Chapter 4
Stability, Structure and electronic Properties of Bimetallic Atomic Chains of Au-Pd, Au-Ag and Au-Pt

This chapter deals with the stability, structure and electronic properties of bimetallic chains of Au-Pd, Au-Ag and Au-Pt. Based on criteria of tension we examine the possibility of chain formation for four different compositions of Au-Pd, Au-Ag and Au-Pt defined in previous chapter. It is found that Au-Pd chains having equal number of Au and Pd atoms do not show any possibility of chain formation while in case of Au-Ag and Au-Pt chains all the compositions can be realised experimentally. Further we judge the most likely composition to occur in an experiment based on cohesive energy criteria.

4.1 Introduction

Experimentally atomic chains can be formed mainly with two different approaches. i) By breaking of point contact in MCBJ experiments and ii) By depositing atoms on suitable substrate using STM [38,110] This chapter aims at discussing structure stability and composition dependent properties of bimetallic chains observed in Break junction experiments.

Theoretical appraoches to predict chain formation involves minimization of enthalpy, string tension and cohesive energy. [54,58,63] It has been specified out that enthalpy can be used as a defining critera for examining possibility of chain formation in several cases [63].

There have been extensive studies on pristine atomic chains of 3d, 4d and 5d elements. [40,55,101,102,111,112] However strongest tendency for chain formation is observed for Au owing to its low reactivity. Though, Ag-atomic chains could not be generated, Au-Ag atomic chains have been formed experimentally. [113]

The string tension of a chain is better a criteria in judging its stability and corresponding geometrics of a structure.[54] Experimental results of Au, Pt, and Ag pristine chains as well as Au-Ag bimetallic chains correlates well with the criteria of string tension and cohesive energy in predicting the chain formation.

4.2 Calculation Details

Free standing infinite chain is modelled along the z-direction of tetragonal unit cell keeping a large vaccum of 20 Å along x- and y-direction, in order to prevent interaction of the chain with its periodic image. The DFT implemented code VASP[87,88] is used to compute stability,structure and electronic properties of bimetallic chains. The GGA, for exchange-correlation functional, has been applied with the use of PBE functional[108]. The plane wave basis set is used for Brilliouin zone sampling. K-point sampling was done using Monkhorst-Pack[95] scheme that uses $1 \times 1 \times 40$ in the full Brillion zone with Gaussian smearing having 0.01 smearing parameter. The kinetic energy cut off was set to 450 eV giving results sufficiently accurate (Convergence within 1meV) to eliminate the possible discontinuity in convergence due to finite points and difference in the unit cell size.[109] The atomic configuration of each atomic chains corresponding to the minimum energy is determined by simultaneously optimizing unit cell size and ionic positions of atoms in the unit cell.

The unit cell size is parameterized by $\bar{d}_z$ which is projection of average interatomic distance along the chain axis. It is to note that since the number of atoms in each type of unit cell are different, the unit cell size of each type is different. For example, For two atom unit cell, unit cell size is $2\times \bar{d}_z$, whereas for the unit cell having three and four atoms the cell size is $3\times \bar{d}_z$ and $4\times \bar{d}_z$, respectively.

For each value of $\bar{d}_z$, cohesive energy was calculated for a range of *x*- and *y*-coordinates of each atoms and a local minimum of cohesive energy is determined. The global minimum is the minimum of the set of local minimums corresponding to a range of $\bar{d}_z$. Further, the ionic relaxation was performed using conjugate gradient minimization scheme, until the minimum force acting on each atom reduces to less than 1 meV/Å.

4.3 Results and Discussion

4.3.1 Structure and Stability

Study of bimetallic chains structuers with different composition involves two main queries:

(1) Whether a particular structure can be formed in the experiment. (2) structure parameters of the stable structure.

Experiments of pristine Au, Ag, Pt and bimetallic chains of Au-Ag have confirmed that string tension is better criteria in confirming possibilities of chain formation.

Since Tension is the first order derivative of energy, the minimum energy configuration corresponds to a point where the tension approaches zero from infinitesimal initial negative value in the plot of tension versus $\bar{d}z$. Here the string tension is defined by, T = dE/d$\bar{d}_z$..While, cohesive energy, E_{coh} of every structure can be computed with the use of;

$$E_{coh} = \frac{1}{a+b}\left(E_{tot} - aE_{atom}^{Au} - bE_{atom}^{Pd,Pt\ Or\ Ag}\right) \qquad (4.1)$$

Where, E_{atom} are the energies of Au, Pd, Ag and Pt atoms in free states, integers a and b are number of atoms of Au and Pd (Ag, Pt) and E_{total} is total energy of bimetallic atomic chain. Our computed T and E_{coh} for types of A, B, C and D atomic chains of Au-Ag and of Au-Pt are displayed in Fig. 1 as the functions of $\bar{d}_z$.

The atomic structure exhibits minima where E_{coh} is minimum, and tension changes its sign. It is seen from Fig. 4.1 that type-A and type-B of Au-Pd chains does not exhibit such minima.

From the earlier reports it is evident that the atomic chains observed in actual MCBJEs possesses a zigzag arrangement of atoms. Likewise, existence of a zigzag minimum is a necessary condition for a finite sized chains to be formed in an MCBJE. This means

that formation of type-A and type-B Au-Pd chains is not possible. Type-C and Type-D of Au-Pd chains and all the four A, B, C and D type atomic chain structures of Au-Ag and Au-Pt shows minimum and thus formation of these structure is possible.

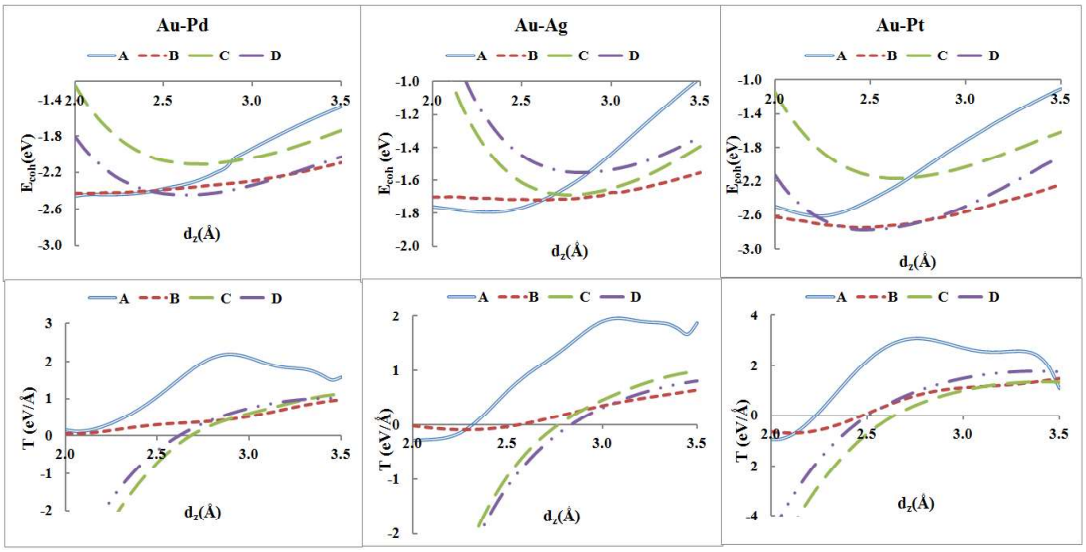

Figure 4.1: Variation of cohesive energy per atom, *Ecoh* and Tension with average z-projected interatomic distance, dz for 4-types of Au-Pd, Au-Ag and Au-Pt chain structures.

The computed $\bar{d}_z$ corresponding to minimum energy structures, for types C and D chains of Au-Pd is equal to 2.50 Å and 2.43 Å respectively. For Au-Ag atomic chains, the minima energy structures of types A, B, C, and D are observed when $\bar{d}_z$ is equal to 2.31 Å, 2.29 Å, 2.49 Å and 2.50 Å respectively. Our computed $\bar{d}_z$, from minimum energy structures, for types A, B, C and D chains of Au-Pt is equal to 2.25 Å, 2.23 Å, 2.40 Å and 2.28 Å respectively.

Further, the minimum energy structures deduced by string tension criteria are relaxed using conjugate gradient algorithm where atoms are allowed to move in *x*- and *y*-directions till the minimum energy state is achieved. The resulting structures of atomic chains of Au-Pd, Au-Pt and Au-Ag are of zigzag geometry which are displayed with optimum bond angles and bond lengths in Fig. 4.2, Fig. 4.3 and Fig. 4.4, respectively. From previous chapter we have seen that average bond length of bimetallic LAC increases with increase in number of Ag and Pd atoms in the Au-Ag and Au-Pd chains. While in case Au-Pt LAC, increase in number of Pt atoms results in decrease in average bond lengths. By comparing bond lengths of zigzag structures with that of LAC, we see

that the general trends of bond mixing and bond length of LAC and Zigzag chains are similar.

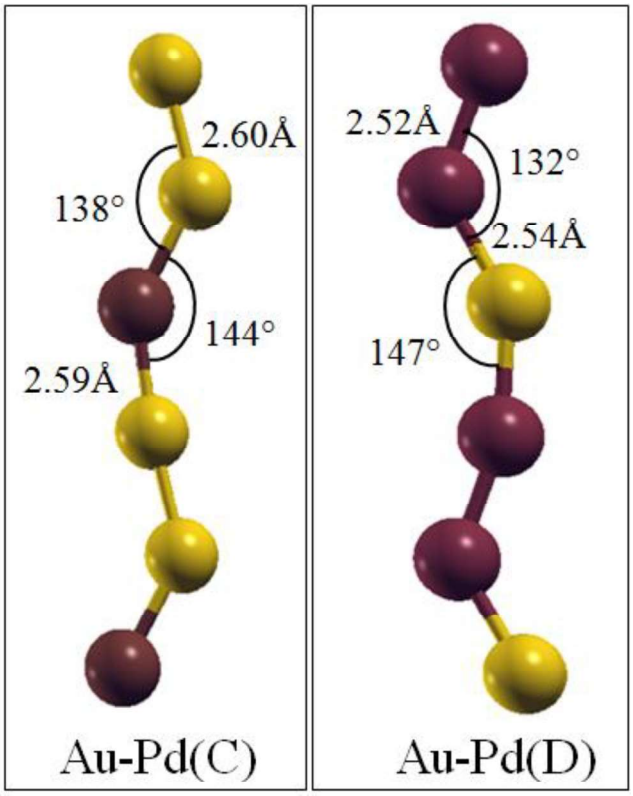

Figure 4.2: Optimized 2-types of chain structures of Au-Pd with bond lengths and bond angles. Yellow and Brown spheres present Au and Pd atoms, respectively.

Our computed cohesive energy of all relaxed structures of Au-Pd, Au-Ag and Au-Pt are exhibited in Table 4.1.

As can be seen from the Table 4.1, C-type of Au-Pd chain has lower cohesive energy than type-D, hence it can be inferred that in MCBJEs involving alloy chain of Au-Pd, the single strand of single atomic chain may have two Au atoms followed by one Pd atom. Similarly lowest cohesive energy among all Au-Ag chains are obtained for type-A and among all the Au-Pt chains D-type chains have lowest cohesive energy.

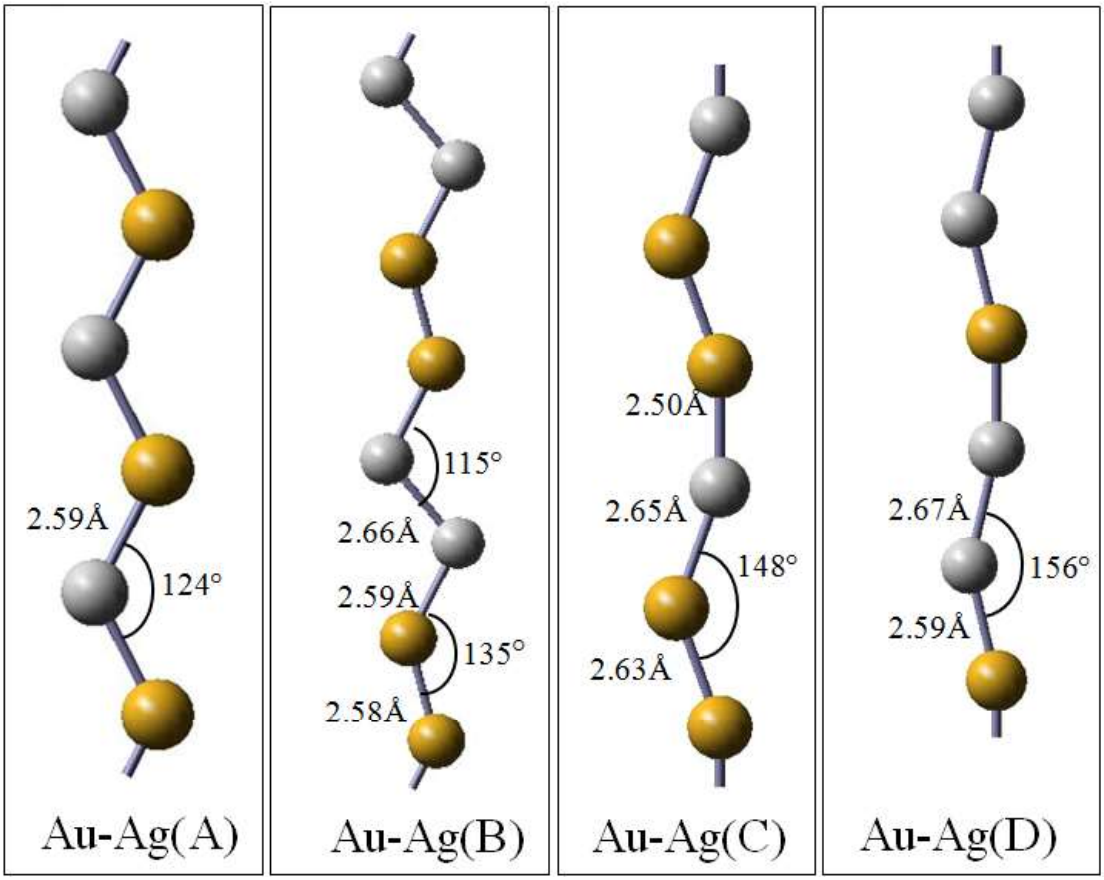

Figure 4.3: Optimized 4-types of chain structures of Au-Ag with bond lengths and bond angles. Yellow and Grey spheres present Au and Pt atoms, respectively.

In present study we find that D-type of Au-Ag chains with higher Ag content shows lowest cohesive energy and higher inter-atomic distance. This correlates well with previous studies[58,68] which considered enthalpy criteria to judge relative stability of bimetallic atomic chains of Au-Ag with different elemental concentration and they concluded that; (i) increase of Ag concentration weakens the relative stability of alloy chain, and (ii) average bond lengths of the alloy chains increases on enhancing Ag contents. This can be attributed to relativistic contraction of 6S orbital of Au atoms which makes Au-Au and Au-Ag bond length smaller than Ag-Ag bond length.

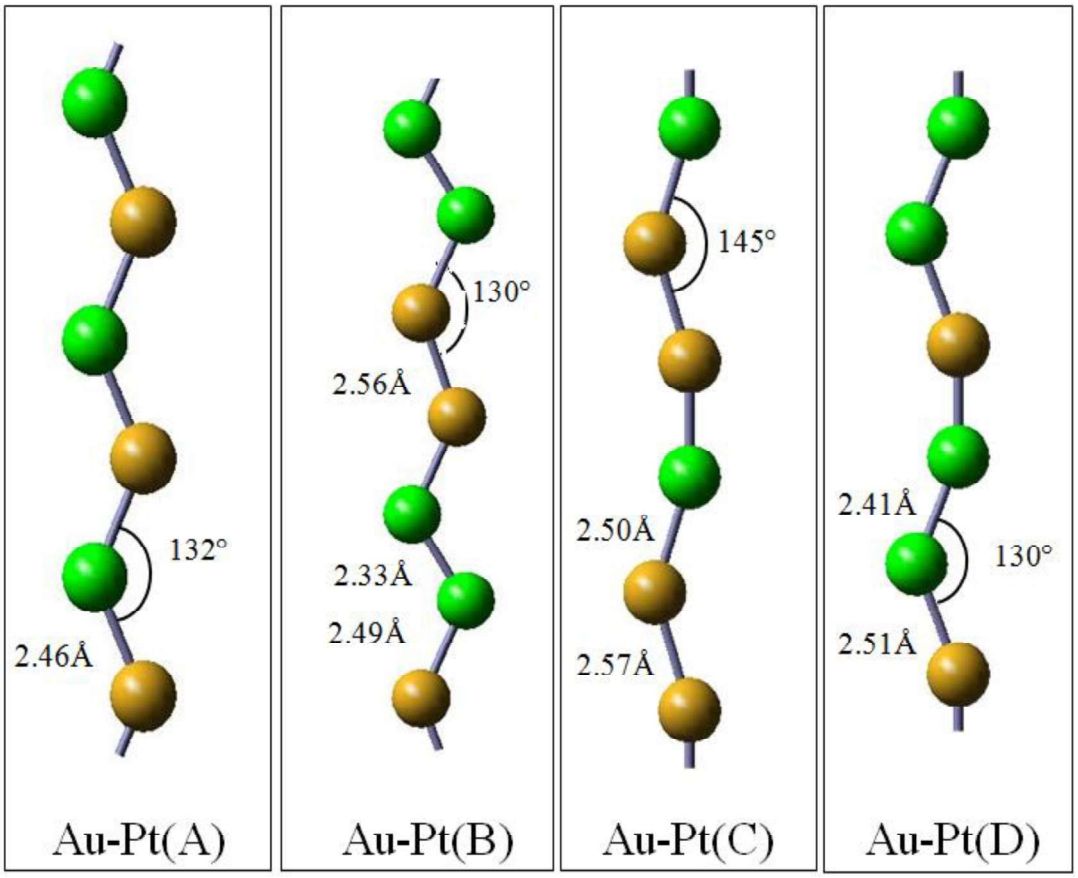

Figure 4.4: Optimized 4-types of chain structures of Au-Pt with bond lengths and bond angles. Yellow and Green spheres present Au and Ag atoms, respectively.

Another study based on thermo dynamical consideration used grand canonical framework to judge most likely composition of alloy chains to occur. It concluded that the atomic chains with alternating arrangement of Au and Ag atoms are most stable composition.[68]

Our results, which are based on criteria of cohesive energy and tension, too suggest that Au-Ag atomic chains with alternating arrangement of Au and Ag atoms termed as type-A is the most stable structure.

To get idea about magnetic state of the bimetallic atomic chains we carried out spin polarized calculation including spin orbit coupling. The ground state of Au-Pd type-C and type-D and all the type-A, B, C and D are magnetic. All Au-Ag bimetallic atomic chains are nonmagnetic.

The difference of total energies of non magnetic (E_{NM}) and ferromagnetic state (E_{FM}), E_{NM}-E_{FM} for Au-Pt chains of type A, B, C and D are found to be: 0.75 eV, 1.43 eV, 1.20 eV and 1.11 eV, respectively suggesting that ground state of all Au-Pt atomic chains are magnetic.

Table 4.1 Cohesive energy and magnetic moment calculated for Au-Pd, Au-Ag and Au-Pt atomic chains.

Composition Type	E_{coh} (eV/atom)	Magnetic Moment (μB)
Au-Pd C	-1.48	0.02
Au-Pd D	-1.39	1.33
Au-Ag A	-1.71	-
Au-Ag B	-1.66	-
Au-Ag C	-1.70	-
Au-Ag D	-1.46	-
Au-Pt A	-2.56	0.61
Au-Pt B	-2.66	0.76
Au-Pt C	-2.29	0.07
Au-Pt D	-2.82	1.15

The value of total magnetic moments are listed in Table 4.1. From Table 4.1 it is seen that Au-Pt chain that has Au atoms more than Pt atoms gives negligibly small magnetism of 0.07 μB.

Values of magnetic moment of Au-Pt chains suggest that relatively higher number of Pt atoms in a chain enhances stability and magnetic moment.

4.3.2 Electronic and Optical Properties

In previous chapter we discussed composition dependent electronic and optical properties of four different structures A, B, C and D of Au-Pd, Au-Ag and Au-Pt. In this chapter we focus our inquiry on possibility of chain formation in break junction experiment and most likely structure to occur. To determine the most likely structure to occur we have used cohesive energy. Based on cohesive energy criteria we infere that type-C of Au-Pd, type-A of Au-Ag chain and type-D of Au-Pt chain are most stable structures and they are most likely to occur in break junction experiment. We therefore computed electronic band structure and Density of states for type-C of Au-Pd, type-A

of Au-Ag and type-D of Au-Pt atomic chains which are displayed in Fig. 4.5 with Fermi energy set to zero.

As is seen from Fig. 4.5, 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.

Ballistic conductance of a wire is related to 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. In past Ballistic conductance of zigzag chain of pristine Au and Ag has been reported to be $2G_0$ and $3G_0$ for Pt.[11] The previous reports of band structure calculation of Au-Ag chains shows semi conducting behavior of the chain having alternate arrangement of Au and Ag atoms.[32,67,101]. We too find that bimetallic Au-Ag chain is semiconducting unlike the pristine zigzag chains of Au and Ag which are known to be conducting.[71] This change in electronic properties from conducting to semiconducting is the effect of alloying.

Existence of gap in our computed electronic structure Au-Ag type-A atomic chain indicates that electronic properties change from metallic to semiconducting on alloying Au and Ag atoms in a chain. It has been suggested that the semiconducting nature of bimetallic chain of Au-Ag may be due to ground state band structure effects.[114]

As is seen from Fig. 4.5, for type-D two bands are crossing Fermi energy level which gives rise to $2G_0$ quantum conductance. One of these two bands that cross Fermi energy is more dispersive. This more dispersive band can be attributed to hybridized S and d_z^2 orbital of Au and Pt atoms. Presence of a larger dispersive band in type-D Au-Pt chain indicates the stronger σ-bond that provides a greater stability to Au-Pt chain structures. For obtaining optical parameters like reflectivity, absorption spectra and electron energy loss spectra we computed frequency dependent real and imaginary part of dielectric function (ε_1) and (ε_2), as a function of photon energy for the most stable structures of Au-Pd, Au-Ag and Au-Pt chains. Our computed results as a function of photon energy are plotted in Fig.4.6.

Since type-D Au-Pt chain is metallic in nature, we incorporated both intra-band and inter-band contributions, while intra band (Drude term) are not included for type-C Au-Pd and type-A Au-Ag chains.

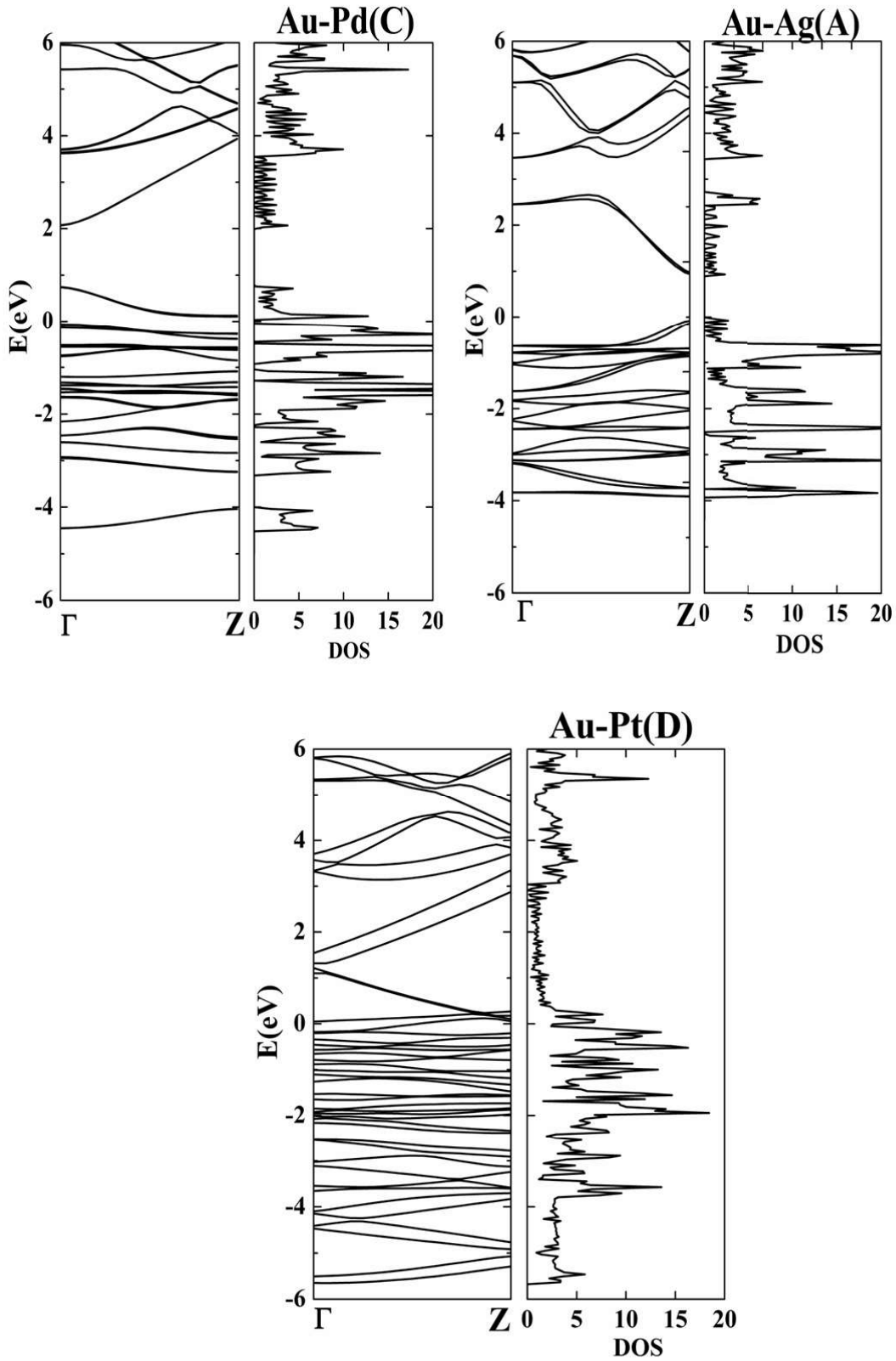

Figure 4.5: Electronic band structure and density of states for the type-C Au-Pd, type-A Au–Ag and the type-D Au–Pt atomic chains depicted in Figure 4.2, 4.3 and 4.4

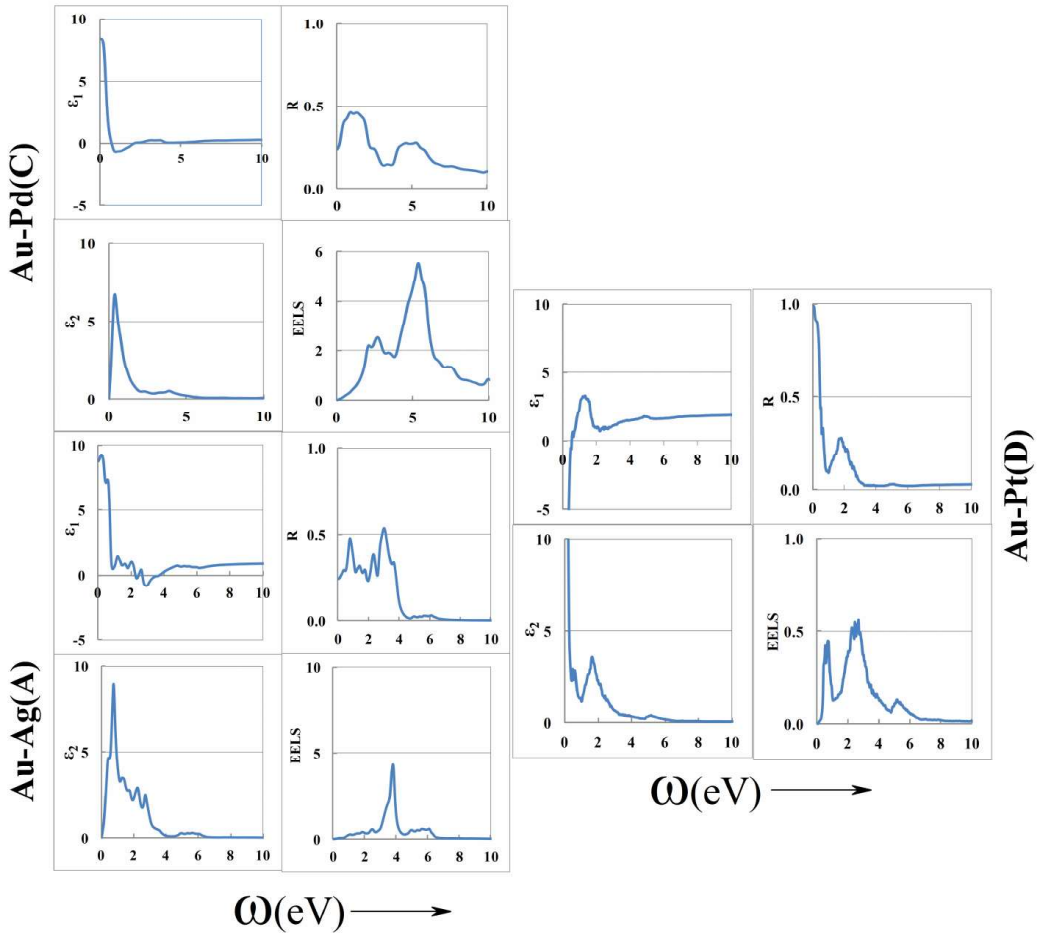

Figure 4.6: Real and imaginary parts of the dielectric function, reflectivity and electron energy loss spectrum for the type-C Au-Pd, type-A Au-Ag and type-D Au-Pt atomic chains

For semiconducting chains, peak in ε_2 corresponds to the transitions across the band gap. Likewise, we observe a peak in ε_2 for C-type Au-Pd and A-type Au-Ag at the photon energy equal to 0.17 and 0.9 eV, respectively. Since Band gap of 0.9 eV falls in infrared regime of the spectrum (0.01 eV to 1.7 eV). A-type Au-Ag chain and C-type Au-Pd chains can be useful for making infra-red devices. A sharp dip in reflectance spectra and the peak in electron energy loss spectra, which correspond to collective excitations, are also seen for type-A Au-Ag chain at around 3.9 eV.

Further a sharp dip in reflectance spectra and the peak in electron energy loss spectra corresponds to collective excitations. From Fig. 4.6, it is seen that EELS of D-type of Au-Pt chain exhibits two peaks at 0.71 and 2.25 eV, respectively.

Optical properties of zigzag chains of Au, Pt and Ag have been reported earlier[71]. Pt zigzag chain show two peaks in EELS at 0.59 ad 1.67 eV, while

plasma frequency for Au zigzag chain has been reported at 1.11 eV. Thus, plasma frequency shifts towards higher frequency for bimetallic chains.

4.4 Conclusion

We intended to inquire possibility for chain formation of bimetallic chains of Au-Pd, Au-Ag and Au-Pt. The possibility of chain formation was judged upon string tension criteria based on which we find that chain formation is possible for type-C and type-D of Au-Pd bimetallic chains. In the case of Au-Ag and Au-Pt atomic chains all the four types of structures can be realised experimentally. Further, we use criteria of cohesive energy to judge the most favored chain structure that can be formed at the last stage of nanowire stretching. We conclude that the most likely arrangement of atoms of the bimetallic chains are (i) an atomic chain with one Pd atom separated by two Au atoms (ii) an atomic chain with alternate arrangement of equal number of Au and Ag atoms and (iii) an atomic chain where two Pt- atoms are separated by one Au-atoms. Calculated electronic band structures of the most stable chains suggest that Au-Pd and Au-Ag atomic chains could be of semi conducting nature, while the most stable Au-Pt chain is metallic in nature. 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.