Chapter 6

Summary

1D structures have attracted great interest with increasing miniaturization. There is a long list of reports on the theoretical studies of one-dimensional structures. Most of these reports are dedicated to nanowires made up of one metal. There are limited number of studies exploring alloyed nano structures. Also, most of the theoretical studies on atomic chains deal with the interplay of properties such as geometry, electronic, transport, and optical properties and very few on the possibility of chain formation relating experimental observations. Gold being the prototype of 1D structures has been the most used element for chain formation. The first ever experimental observation of 1D structure was of Au atomic chains. As gold nanowires offer highest stability, Au atomic chains are most convenient samples to study effect of alloying different transition and noble metals. Transitional metal nanowires are interesting in itself because of the varied magnetic properties and their prospective utilization in spintronic applications.

Our motive for the work presented in this thesis is to systematically study both the aspects: (i) Formation possibility. (ii) Composition dependence of different properties of bimetallic atomic chains.

The experimental methods for formation of atomic chains are broadly classified into two categories. (a) Suspended chains by using breaking of point contacts. (b) Formation of atomic chain by atom manipulation on a substrate. We have tried to cover above four aspects in our study of bimetallic chains of Au-Pd, Au-Pt and Au-Ag.

The present thesis titled "Ab-initio investigations on structure, electronic, transport and optical propertied of bimetallic nano structures such as Au-Pd, Au-Pt, Au-Ag" can be summarized as follows.

Chapter 1 deals with the introductory aspects of the subject, that is nano structures specifying the focus on one-dimensional structures. It starts from the definition of 1D structures followed by the discussion of its possible applications. A detailed review of the pioneering work on 1D structures with the emphasis on theoretical aspects of early

experiments is presented. The review section ends with briefing about the work done so far and our motive and aims of the present study.

Chapter 2 is dedicated to essential theory and computational methods. Theoretical concepts behind each computational tools incorporated in VASP. For sake of continuity and completeness this chapter in the beginning mentions the historic development of formulation and basics of a DFT calculations.

The aim of the study reported in **Chapter 3** limits to interplay of properties and composition of bimetallic chains. We modelled four different compositions for bimetallic chains based on some experimental studies on alloy nanowire. The simple model of four types A, B,C and D are based on the idea of having smallest possible unit cell of atomic chain representing, uniformly mixed, Au-rich and Pd/Pt or Ag rich atomic chains. Any bimetallic alloy formation does have these three possibilities only. Our choice four compositions cover all possible composition a bimetallic chain can have.

The structural parameters of relaxed geometry and comparison of cohesive energy gives an idea about relative stability of each composition. We find that the most stable structures are C-type of Au-Pd LAC, A-type of Au-Ag LAC and D-type of Au-Pt LAC. This means that, Au-Ag atomic chains prefer uniform mixing, while Au-Pd and Au-Pt atomic chains prefers non uniform mixing of two species. An important information that emerges from relative study of cohesive energy and bond length is that local arrangement of atoms play an important role in deciding the properties of chains. For example, chains having equal number of two species but differing in ordering of atoms exhibits properties quite different from each other. The presented theoretical data of composition dependent properties can be useful in experimental characterization of atomic chains.

Magnetism is an important aspect in study of any condensed matter system. Nano structures are known to have dimensionality dependent magnetic properties. In present study Au-Pd and Au-Pt atomic chains are magnetic in nature and all composition of Au-Ag LAC are nonmagnetic.

Chapter 4 is devoted to stability, structure and electronic properties of bimetallic chains Au-Pd, Au-Pt and Au-Ag. Similar to chapter 3 this chapter also deals with the free-standing chains however the study conducted here is on different aspect of chain

study. We address the question of possibility of chain formation and the most likely composition of bimetallic chain to occur in an experimental set up. In an important report regarding chain formation, it was shown that the actual ground state of an atomic chain corresponds to the minima in the string tension and not the energy. Based on criteria of string tension the possibility of chain formation is judged. Since tension is first order derivative of energy, the table structure that corresponds to minimum total energy can be realized where the tension approaches zero from infinitesimal initial negative value. We identified such points of minimum tension and related it to the most stable structures. Further the comparison of cohesive energy gives idea about the most probable structure to be realized in break junction experiment. Based on this criterion following points are observed:

i) For the case of Au-Pd chains, the atomic chains having equal number of Au and Pd atoms are do not have any minima in string tension meaning that these chains cannot be formed in an experiment. Comparing the cohesive energy of remaining two compositions that is Au-rich and Pd rich atomic chains, we find that Au-rich atomic chain is most likely to occur in experiment. That is termed as type-C Au-Pd chain.

ii) For the case of Au-Pt chains, the minima of string tension are obtained for all the four compositions however the most probable composition is the one having a greater number of Pt atoms than Au atoms. That is termed as type-D Au-Pt chain.

iii) All the four types of Au-Ag atomic chains also fulfil string tension criteria. The most likely structure is the one having equal number of Au and Ag atoms with an alternating arrangement of Au and Ag atoms. That is termed as type-A Au-Ag chain.

Further, electronic and optical properties of the most stable structures are studied.

The band structures of the most stable chains reveal that type-C chain of Au-Pd and type-A chain of Au-Ag exhibit a band gap of 0.16 eV and 0.9 eV, respectively, hence they could be termed as semiconducting chains. Type-D of Au-Pt atomic chains have two bands crossing Fermi level hence it can be considered as metallic chain.

To get an idea about transport properties of atomic chains having metallic character, that is Au-Pt type D chain, we analysed number of bands that cross the Fermi level. For n number of bands that crosses Fermi level, the ballistic conductance is G_0, where G_0 is the unit of quantum conductance. Spin polarised calculation with the inclusion

of Spin Orbit Coupling shows that Au-Pd and Au-Pt atomic chains are magnetic, while Au-Ag atomic chains are non-magnetic.

Chapter 5 deals with the atomic chains adsorbed on substrate. The another important class of one-dimensional structures apart from suspended atomic chains. The chapter reports DFT calculations on structure and electronic properties of bimetallic chains of Au-Pd, Au-Pt and Au-Ag on two different substrates NiAl(110) and Cu(110). These two substrates are most widely used substrates for absorption of transition metals and noble metals. It is evident from a good number of research reports on NiAl (110) and Cu(110) substrate that the most favourable direction of growth for both the substrate is [001] direction and the most favoured site of adsorption of metal atoms on the substrate is Ni-Ni bridge site and Cu-Cu bridge site.

We modelled out chain-substrate accordingly where bimetallic chains are formed by placing atoms of two different species on Ni-Ni bridge site along [001] direction.

The chapter reports structural parameters of relaxed geometry of chain-substrate systems.

The strength of bond, interaction of chain atoms with the substrate atoms and stability of chains are discussed based on interaction energy, binding energy and plots of projected Density of States.

Among the three bimetallic chains, Au-Pt chain exhibit highest magnitude of binding energy, followed by Au-Pd and Au-Ag chains in both the cases of substrates.

The inquiry on how the presence of substrate affects structure and electronic properties of atomic chains yields following observations:

i) Pristine chains of Au, Ag, Pd and Pt are reported to be having linear structures over the substrate while bimetallic chains exhibit zigzag geometry over the substrate. The deviation from linearity can be attributed to the difference in atomic radii of alloy atoms, Au, Pd, Pt and Ag, which makes each of these atoms in alloy chain sit at different heights on the Ni or Cu troughs, which results into zigzag geometry of bimetallic chains.

ii) The magnetic moment of Au-Pd and Au-Pt chains on NiAl (110) and Cu(110)

substrate vanishes due to interaction of d-orbital of Ni and Cu atoms with that of chain atoms. The reason for this vanishing magnetic moment is reflected in plots of PDOS. Shifting of d-band edge away from Fermi level, and the stronger interaction of Pd/Pt atoms in chain with the Ni/Cu atoms of the substrate, as compared to interaction between Au and Pd; or Au and Pt atoms. Shifting of d-orbital away from Fermi energy in chain-NiAl system lowers the total density of states at Fermi level and neutralize spin polarization originated from reduced dimension of Pd and Pt d-orbital.

iii) Presence of NiAl(110) substrate reduces the chain-atom interactions and enhances chain-substrate interaction.

iv) The way round in the presence of Cu substrate chain atom interactions are stronger than chain-substrate interaction.

iv) The plots of projected density of states shows strong interaction of d-orbital of Pd and Pt atoms of the Au-Pd and Au-Pt chains with the d-orbital of Ni atoms of NiAl(110) substrate. Ag atoms of Au-Ag chains are found to have almost no interaction with the NiAl(110) substrate atoms.

v) Cu-atomic orbital, which are spread over wider energy range, shows good orbital overlap with Au, Pd, Pt and Ag atoms.

We compared results of single chains adsorbed on two substrates NiAl(110) and Cu(110) and find that the Atoms of Au-Pd, Au-Pt and Au-Ag chains bind more strongly with Ni atoms of NiAl substrate, as compared with Cu atoms in Cu(110).

Further to explore more possibility of alloying by making different compositions with bimetallic chains we placed double chains of Au-Pd, Au-Pt and Au-Ag on Cu(110) substrate in three different configurations. Au-Pd and Au-Pt chains on Cu(110) substrate settles with a double zigzag geometry while Au-Ag chains exhibits ladder topology in Cu(110) substrate.