrated circuits and reached to truly a nano scale technology by 2007 when the printed gate length of production micro processor transistors was 45 nm. Currently, the down scaling of commercial integrated circuits has reached to 5nm gate length and have been envisioned to further reduce to 3nm gate length in next couple of years by International Roadmap for Devices and Systems. Such miniaturization is possible only with efficient and multifunctional small-scale devices and interconnects. For manufacturing such small-scale multifunctional device, the smart choice of nano structures is inevitable. The reduced dimensionality of nano structures offers a wide range of properties which are sensitively dependent on geometry and size. Alloy nano structures goes one step further in the prospects of tailoring desired properties by adding the composition dependence of the properties. However, it is extremely challenging to manufacture and have precise control over the operation of such small-scale electronic circuits.

1.2 One dimensional structures

This section briefs about definition and concepts related to one dimensional (1D) structures. Confinement in at least one dimension up to 100nm is generally considered as nano structures. As per number of confined dimensions, nano structures are classified into Two dimensional structures (Nano films), one dimensional (Nano rod, atomic chains, nano ribbons) and Zero dimensional (0D) (atomic clusters, Quantum dots) structures.

A typical example of 1D structure is atomic chain in which a series of atoms are sequentially bonded together. Study of 1D structures has two main prospects. First their usage as contacts in molecular electronics and second as an excellent theoretical test ground for 1D physics. One of the aims of such theoretical test ground is to check whether the models of truly 1D-physics is applicable to these structures or a picture of quasi-1D structure is more correct. Quasi-1D picture renders the interaction of atoms in one direction much higher than other two directions. We may imagine a 1D world where electrons are free to move in one dimension, however our world is three dimensional and even forming a chain of atoms is not going to be truly 1D as the atoms are three dimensional and the electrons will be moving in three-dimensional space. Thus, these structures are referred as quasi-1D.

A typical 1D structure is spatially confined perpendicular to the system axis which induces pronounced discretization of electronic states.[1,2] In some cases the enhanced electron-phonon coupling in 1D structures forms new zone boundaries in reciprocal space which results in static rearrangements of the atom positions (Peierls distortion). [3]Also, low dimensional electronic systems possess anomalously long interaction lengths owing to the reduced screening efficiency. [4]

A strong interaction between electrons in 1D structures leads to departure from normal metallic (Fermi liquid) behaviour and follows concepts introduced by Tomonaga-Luttinger and Wigner[5]. Other effects that come into play for 1D-structures are coulomb repulsion, Coulomb blockade, Kondo effect, interactions with vibrational degrees of freedom and Quantum Decoherence.

Study of atomic chains is an interesting topic for number of reasons. They are at the boundary between the Physics of itinerant electrons in bulk and localised electrons in molecules. Being at this boundary makes them a fruitful playground for testing the validity and limitations of model's characteristic of both branches.

One of the striking characteristics of 1D Physics is appearance of magnetism in many of the atomic chains despite the less number of neighbouring atoms compared to bulk. The reason is, since the electrons in atoms of 1D structures are confined in two dimensions their dynamics are restricted to one dimension. This restriction compensate the reduced hopping due to less neighbouring atoms and favours exchange.[6] As a result magnetization is observed even in atomic chains of sp-metals which are non-magnetic in bulk - for example, Al.[7]

The interest in 1D systems is not only of scientific origin but also of technological implications, specifically the unbroken trend in miniaturization of electronic devices. Nanowires can be utilized with more efficiency in gas sensors and heterogeneous catalysis as they have large surface-to-volume ratio.[8,9]

Although existence of such atomic chains is mostly transient in nature, this has been observed in number of experiments for short duration of time.[10–12] The methods that involve preparation of 1D systems on extended surface area are the most popular.

There are several approaches that have been implemented over the years for manufacturing 1D structures on a surface. In one approach vicinal surfaces are used for metal depositions which leads to decoration of step edges and formation of nanowires.[9,13,14] Figure 1.1 shows one such example.

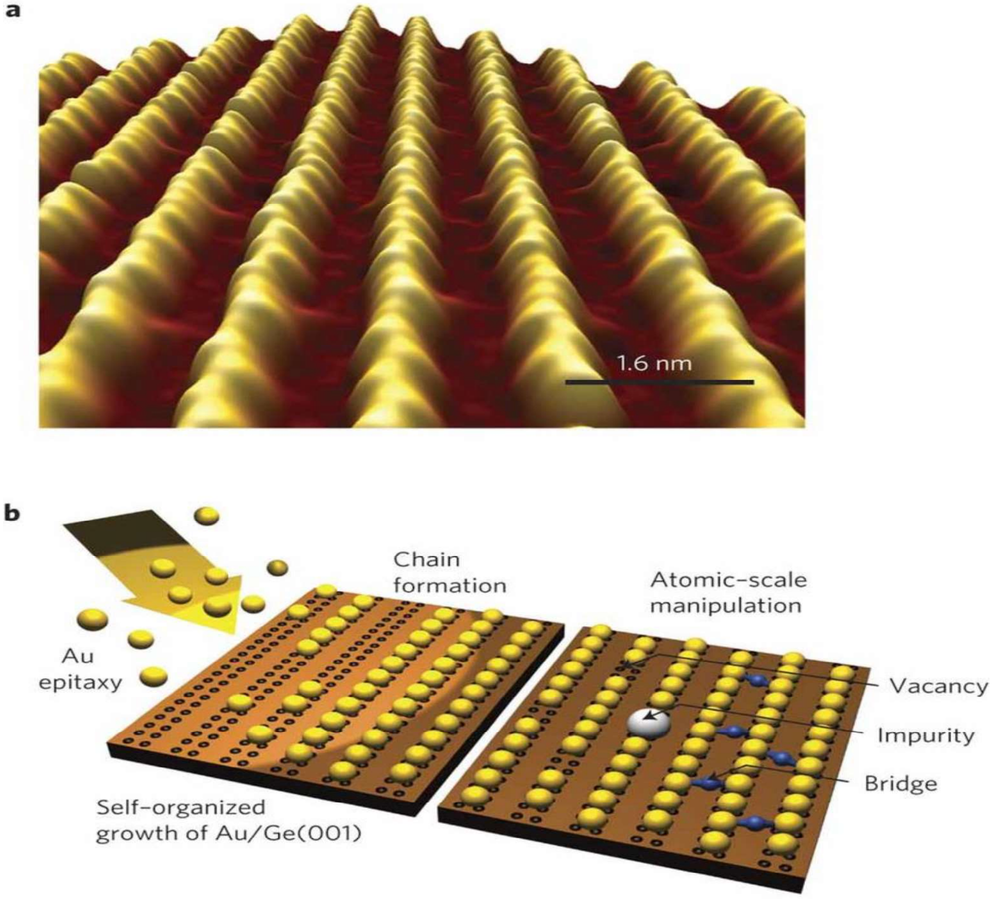

Figure 1.1: Atomic arrangement of self-organized gold chains on Ge (001). (a) Topography from STM, showing parallel alignment of Au-induced chains, spaced by 1.6 nm (bias −1.0 V, 0.4 nA). The elevated chain architecture exposes a single-atom ridge, including a small buckling, which hosts the 1D electron liquid under study. (b) Schematic representation of chain formation and atomic modification possibilities. Epitaxy of Au leads to self-organized chain formation at elevated temperatures.[37]

In another approach a well-defined geometry of template surface is used for adsorption of metal atoms resulting in directional growth of atomic chains.[15] For some substrate-adsorbate systems, a self-assembly of 1D structures have been observed driven by the minimization of surface energy and stress relief.[16–19] However these methods have some serious limitations. They are not devoid of statistical disorder, defects, and imperfections. Also, these methods do not allow control over the exact length of the wires, atomic position and type of atoms in the structure. To overcome these limitations, Scanning Tunnelling Microscope (STM) are used. STM allows assembly of linear aggregates with atomic precision.[20–22] In addition to imaging, the spectroscopic modes of STM can be used to investigate structures on the atomic scale.[23]

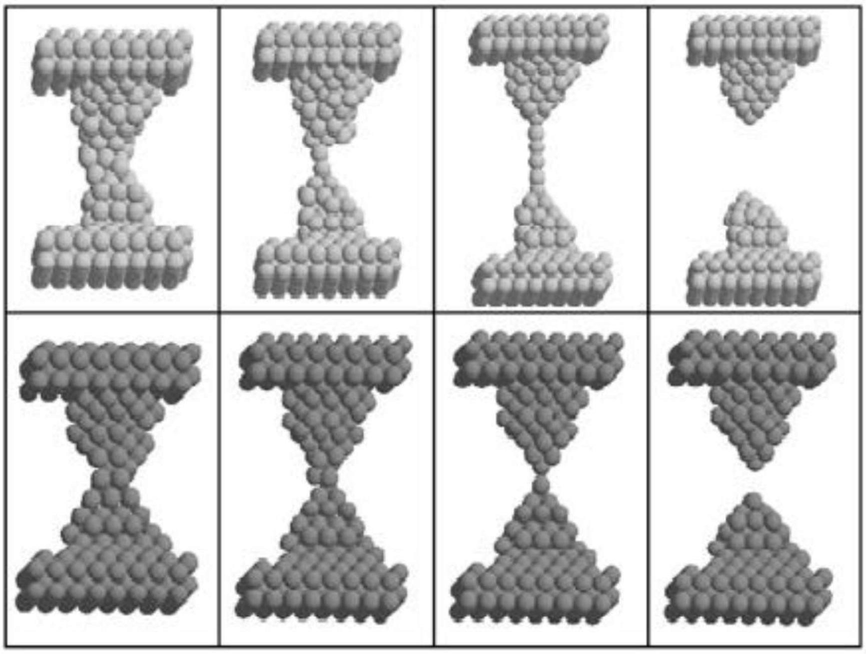

Figure 1.2: Snapshots from simulations of breaking gold (upper row) and copper contacts (lower row). The gold contact exhibits the formation of a single-atomic chain, while the copper contact breaks after a single-atom contact is formed. Out of the six metals studied (Cu, Ag, Au, Ni, Pd, and Pt) only Au and Pt form chains.[32]

In general, the atomic chains can be classified into two main groups based on the methods of preparation. One group consists of Atomic chains realised either by depositing metal atoms on any surface, mainly, semiconducting chains or transition metal atoms chain deposited on variety of surfaces or atomic chains grown in interior of nano tubes.[12,24–26] Another group is comprised of atomic chains produced by narrowing a junction between two metal tips. The narrowing junction between two metal tips is termed as Quantum Point contact which is made up of a few atoms thick bridge between two metal electrodes. Such Quantum Point contact can be made either by contacting a metal tip with STM tip or by 'breaking' of a metallic contact. Figure 1.2 exhibits an example of chain formation from a contact breaking experiment.[32] In either way, the contact area undergoes series of retractions and structural rearrangements until it consists in its final stage only a few bridging atoms. However, Atomic chains made by these methods are short in contrast to theoretical modelling of extended chains.

The experiments intended to find formation probability and structure of 1D atomic chains involve study of conductance histograms. The conductance histograms show decrease in conductance in series of sharp vertically descending steps with a gradual slope on the plateaux in between. It is shown that these steps are result of atomic rearrangements.[27,28] It was argued that the remarkable length of the last conductance plateau just before rupture of point contact corresponds to a contact with a single atom at the narrowest cross-section.

The connection between long stretched plateau and one atom thick point contact became clear when it was confirmed that the conductance of a point contact is determined predominately by the size of its narrowest cross-section during contact elongation and all structural transformations are localized to this narrow neck region.[28–30]

During retraction or elongation of Quantum Point contact an abrupt transition to ballistic conduction occurs. At this time the conductance histograms show quantised conductance close to value of $2e^2/h$, where e is the charge on an electron and h is Planck's constant. The occurrence of one quantum unit of conductance marks formation of a 1D structure. When the radius of an electrical contact or constriction between two metals is small compared to the mean free path of the electrons, the electrons are accelerated due to the electric field caused by the applied voltage and are injected from one metal side to the other by passing through the contact. The transport of electrons is then said to be ballistic.

Quantization effects in conductance in point contact is observed as the tip is pressed against the sample. Such quantum size effects are observed due to quantization of transverse momentum in the constriction having diameter of the order of the Fermi wavelength.

Realisation of atomic chains through point contact is associated with the Experimental techniques such as Mechanically Controlled Break Junctions (MCBJ) combined with STM and AFM. Most of the pioneering work on 1D chains was carried out utilizing the breaking of point contact. Although extremely relevant as a pioneering technique, point contact breaking does not offer a definitive solution to the atomic chain fabrication problem. The fine control of the geometry and composition of the chains is not feasible in the point breaking experiments as it involves lot of structural rearrangements at the site of breaking.[18,31–33] An alternative approach is to assemble long and stable atomic chains on a supporting substrate, such as a semiconductor or metal surface. The supporting substrate works as a template for assembling of atomic chains. Along these lines the pioneering work was carried out by Ho and co-workers. It was demonstrated that it is possible to assemble long gold chains, depositing Au atoms onto a metallic NiAl(110) surface with a STM tip.[25,34,35]

The final chain obtained by such procedure is highly ordered and stable against atomic relaxation and shows true metallic electronic properties in 1D. One more advantage of the chains realised on substrate is the ease of adsorption of individual atoms such as CO to fine-tune their electronic characteristics.[34]

In the following two sections brief idea about two main experimental methods of preparing 1D chains are discussed along with some key results.

1.3 Experimental Methodologies for atomic chains

1.3.1 Scanning Tunnelling Microscope

Study of small-scale structures was stimulated by the development of STM by Binnig and Heinrich Rohrer, for which they were awarded the Nobel prize in 1986. Inspired by STM, many related scanning probes were further developed which measure a great variety of properties with atomic resolution.[36]

In addition to scanning surfaces, STM has the ability to vary the contact area in controlled manner in increments as small as atomic size. This has been very effectively exploited to study extensively different conductance regimes and transitions among them, for example, ballistic to contact regime. Such studies have opened avenues to study molecular junctions and 1D structures.

In a typical STM experiment, the tip is driven to a metal substrate and simultaneously conductance is measured during subsequent retractions. During this very slow retraction the contact area undergoes structural rearrangements until it consists in its final stage only few bridging atoms.

1.3.2 Mechanically Controlled Break Junction

In these experiments two electrodes are displaced by small fraction of atomic distances until the elongation or retraction makes the width of the contact to single atom before breaking. In the study of Molecular electronics, a molecule or single atom is then inserted between the atomic size gap of two electrodes. As compared to STM, MCBJ technique is orders of magnitude less susceptible to vibrations than the STM and it offers a continuously tuneable gap size between two tip-shaped electrodes.

Also, MCBJ techniques can be easily combined with other techniques, such as Raman Spectroscopy, inelastic electron tunnelling spectroscopy and noise spectroscopy. However, there are some limitations and challenges to this technique. For example, the chips use polyamides as an isolating layer, which always suffer from a varied gap size due to its variable deformation at different temperatures. Also, MCBJs are incapable to measure the force and surface morphology. Such limitations restrict the utility of MCBJ techniques.

The nanowires are suggested to have important applications as interconnects in fabrication of next generation lightweight display, mobile computing and information storage applications.[37]

1.4 A brief account of work done on Atomic chains

In the pioneering work of atomic chain, 1998 Ohnishi and Kondo[38] first observed strands of gold atoms suspended between the tip of STM and metal surface. The one atom thick strand was about one nanometre long and showed quantised conductance in the unit of $2e^2/h$. It was observed that the conductance of a single strand of atoms is $2e^2/h$ and that of double strand is twice as large, verifying that law of equipartition holds for such quantum systems. In the same report the structure of bridge atoms arrayed in a linear strand has also been studied for (001) and (110) films. It was observed that for the (001) film, a nano bridge of 10nm long and four atoms thick in diameter was formed in [110] direction. When (110) film was used the single strand of atoms was continuously observed for two or more minutes.

Yanson et al[10] in their study observed breaking of contact resulting in one atom thick and four atoms long atomic chain. The conductance of these chains never exceeds $2e^2/h$

even after pulling them. These chains possessed high stability and ability to support Ballistic transport. Some of the chains were found to be stable for duration as long as an hour. Large current density up to $8x10^{14}$ Am-2 proved that the transport is truly ballistic, and they were considered to be suitable for investigations of atomic-scale electronics.

Rodrigues et al[39] in their studies tried to correlate gold NW structure and quantised conductance behaviour using High-Resolution Transmission Electron Microscopy HRTEM. It was observed that just before rupture gold nanowires are crystalline and display only three possible atomic configurations where elongation direction is roughly parallel to either [100], [110], or [111] crystalline direction. Their experiment has shown predominance [110] rod like configuration.

The theoretical study using molecular dynamics simulation of breaking of contact of metals like Au, Pt, Pd, Ag, Ni and Cu by Bahn et al[32] revealed that Pd, Ag, Ni and Cu contact breaks without chain formation and the tendency of chain formation is strongest for Au and Pt.

The reason for the stronger tendency of chain formation in these two metals is claimed to be due to the stronger bond in low coordinated system compared to bulk bonds. This is a typical character of metallic bond in which bond strength increases as the coordination number reduces. Further the theoretical simulation of chain formation showed that chain formation can occur if the bonds in the chain are much stronger than the bonds in the bulk so that it is harder to break the chain than to pull out an atom of the shoulders at the contact region.

Also, bond strength depends on how difficult it is to break bonds in the chain relative to other bonds in region close to the chain.

Out of all the metals considered for possibility of chain formation in various studies, Au and Pt show strong variation of bond strength with coordination number.[40,41] Compared to noble metals, transition metals show less clear evidence of quantised conductance in conductance histograms. Early experiments on Pd, Pt, Rh and Ru showed that none of these metals exhibited clear nG_0 peaks in their histograms. Meaning that chain formation is not possible in these metals[42]. It was suggested that the absence of peaks in conductance histograms of Pd is due to its d state valence electrons the conductance channel of which do not exhibit clear quantization.[43,44] However atomic contacts from practically all 3d-,4d- and 5d-metals at room temperature has been observed by means of TEM. For example, nanocontacts have been formed from Co[45], Cu[46], Pd[45], Ag[47], Pt[45,48] and Au.[49,50] In another first principle study the structure and stability of gold was investigated in which gold monatomic wires were found to exhibit a zigzag shape under tension becoming linear just before breaking[31]. The theoretical studies of 1D structures are carried out mostly using classical atomistic models, as well as the first principles.[31,51–55]

In a most recent report a group of scientist have demonstrated novel method to simultaneously image monatomic platinum chains with a transmission electron microscope while measuring their bond strength and conductance during mechanical stretching.[56]

Since ancient times alloying has been found a route to enhance, change and modulate properties of material. By changing elemental composition and alloying condition the specific properties of alloy can be adjusted over a wide range. With no difference to nano structures, alloying provides large possibility to tune specific property and enhance stability. For example, stability of nanocontacts can be increased by alloying of several elements with Au.[57,58] The change in elemental composition of alloy nano particles affects significantly to the optical properties. For example, the change of Au and Ag mass ratio in Au-Ag nano particle results in a shift of optical absorption band.[59]

For the case of alloyed nano structures, in addition of reduced dimension, alloying adds an extra degree of freedom to have different properties. However in the realm of atomic chains alloying was not much explored until the very first experimental realisation of Au-Ag atomic chains in break junction experiment.[49] The initial work on alloy nano contacts were reported by Akihiro et al.[57] They measured the quantized conductance in Au-Pd and Au-Ag alloy nano contact for a wide range of Pd and Ag concentration to study effect of alloying on the quantised conductance in Au nanocontacts. It is found that $1G_o$ conductance peak corresponding to one atom thick chains appears for whole range of Ag concentration. In Au-Pd the $1G_o$ peak survive at least in Au rich nanocontacts. It was speculated that in case of Au-Pd, Pd atoms might be acting as a blocking element of the *sp* conductance channel of Au because of their small *sp* valency. Thus, conductance peak is observed only if the link between the contact is Au rich. While in case of Au-Ag alloy nano contact, the 1*G₀* peak height can be well described as a liner average of those of pure Au and Ag.

An experimental study of alloying Au nano contact with four different metals namely Pd, Pt, Cu and Ag clarified effects of alloying on the formation probability of the $1G_0$ contact and the average plateau length of the $1G_0$ peak.[57] They termed the probability of appearance of $1G_0$ peak and the chain formation as *p*. It was concluded that alloying appreciably affects the probability of appearance of $1G_0$ peak but the effect of alloying on average plateau length was negligible. This means that the contact of Au alloy consists mostly of Au atom and other metal atoms hardly participate into the conduction. It was also found that alloying Au with Pd and Pt atoms gives rise to rapid suppression of probability of chain formation with increasing the bias. While Ag and Cu yields weak bias dependence of *p* which is not much different than that of pure Au contacts. It has been found that Au-Ag nanocontact are more stable than pure Au and Ag nanocontacts.[58] In addition to enhanced stability, presence of Ag atoms in Au-Ag nano contact increases the range for which the nanowire is stable. In other words, Au-Ag nanowires are stable at the distance where Au or Ag nanocontacts would break.

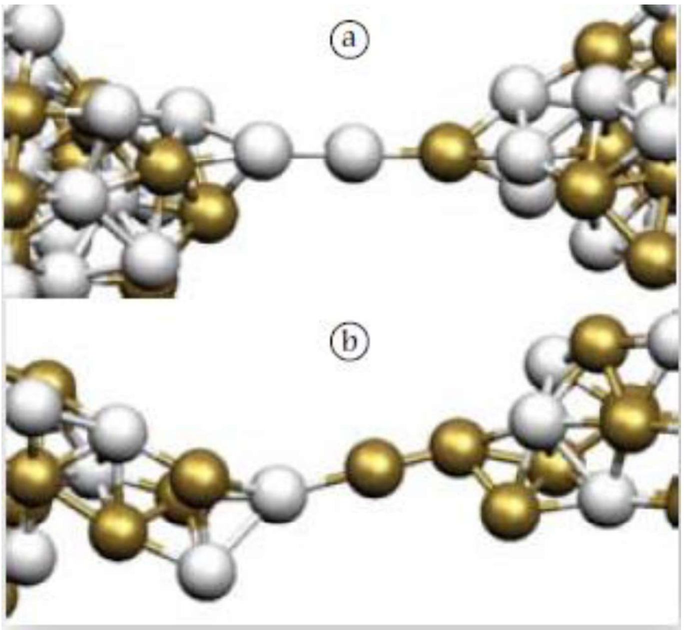

Figure 1.3: Snapshots of the molecular dynamics simulations showing the formation of mixed LACs from alloys: a) Au40Ag60; and b) Au60Ag40. Yellow (grey) indicates gold (silver) atoms.[50]

It was reported that Ag-Au[57] Au-Zn, and Au-Mg alloy monatomic wires are more stable than pure Ag, Zn and Mg ones.[60] In case of alloy nano contacts, the formation strength, stability, rupture point and electronic properties depend on the species composition, local species arrangement and stretching direction.[61–63] It was also found that interatomic distance of an atomic chain is dependent on their component compositions. Properties like giant magneto resistance, magnetism, electronic structure, and optical properties also depend on elemental composition of bimetallic chains. The molecular dynamics study on bimetallic Pd-Pt nanowires have revealed that mechanical properties of alloy nanowire is dictated by applied strain rate, alloy composition as well as structural rearrangements associated with nanowire elongation.[64]

Impurities or alloying also change conductance, electronic and magnetic properties of contacts. For example, Au nano contact is not magnetic and electronic transport through it cannot be spin polarized, however, stable quasi-1D Au-Co contact is found to have the giant magneto resistance.[65] The molecular dynamics simulation for Co-Au and Ag-Au alloy nano contact have found that the mechanical properties of alloy nanocontacts and structure before rupture depends on crystallographic orientation of elongation and concentration of components.[66] Despite so many benefits of alloying nano structures, most of the experimental and theoretical studies for 1D structures were carried out for pure metals. Nevertheless, the very first experimental realisation of alloy chains of Au and Ag motivated many studies aimed for bimetallic nano structures.[58,61,62,67–70]

Along the continuum of already done work so far on alloy chains of transition metal and noble metals, we find a gap of a systematic study dedicated to investigating effect of composition on various properties of alloy chains. As stated earlier, Au and Ag are metals which sit on two extremes of positive and negative for chain formation possibility.[40,58] On the other hand Pt is known to be making most stable 1D chains. [40,50,71] As to appearance of quantised peak in conductance histograms Au and Pd represents the most positive and most negative examples.[57] Thus an interesting issue is then to see how alloying Au with Pd, Pt and Ag will change chain formation possibility and to compare the properties of pristine and alloy chains. This thesis is aimed at a systematic study of interplay between atomic composition, structure, electronic and optical properties of bimetallic chains of Au-Pd, Au-Ag and Au-Pt. The study covers two main class of experimental techniques of chain formation namely: (1) Point contact breakings, chapter 3 and chapter 4 of this thesis are related to this method. (2) Atom by atom assembly on a substrate, chapter 5 of the thesis is related to this method.

1.5 Outline of the thesis

The thesis is organised as follows:

Chapter 2 highlights basics of Density Functional Theory (DFT) and computational tools used for carrying out calculations of the work reported in the thesis. We report composition dependent properties of bimetallic linear atomic chains of Au-Pd, Au-Ag and Au-Pt in Chapter 3. The geometry of the atomic chains is restricted to linear atomic chains. Chapter 4 broadly relates the computational results with the MBJC experiment. It reports results of the possibility of chain formation, structure, relative stability and electronic properties of bimetallic atomic chains. Unlike chapter 3, here we do not restrict the geometry of atomic chains to be to linear chains and searched for the most stable geometry and most likely composition to be observed in actual break junction experiment. The work on chain formation on a substrates is reported in chapter 5. Structure and electronic properties of Au-Pd, Au-Pt and Au-Ag bimetallic atomic chains absorbed on NiAl(110) and Cu(110) substrate are discussed in this chapter. We compare structure and electronic properties of bimetallic chains on NiAl(110) and Cu(110) substrate. Further, to study the effect of change in positions of atoms in bimetallic chains in the presence of substrate double chains of Au-Pd, Au-Pt and Au-Ag are placed on Cu(110) substrate in three different configurations. Chapter 6 presents the summary of the thesis.