Chapter 3

Composition Dependence of Electronic, Magnetic and Optical Properties of Bimetallic Linear Atomic Chains of Au-Pd, Au-Ag and Au-Pt

This chapter deals with the linear geometry of bimetallic atomic chains of Au-Pd, Au-Ag and Au-Pt. The computational results of structure, electronic, magnetic and optical properties are presented. Four different compositions of linear atomic chains are modelled representing uniformly and non-uniformly mixed bimetallic chains. They are termed as A, B, C and D. How the variation in composition affects electronic, magnetic and optical properties of atomic chains is discussed in this chapter.

3.1 Introduction

With the experimental realisation of free standing atomic chains of gold in 1998[10,38] the field of nano science evolved one step closer to ultimate miniaturisation of electronic devices. This pioneering work lead to numerous studies on Gold atomic chains investigating the properties such as structure, stability, breaking force, conductance etc.[11,31,39,100,101] All these detailed studies using various approaches made the Gold nanowires a "prototype" of atomic chain studies. The search for the most stable geometry of gold atomic chains has found that zigzag structure of gold is more favoured against strictly linear geometry.

However, there are studies claiming that truly one atom thick linear atomic chains do exist as a very short and transient objects during thinning process of the break junction experiments which eventually breaks by further stretching. [102] Despite the fact that zigzag geometry is found to be the most stable structure of the atomic chains,[31,40] there are good number of theoretical studies devoted to strictly linear geometry of the infinite mono strands for a number of reasons.[67,71,101–103]

Firstly, for a tip suspended nano wire set up, the stability of nano contact is essentially determined by monatomic part of the contact. In other words, infinite monatomic chains correctly describes the properties of atomic chains.[31] Moreover it is found that stability of an infinite chain is at least necessary condition for the formation of a finite sized atomic chain in MCBJ experiments.[40] Thus, a good number of studies which aimed to examine possibility of chain formation in different metals considered the simple model of Linear Atomic Chains(LAC) with all the atoms placed at equal distance from each other and ignored any possibilities of other structures such as Peierl's dimerisation.[40,41,100,101,104,105]

Secondly, the initial images of Transmission Electron Microscopy (TEM) experiments of mono strand nanowire and some Molecular Dynamics simulations indicated straight wire geometries which motivated many theoretical studies to take into account LAC.[45,106,107]

Thirdly, study on structure and electronic properties of monatomic chains of Au, Ag and Pd reveals that the zigzag configuration of atomic chains can be interpreted as two linear chains put side by side but dislocated from each other in the longitudinal direction by half the inter atomic distance.[41] As a result, the electronic properties of linear chains shows similar features as that of zigzag chains.

Despite such huge number of studies dedicated to investigating possibility of chain formation for various elements, there are limited number of studies on alloy or bimetallic nanowires.

In addition to having dramatic effects of reduced dimensionality on various properties, bimetallic nanowires possess dependence of properties on composition and local atomic ordering which makes them more interesting. Electronic, magnetic, optical and transport properties of atomic chains depend on number of atoms of each species, topology, as well as local compositions of the atoms. In a report, A. Kumar et al have reported topology dependent properties of bimetallic chains of Au-Ag and Au-Pt.[67] However , to best of our knowledge there is hardly any studies reported till date aimed at investigating composition dependent properties of bimetallic linear atomic chains of Au-Pd, Au-Ag and Au-Pt.

This chapter describes structure, electronic and optical properties of bimetallic linear chains of Au-Ag, Au-Pt and Au-Pd. At this juncture we specify and limit our aim of study to check how the alteration of composition and atomic ordering of bimetallic

LAC would affect structure, magnetic, electronic and optical properties. We use the simplest geometry of atomic chains that is linear geometry . For studying composition dependence of different properties, we model four different types of compositions and term them as A, B, C and D. They are depicted in Figure 3.1. The idea behind such modelling is as follows.

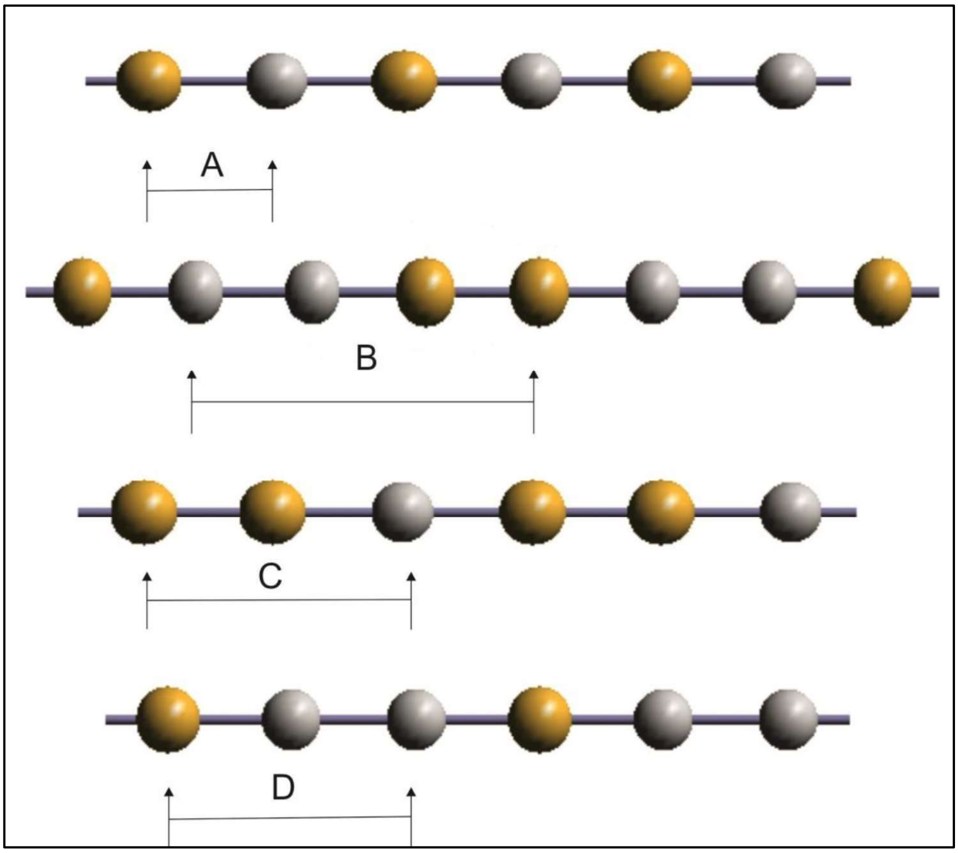

Figure 3.1: Atomic arrangements and unit cell for LAC of Au-Ag and Au-Pt with four different compositions labelled as A, B,C and D. The horizontal line with the arrow shows unit cell considered for the calculation for each composition, Yellow sphere shows Au atoms, grey spheres shows Pd (Ag or Pt) atoms in LAC.

For any bimetallic structure there are two main categories of alloying: (i) uniformly mixed and (ii) non uniformly mixed. The term uniformly mixed is crudely used to describe structures which have equal number of atoms of both the species. Non uniformly mixed structures refers to structures which have unequal proportion of both the species. Type A and B describes uniformly mixed chain structures where number of Au and Pd(Pt, Ag) atoms are equal. Type C and D describes non uniformly mixed structures where number of Au atoms are more or less in number than other metal atoms. Further, there are two ways to arrange uniformly mixed structures. Type-A, with alternate arrangements of two metal atoms, evenly mixed. While the linear arrangement in type B has two Au atoms followed by two Pd(Pt, Ag) atoms. The unit cells of each type of structures are shown in Figure 3.1.

3.2 Methodology

Free standing atomic chains are modelled as infinitely long bimetallic LAC. Unit cell consists of two, three and four atoms depending upon the composition of the bimetallic LAC, as is shown in Fig. 3.1. The atomic chains are 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. For exchange-correlation functional, the GGA with Perdew-Burke-Ernzerhof (PBE)[108] parameterisation is used. All calculations were performed including spin orbit coupling. K-point sampling was done using -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]

Minimum energy configuration for each composition are obtained by locating minimum in the calculated total energy as a function of interatomic distance. The bimetallic LAC were further relaxed using conjugate gradient minimization scheme, until the minimum force acting on each atom reduced to less than 1 meV/Å.

3.3 Structural Parameters and relative stability of LAC

Our computed bond length and cohesive energy for bimetallic chains of Au-Pd, Au-Ag and Au-Pt LAC are listed in Table 3.1, 3.2 and 3.3 respectively. From the tables it is seen that the bond lengths of bimetallic chains are between two bond lengths of pristine chains eg. bond length of Au-Au is 2.60 Å and bond length of Pd-Pd is 2.41 Å. The bond length of Au-Pd in all the four structures A, B, C and D of Au-Pd LAC is around 2.50 Å which is intermediate to Au-Au and Pd-Pd bond lengths. Similarly, bond lengths of Au-Pt in all the four structures A, B, C and D of Au-Pt LAC are intermediate to Au-

Au (2.60 Å) and Pt-Pt (2.35 Å) atomic chain. Same applies to the bond lengths of Au-Ag in all the structures of Au-Ag LAC.[71]

Properties of LAC with alternate arrangement of Au and Pt(Ag) have been studied earlier.[50,67] A Kumar et al[67] reports bond length of Au-Ag LAC chains 2.62 Å which is same as our calculated value. However our obtained value of Au-Pt bond length 2.45 Å is quite lower than earlier reported values of Au-Pt bond length of 2.61 Å[50] and 2.51 Å[67]. This difference between our calculated bond length and earlier reported values may be due to difference in basis set used for calculating total energy. Comparing the interatomic distances of type A, B, C and D of LAC, it is seen that average bond length of bimetallic LAC increases with increase number of in 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.

Table 3.1 Inter atomic distance, cohesive energy, Magnetic moment per atom and Spin polarisation factor calculated from Density of states at fermi energy for Au-Pd LACs.

Composition	**d_{Au-Pd} (Å)**	**d_{Au-Au} (Å)**	**d_{Pd-Pd} (Å)**	**BE/atom (eV)**	**Magnetic Moment(μB/atom)**	**P**
A	2.50	-	-	-1.55	0.47	-1.00
B	2.50	2.55	2.50	-1.49	0.49	-0.53
C	2.55	2.55	-	-1.57	0.29	-0.42
D	2.54	-	2.43	-1.41	0.51	-0.65

Table 3.2. Inter atomic distance, cohesive energy, Magnetic moment and Spin polarisation factor calculated from Density of states at fermi energy for Au-Ag LACs.

Composition	**d_{Au-Ag} (Å)**	**d_{Au-Au} (Å)**	**d_{Ag-Ag} (Å)**	**E_{coh} (eV/atom)**	**Magnetic Moment (μB/atom)**	**P**
A	2.62	-	-	-1.48	-	-
B	2.60	2.60	2.67	-1.39	-	-
C	2.63	2.59	-	-1.45	-	-
D	2.62	-	2.66	-1.34	-	-

Table 3.3. Inter atomic distance, cohesive energy, Magnetic moment and Spin polarisation factor calculated from Density of states at fermi energy for Au-Pt LACs.

Composition	d_{Au-Pt} (Å)	d_{Au-Au} (Å)	d_{Pt-Pt} (Å)	E_{coh} (eV/atom)	Magnetic Moment (μB/atom)	P
A	2.45	-	-	-1.93	0.48	0.74
B	2.56	2.67	2.35	-2.09	0.68	0.43
C	2.45	2.49	-	-1.78	0.51	0.66
D	2.45	-	2.35	-2.24	0.31	0.16

The cohesive energy can be used as an important parameter to estimate the relative stability of materials; larger negative magnitude of E_{coh} indicates higher stability of a system. In order to assess relative stability of structures, we computed cohesive energy, E_{coh} with the use of

$$E_{coh} = \frac{1}{(a+b)}\left(E_{total} - aE_{atom}^{Au} - bE_{atom}^{Pd,Pt\ or\ Ag}\right) \qquad (3.1)$$

E_{atom} are the energies of Au, 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.

On comparing relative stability, 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. The trend of chain formation and stability for pristine chains follows Pt>Au>Pd>Ag. The trend of relative stability in case of bimetallic chains is also similar to monatomic chains. It is seen that D-type of Au-Pt chains which have a greater number of Pt atoms than Au atoms are most stable which follows the order that Pt atomic chains are more stable than Au atomic chains. Similarly, type-C of Au-Pd chains where Au atoms are more in number than Pd atoms is most stable composition following the order that Au LAC is more stable than Pd LAC. In other words, increase of Ag and Pd concentration to alloy chains of Au-Ag and Au-Pd weakens the relative stability of alloy chain. While increase of Pt concentration enhances the relative stability of the alloy chains.

Another important information that emerges from our investigations is that both sequence and number of atoms play equally important role in formation of an atomic chain. Type-A and Type-B of LAC have same ratio of Au and Pd (Ag, Pt) atoms and they differ only in the sequence of the atoms. Type-A have alternate arrangement of the atoms and Type-B have two atoms of Au followed by two atoms of other species. Cohesive energy for both the A-type and B-type are quite different from each other for all the three alloy chains studied here.

3.4 Magnetic Properties

Pristine LAC of Pd and Pt with partially filled d-orbital is known to be magnetic. Ag atomic chains are non-magnetic, while Au atomic chains exhibit magnetic moment less than 0.1 μB[71,102,103,105]. In previous studies ultra-thin Au-Pt nanowire have been found magnetic.[50,61] It is suggested that the ferromagnetism observed in Au-Pt chains is due to charge transfer mechanism. Our calculations that include spin polarisation show that Au-Pd and Au-Pt atomic chains are magnetic in nature and all composition of Au-Ag LAC are non-magnetic. The magnetic moment of each composition of Au-Pd and Au-Pt LAC are reported in Table 1,2 and 3. The highest value of magnetic moment is obtained for type-B of Au-Pt structure. On the other hand, in case of Au-Pd LAC type-D shows highest value of magnetic moment. Similar to cohesive energy magnetic moment also is influenced by ordering of atoms of LAC. In other words, apart from the number of atoms, how these atoms are arranged in a linear chain influences magnetic properties. For example, type-A and type-B of Au-Pt chains are made up of equal number of Au and Pt atoms and they differ only in the ordering of atoms, however the magnetic moment per atom for these two compositions are quite different from each other. On the other hand, magnetic moment of Au-Pd type-A and type-B does not show much difference.

Spin polarisation factor plays important role in deciding the application of a nanostructure in spintronics devices. Spin polarisation Factor quantifies amount of spin polarisation near Fermi energy. Since electronic transmission depends on density of states near Fermi energy, higher value of Spin Polarisation Factor suggests better the possibility of spin transport of the material. We computed spin polarisation factor with the use of $P = (N(\uparrow)N(\downarrow))/(N(\uparrow)+N(\downarrow))$, where $N(\uparrow)$and $N(\downarrow)$ are density of states at Fermi energy for spin up and spin down electrons, respectively. Our computed values of spin polarisation factor for different LAC are listed in table1, table 2 and table 3. An important observation from Table 1 is that Spin polarisation factor of type-A Au-Pd LAC is found to be -1. This means that type-A Au-Pd LAC is half metallic material. These materials have one spin channel conducting and other insulating. In other words, the electron transport through such materials is totally spin polarised. Such materials are very important for making spintronic devices. In case of Au-Pt LAC, type-A shows highest value of spin polarisation factor.

3.5 Electronic Properties

The study of electronic band structure and Density of State of a structure gives an insight into conduction properties. The distribution of bands below and above Fermi energy gives idea about type of bonding and orbital overlap that contribute to bonding. Figure 3.2, 3.3 and 3.4 exhibits Band structure and Density of States of Au-Pd, Au-Ag and Au-Pt LAC, respectively. The Fermi energy is set to zero and the band structures are drawn from Gamma point to X along the direction of chain axis. From Figure 3.2, it is seen that all the LAC of Au-Pd is conducting with several bands crossing the fermi energy.

The quantum ballistic conductance of a wire under ideal situation can be determined by the number of bands crossing Fermi energy. For each band that crosses the E_F, ballistic conductance is G_0,(G_0= $2e^2/h$, quantum of conduction) which results into nG_0 for n number of bands crossing E_F. Counting of number of bands for each different type of configuration, number of bands crossing Fermi energy gives indication of finite conduction parameter.

Au-Ag A-type and B-type LAC show semiconducting nature with band gap of 0.6 eV and 0.12 eV, respectively. All other LAC of Au-Pd, Au-Ag and Au-Pt are conducting in nature with several bands crossing Fermi energy. Au-Pd A, B, C and D have one band crossing E_F showing ballistic conductance $1G_0$. Au-Ag LAC of type-C and type-D also have one band crossing E_F showing ballistic conductance $1G_0$. Type-A and type-

D of Au-Pt LAC have three bands crossing E_F, showing that it has ballistic conductance of $3G_0$. Type-B and type-C of Au-Pt LAC having two bands crossing E_F shows ballistic conductance 2 G_0. Au-Ag A-type and B-type LAC show semiconducting nature with band gap of 0.6 eV and 0.12eV, respectively. All other LAC of Au-Ag are conducting in nature with several bands crossing Fermi energy. The bands that cross the Fermi energy are mostly comprising of d-orbital of Au-atom. Similarly, all the four types of Au-Pt LACs are also conducting in nature with several bands crossing Fermi energy.

From figures 3.2, 3.3 and 3.4 it is seen that band structures representing C and D types are strikingly similar for the region below Fermi energy with only few rearrangements of bands. As compared to D-type structures, band structure of C-type shows narrowing of bands. Since all the C-type of structures have more Au atoms than Pd, Ag or Pt atoms, the stronger tendency of bond formation of Au atoms results in increased hybridization and thereby narrowing the bands and reducing the gaps between bands in C-Types of structures. These band rearrangements may have some effect on optical properties. It can be said that electronic and optical properties of type-C and type-D do not differ much, However similar conclusion cannot be made for magnetic properties of C and D types of LAC. Increase in number of Pd atoms in D-type Au-Pd LAC results in enhanced magnetic moment. Whereas D-type Au-Pt LAC with more number of Pt atoms shows less magnetic moment than C-type.

3.6 Optical Properties

Knowledge of optical properties of a bimetallic LAC is crucial for their use in both technological applications and experimental identification or characterisation. Our computed results for both for $E\perp C$ and $E\parallel C$ show that real and imaginary parts of dielectric function are anisotropic in nature. Our results are plotted for $E\parallel C$ polarization only. Since most of the LAC studied in present study are conducting except Au-Ag type-A and type-B, we have taken into account the intra band contribution to the dielectric function which is crucial for metallic system.

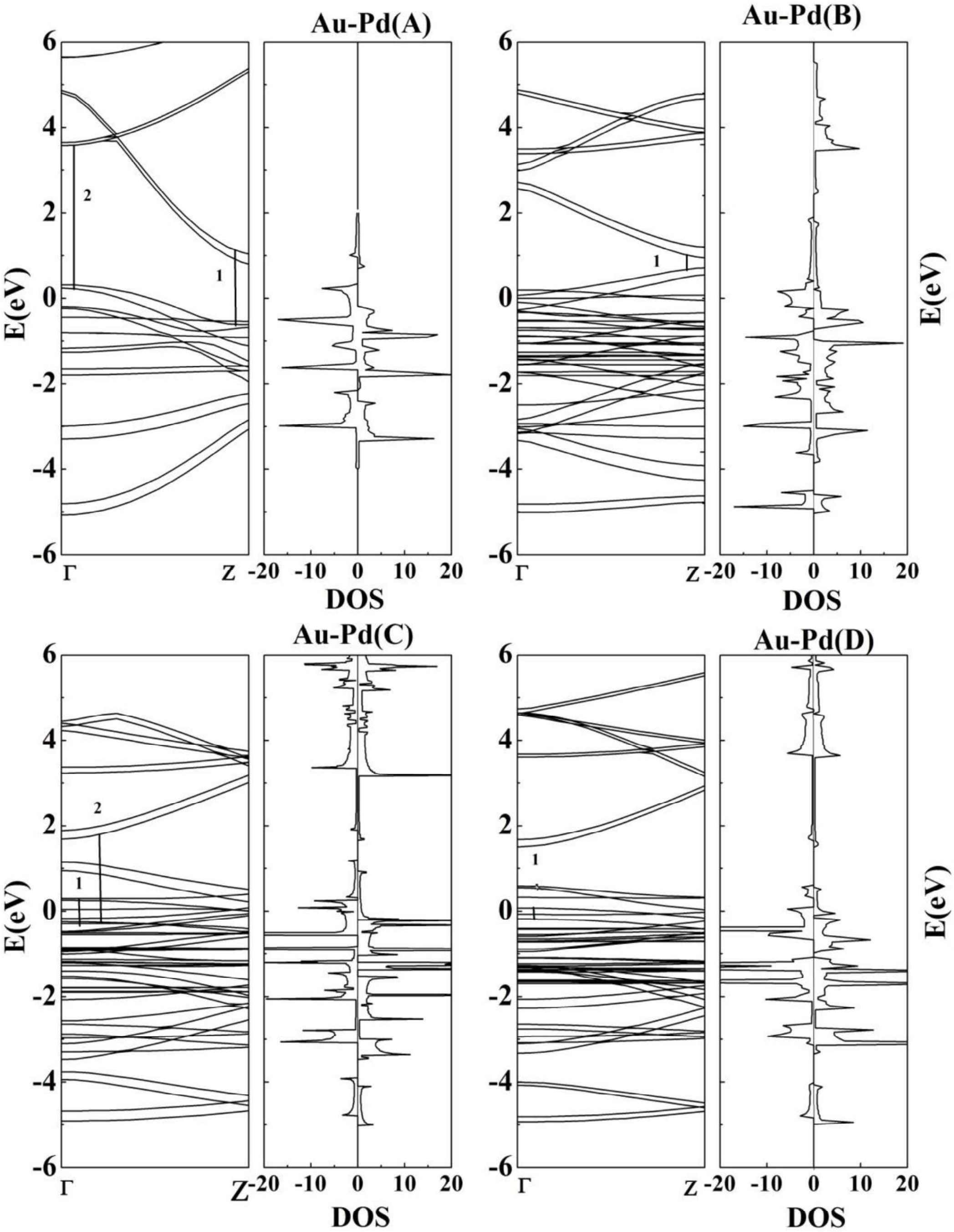

Figure 3.2: Electronic band structure and Density of states for Au-Pd LAC for different compositions described in Fig 3.1.

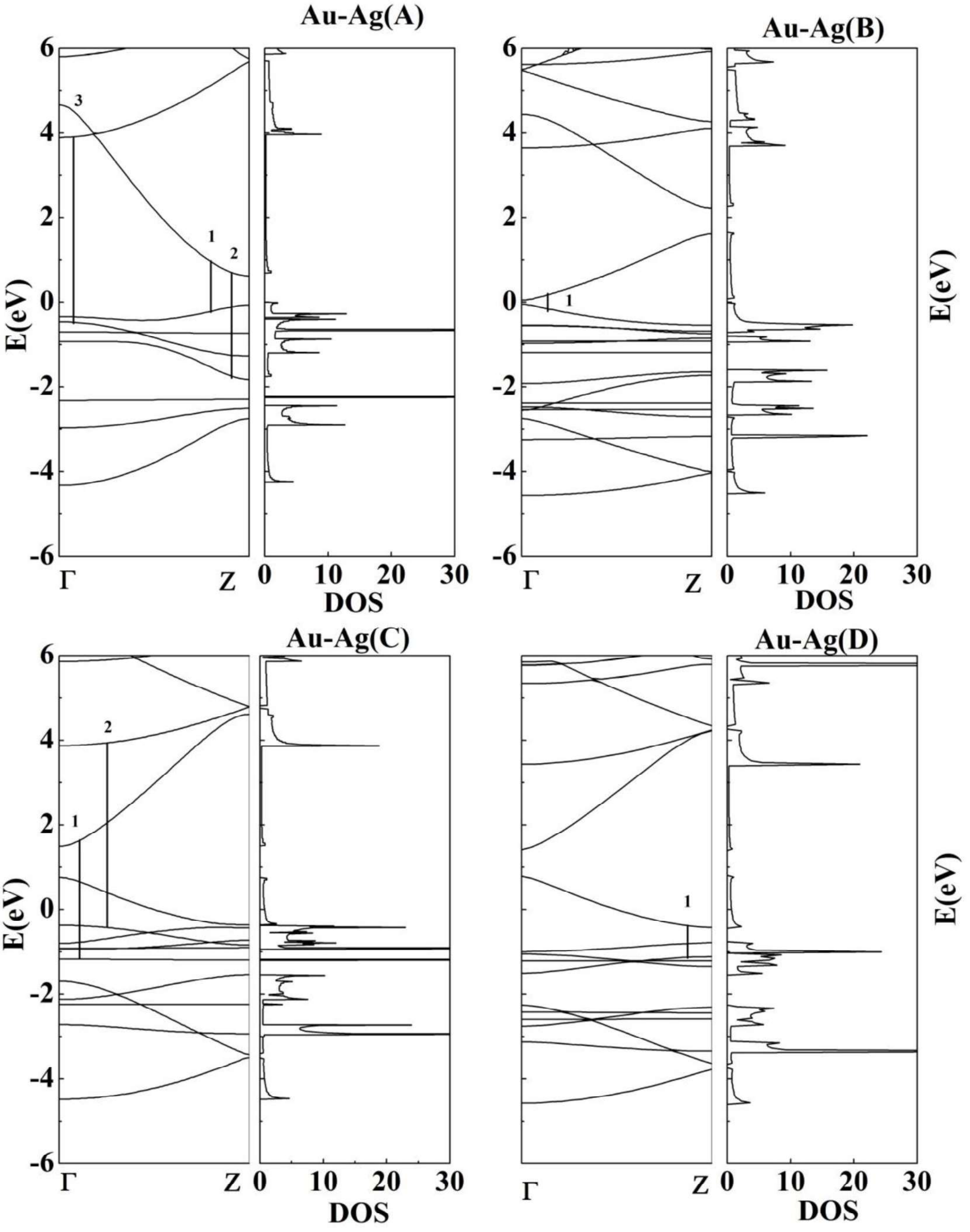

Figure 3.3: Electronic band structure and Density of states for Au-Ag LAC for different compositions described in Fig 3.1.

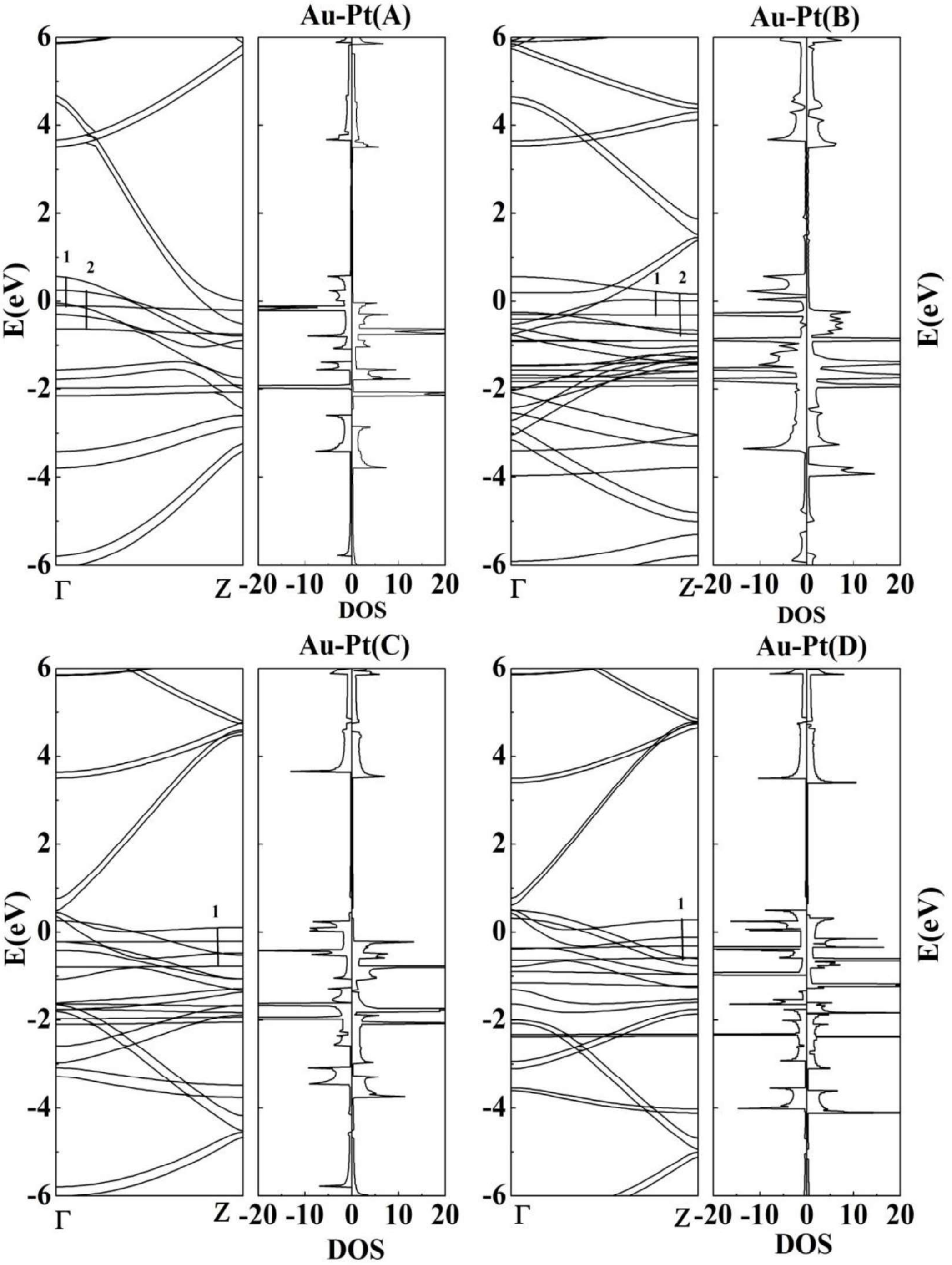

Figure 3.4: Electronic band structure and Density of states for Au-Pt LAC for different compositions described in Fig.3.1, are exhibited.

Figures 3.5, 3.6 and 3.7 represents optical properties of Au-Pd, Au-Ag and Au-Pt LAC respectively. We plotted real and imaginary part of dielectric function to compare and study the peak positions. We also plotted reflectivity, absorption coefficient and electron energy loss spectra of each composition. The plots of dielectric function clearly demonstrate that dielectric properties of a bimetallic LAC strongly depend on its chemical composition and sequence of atomic arrangement. The composition dependence of the primary peak position of imaginary part of dielectric function suggests that it is possible to tune optical properties with greater precision in case of bimetallic nano structures. Peak position in R(ω) and α(ω) strongly depends on the topology of LAC. This information can be very useful in identification criteria of formation of linear atomic chain in break junction experiments, where LAC are observed at final stage. On comparing dielectric function of bimetallic LAC from Figures 3.5, 3.6 and 3.7 with that of pristine chains of Au, Pd, Ag and Pt, it is seen that imaginary part of dielectric function is observed to be shifting towards lower energy compared to pristine LACs.[71]

As is seen from Figure 3.5, 3.6 and 3.7, the peak position of highest peak of reflectance spectra for almost all the compositions lies between energy range or 0.3 to 0.9 eV except Type-C of Au-Ag and Au-Pd LAC. Reflectance peak of type-C Au-Ag LAC chain lies in visible range at 2.47 eV. While reflectance peak of type-C Au-Pd LAC is at 1.4 eV which is in near Infra-red region. The electronic band transitions at critical points contributes most to absorption peaks. This has been a useful tool to predict electronic properties of materials from absorption coefficient and reflectance spectra obtained from experimental data. Similarly, it is possible to find band transitions responsible for peaks appearing in $\varepsilon_2(\omega)$. The electronic transitions that correspond to majority of peaks in $\varepsilon_2(\omega)$ can be identified from band structure calculations by vertical lines labelled as 1,2 and 3 as is shown in figures 3.2, 3.3 and 3.4. In general, the transitions from hybridised orbital of d_{xy}, d_{yz}, d_{zx} and d_x^2 to a more dispersive s+dz^2 or empty bands, at higher energy, contributes to major peaks.

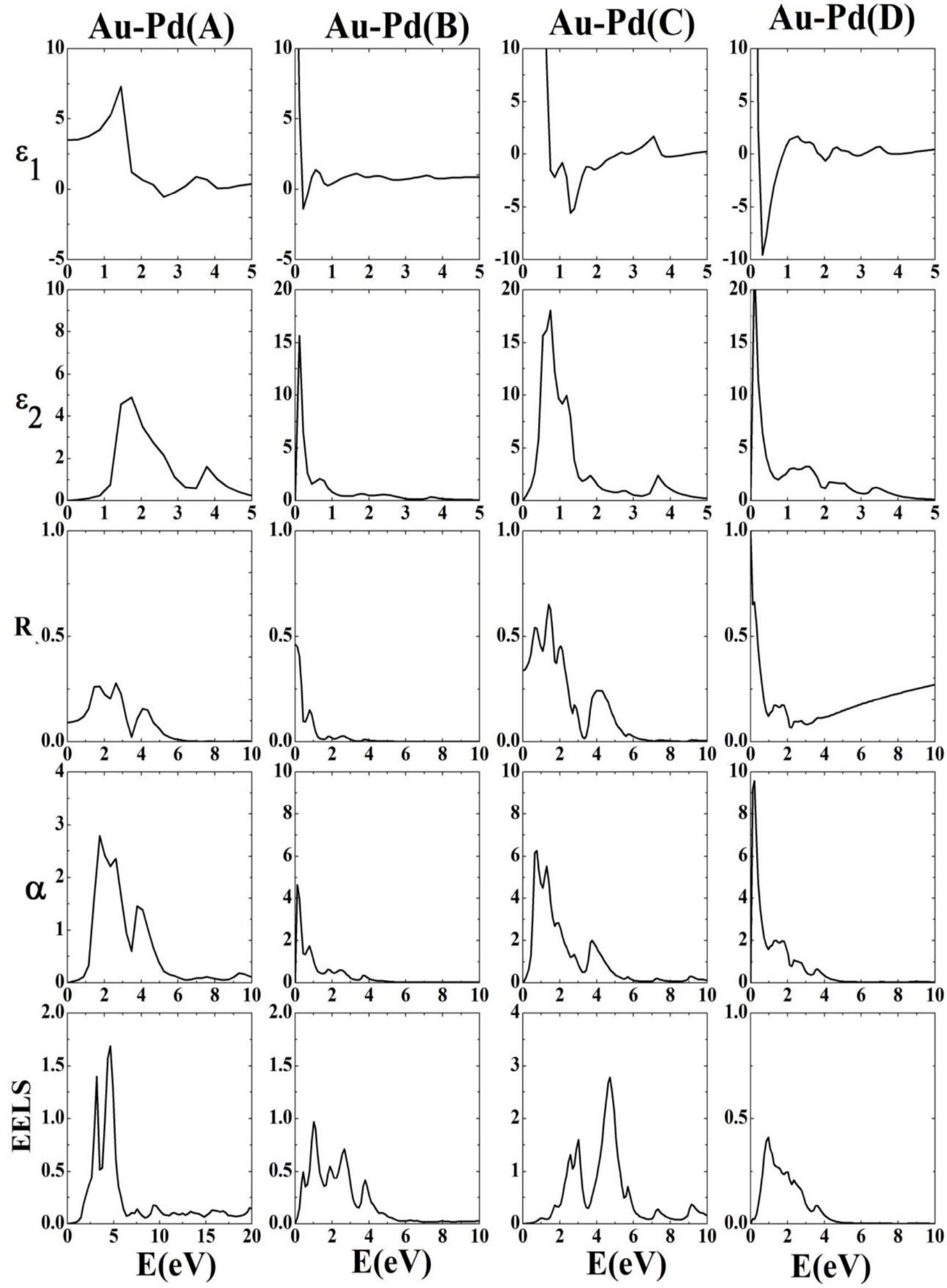

Figure 3.5: Computed real part $\varepsilon_1(\omega)$ and imaginary part of dielectric function, $\varepsilon_2(\omega)$,reflectance spectra, R(ω) absorption spectra, α(ω) and EELS spectra L(ω) of Au-Pd bimetallic LAC with different compositions A,B,C and D defined in Figure 3.1, are displayed as function of energy.

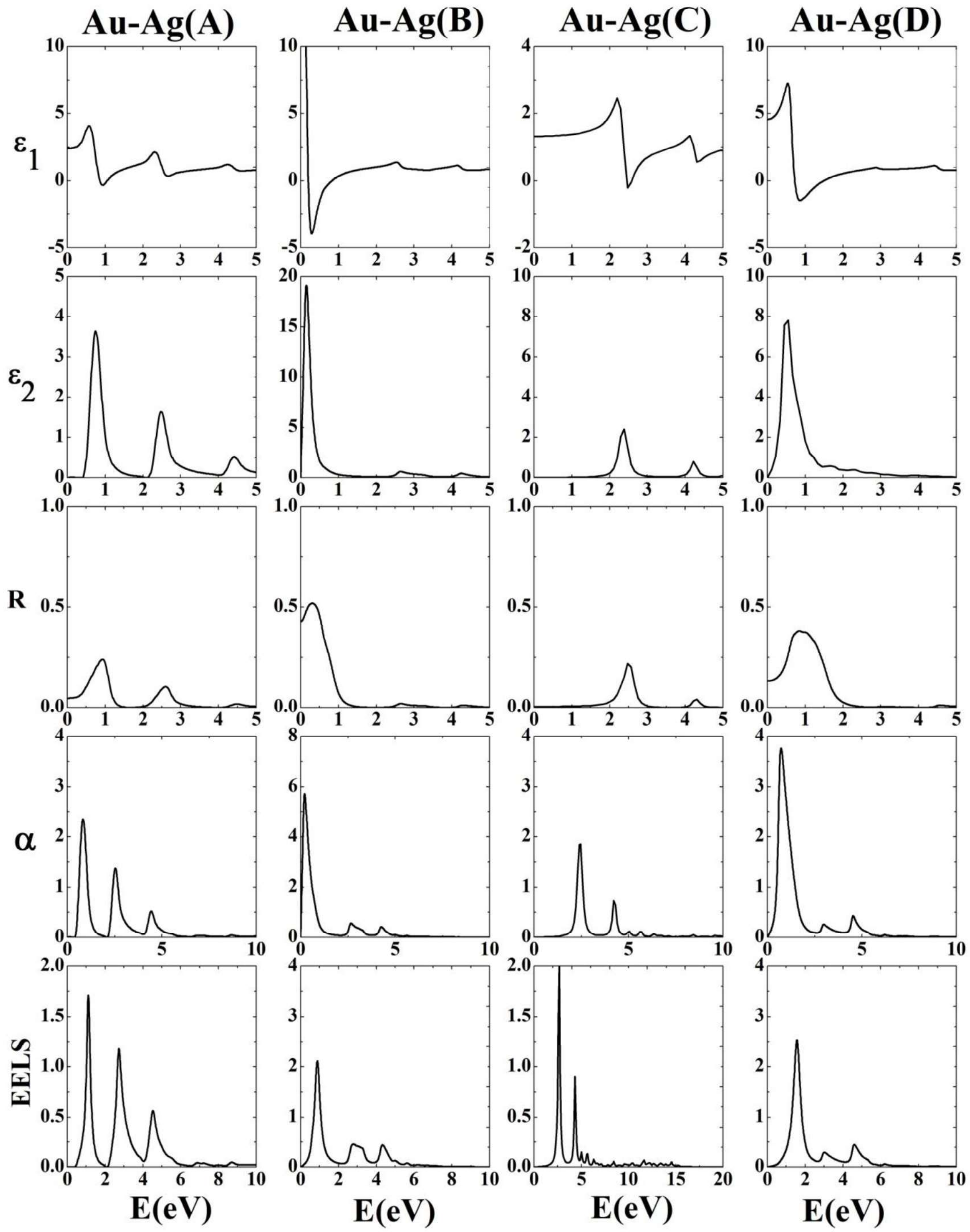

Figure 3.6: Computed real part $\varepsilon_1(\omega)$ and imaginary part of dielectric function, $\varepsilon_2(\omega)$,reflectance spectra, $R(\omega)$ absorption spectra, $\alpha(\omega)$ and EELS spectra $L(\omega)$ of Au-Ag bimetallic LAC with different compositions A,B,C and D defined in Figure 3.1, are displayed as function of energy.

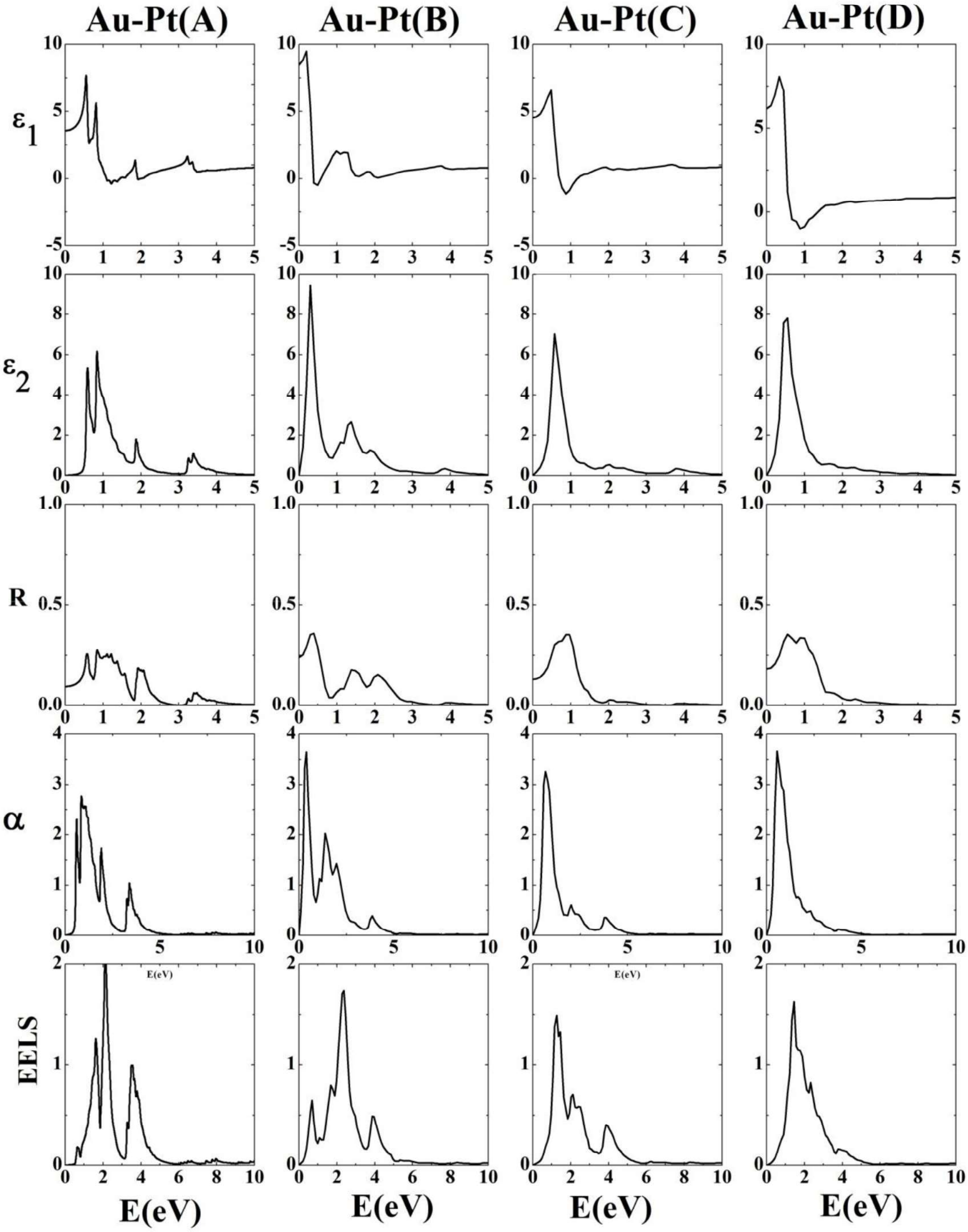

Figure 3.7: Computed real part ε1 (ω) and imaginary part of dielectric function, ε2 (ω),reflectance spectra, R(ω) absorption spectra, α(ω) and EELS spectra L(ω) of Au-Pt bimetallic LAC with different compositions A,B,C and D defined in Figure 3.1, are displayed as function of energy.

3.7 Conclusion

We analysed structure parameters, magnetic, electronic and optical properties of bimetallic linear atomic chains of Au-Pd, Au-Ag and Au-Pt. The bond length of bimetallic chains are found to be intermediate to bond lengths of pristine chains. Comparison of calculated cohesive energy of each structures shows that increase of Ag and Pd concentration to alloy chains of Au-Ag and Au-Pd weakens the relative stability of alloy chain. While increase of Pt concentration enhances the relative stability of the alloy chains. Spin polarized calculation of bimetallic chains reveals that all the compositions of Au-Pd and Au-Pt LAC are magnetic. The magnetic moment per atom increases with increase in number Pd atoms. However, such trend is not observed in case of Au-Pt chains where magnetic moment is least for D-type Au-Pt chains which have more number of Pt atoms in a unit cell. The electronic band structure and Density of state reveals that all the compositions studied here are conducting except type-A and type-B of Au-Ag linear atomic chains which shows semi conducting behaviour.

On comparison the band structures and optical properties of type C and D of bimetallic chains do not differ much. In other words, electronic and optical properties are less composition dependent than magnetic properties. Magnetic moment of type-C and type-D shows striking difference. Such analysis of composition dependence of different properties might be useful in experimental characterisation. Composition dependent peaks of reflectance spectra shows possibility of tuning optical properties. For most of the structures reflectance peaks lies in infra-red region except C-types of Au-Ag and Au-Pd LACs. Reflectance peak of Au-Ag and Au-Pd LAC lies in visible and near infra-red region respectively.