Synopsis of the thesis

Title : ab-initio investigations on Structural, Electronic, transport and Optical properties of bimetallic nano structures such as Au-Pd, Au-Ag, Au-Pt

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BY

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The synopsis is organised as follows: Brief introduction and the highlights of the literature review, our objectives for carrying out this research work , and the important outcomes of our investigations discussed in detail in various chapters of the thesis.

1 Introduction

Quantum effects and surface effects make properties of materials dependent on size, structure and local atomic arrangement at nano scale. This offers a superb opportunity to tailor the properties of the materials. Atomic chains which are the smallest one-dimensional (1D) nano system have been studied extensively theoretically and experimentally for two main prospects: [1–6] (a) Their usage as contacts in molecular electronics. (b) As an excellent theoretical test ground of one dimensional physics.

There is a long list of reports on the theoretical studies of 1D structures. Most of these reports are dedicated to nanowires made up of one metal. [5–12] There are limited number of studies exploring alloyed nano structures. [4,8,13–15]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 to the possibility of chain formation relating experimental observations.[4,14,16] 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. [5,10]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.

There are two main experimental methods for chain formation. One class consists of Atomic chains realised either by depositing metal atoms on any surfaces, mainly, semiconducting chains or transition metal atoms chain deposited on variety of surfaces or atomic chains grown in interior of nano tubes. Another class is comprised of atomic chains produced by narrowing a junction between two metal tips. The narrowing junction between two metal tips are 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. 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. In the thesis, we address the theoretical aspects of both of the above mentioned class of atomic chains. Our aim was to carry out a systematic study covering most of the important aspect of chain study. That are formation possibility, stability, structure and interplay of properties with varied composition of bimetallic atomic chains.

2 Research Objectives

Our motive for the work presented in this thesis was 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.

3 Outline of the thesis

The thesis titled "ab-initio investigations of structure, electronic, transport and optical propertied of bimetallic nano structures such as Au-Pd, Au-Pt and Au-Ag" is divided in 6 chapters as follows:

Chapter 1 is devoted to the introductory aspects of the subject, that is nano structures specifying the focus on 1D structures. Starting from the definition of 1D structures and it possible application, a brief about two experimental methods, Scanning Tunnelling Microscope and Mechanically Controlled Break Junction experiment for fabrication of 1D structure is discussed. 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 presents essential theory and computational methods. The computations reported here are carried out using computational code Vienna Ab initio Simulation Package(VASP). VASP is a computer program for atomic scale materials modelling, e.g. electronic structure calculations and quantum-mechanical molecular dynamics, from first principles. VASP

computes an approximate solution to the many-body Schrödinger equation, either within density functional theory (DFT), solving the Kohn-Sham equations, or within the Hartree-Fock (HF) approximation.

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.

Chapter 3 reports results and discussion of our study related to Linear Atomic Chains. The aim is limited 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. They are exhibited in Figure 1. Any bimetallic alloy formation does have these three possibilities only. Our choice of four compositions covers all possible composition a bimetallic chain.

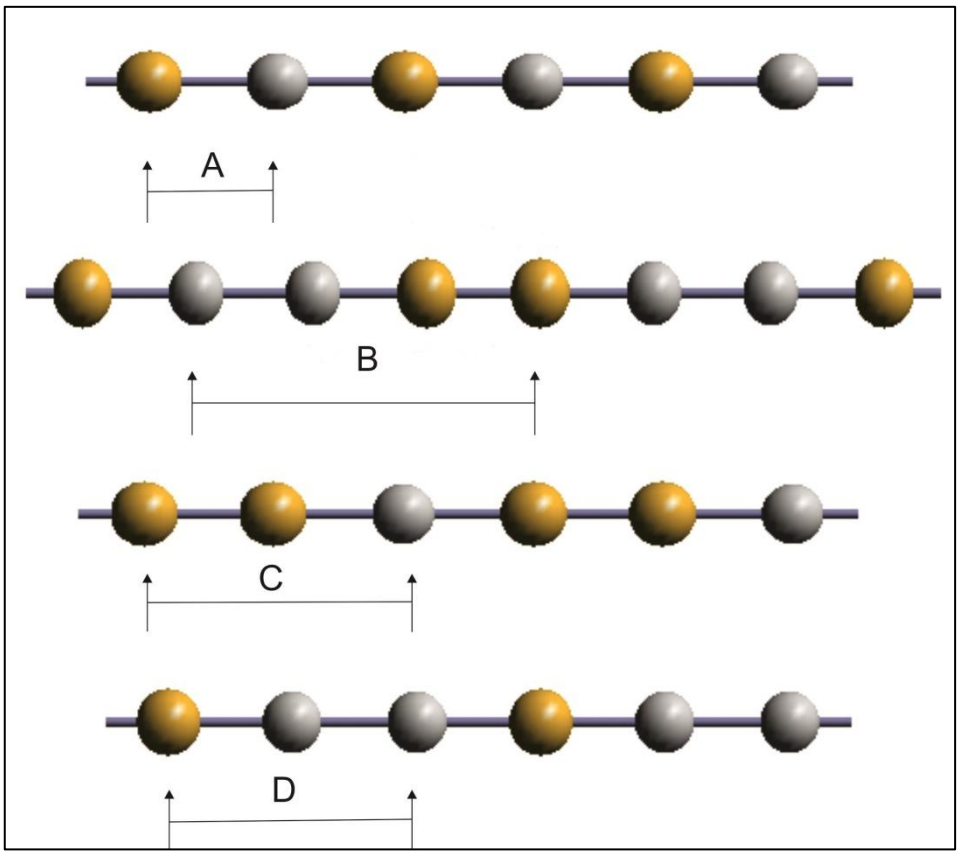

Figure 1 Atomic arrangements and unit cell for LAC of Au-Ag and Au-Pt with four different compositions labelled as A,B,C and D. The horizontal line with the arrow shows unit cell considered for the calculation for each composition, Yellow sphere shows Au atoms, grey spheres shows Pd(Ag or Pt) atoms in LAC.

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 non magnetic.

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 stable 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 criteria following points are observed:

i) For the case of Au-Pd chains, the atomic chains having equal number of Au and Pd atoms 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 is obtained for all the four compositions however the most probable composition is the one having more 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 fulfils 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 reveals 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 analyzed 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. Another important class of 1D 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 which is exhibited in Figure 2.

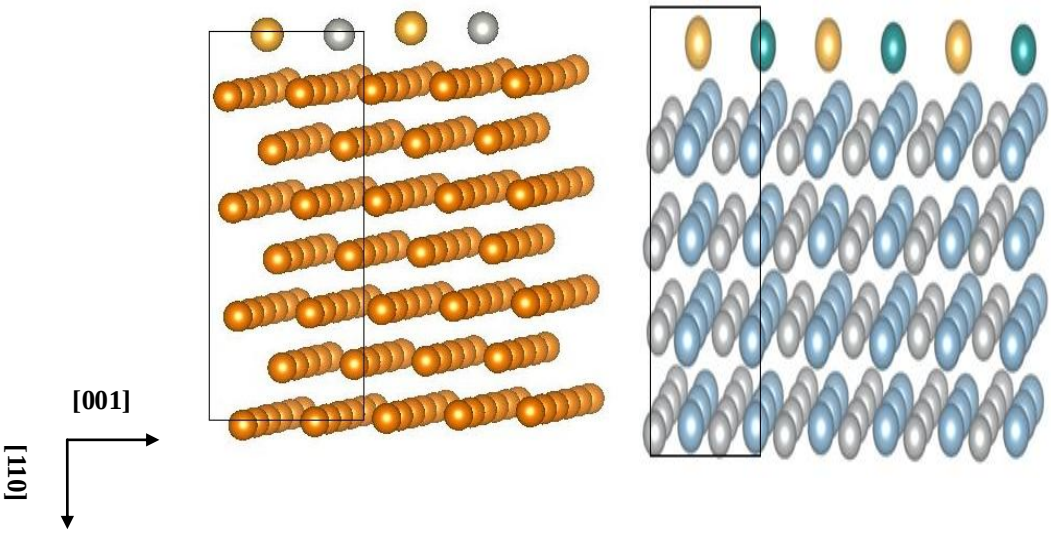

Figure 2 Au-Pd, Au-Pt and Au-Ag chains over Cu(110) substrate (left side figure) and NiAl(110) substrate (right side figure). The copper atoms are represented by reddish yellow spheres. Al atoms are shown by light blue spheres while light grey spheres display Ni atoms in NiAl substrate. The chains atoms are shown by blue(Pd(Pt, Ag)) and yellow (Au) spheres, respectively, when are placed chain on Cu(110) substrate. The rectangle is the supercell used for the calculation.

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 be having linear structures over the substrate while bimetallic chains exhibits zigzag geometry. 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.

Chapter 6 summarises the entire work of thesis.

4 List of Publications

1. Mudra R. Dave and A. C. Sharma, "*First principles calculation of the structural, electronic, and magnetic properties of Au-Pd atomic chains*", AIP Conf. Proc. **1665**, 050105 (2015).

2. Mudra R. Dave and A. C. Sharma, "*Ab Initio Calculations of Dielectric Function of Bimetallic Linear Atomic Chains of Au-Pd",* Advanced Materials Research, Vol. **1141,** pp 171-175 (2016)

3. Mudra R. Dave and A. C. Sharma, "*Structure, stability and electronic properties of bimetallic atomic chains of Au–Ag and Au–Pt*" Pramana – J. Phys. 93:55 (2019)

4. Mudra R. Dave and A. C. Sharma, " *Effect of Substrate on Structural and Electronic Properties of Au-Pd, Au-Pt and Au-Ag Atomic Chains*" Asian Journal of Physical and Chemical Sciences 8(3): 7-18 (2020)

5 References

1. Tung JC, Wang Y-K, Guo GY. Magnetic anisotropy and spin-spiral wave in V, Cr and Mn atomic chains on Cu (0 0 1) surface: first principles calculations. *J Phys D Appl Phys*. 2011;44(20):205003.
2. Singh P, Nautiyal T, Auluck S. Electronic and optical properties of free-standing and supported vanadium nanowires. *J Appl Phys*. 2012;111(9):93506.
3. Nilius N, Wallis TM, Ho W. Building alloys from single atoms: Au- Pd Chains on NiAl (110). *J Phys Chem B*. 2004;108(38):14616-14619.
4. Alves Da Silva Autreto P, Galvao DS, Artacho E. Species fractionation in atomic chains from mechanically stretched alloys. *J Phys Condens Matter*. 2014;26(43). doi:10.1088/0953-8984/26/43/435304
5. Ohnishi H, Kondo Y, Takayanagi K. Quantized conductance through individual rows of suspended gold atoms. *Nature*. 1998;395(6704):780-783. doi:10.1038/27399
6. Bahn SR, Jacobsen KW. Chain formation of metal atoms. *Phys Rev Lett*. 2001;87(26):266101-1-266101-266102. doi:10.1103/PhysRevLett.87.266101
7. Tung JC, Guo GY. Magnetic moment and magnetic anisotropy of linear and zigzag 4d and 5d transition metal nanowires: First-principles calculations. *Phys Rev B - Condens Matter Mater Phys*. 2010;81(9):1-14. doi:10.1103/PhysRevB.81.094422
8. Singh P, Nautiyal T, Auluck S. Electronic and vibrational properties of vanadium-carbide nanowires. *J Appl Phys*. 2012;112(6). doi:10.1063/1.4752020
9. Kumar A, Kumar A, Ahluwalia PK. Ab initio study of structural, electronic and dielectric properties of free standing ultrathin nanowires of noble metals. *Phys E Low-*

Dimensional Syst Nanostructures. 2012;46:259-269. doi:10.1016/j.physe.2012.09.032

10. Yanson AI, Rubio Bollinger G, Van Den Brom HE, Agraït N, Van Ruitenbeek JM. Formation and manipulation of a metallic wire of single gold atoms. *Nature*. 1998;395(6704):783-785. doi:10.1038/27405
11. Delin A, Tosatti E. The electronic structure of 4d transition-metal monatomic wires. *J Phys Condens Matter*. 2004;16(45):8061-8074. doi:10.1088/0953-8984/16/45/028
12. Delin A, Tosatti E, Tosatti E. Magnetic phenomena in 5d transition metal nanowires. *Phys Rev B - Condens Matter Mater Phys*. 2003;68(14):1-8. doi:10.1103/PhysRevB.68.144434
13. Kumar A, Ahluwalia PK. Transport properties of pristine and alloyed free standing ultrathin nanowires of noble metals. *J Alloys Compd*. 2014;615:194-203. doi:10.1016/j.jallcom.2014.05.210
14. Fa W, Dong J. Stability of suspended gold and silver alloy monatomic chains. *J Chem Phys*. 2008;128(24). doi:10.1063/1.2940332
15. Bettini J, Sato F, Coura PZ, Dantas SO, Galvão DS, Ugarte D. Experimental realization of suspended atomic chains composed of different atomic species. *Nat Nanotechnol*. 2006;1(3):182-185. doi:10.1038/nnano.2006.132
16. Tosatti E, Prestipino S, Kostlmeier S, Corso AD, Tolla FD Di. String Tension and Stability of Magic Tip-Suspended Nanowires. 2001;291(January):288-290.

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Endorsement of the Supervisor:

Synopsis is approved by me

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