Structural, Electronic, Optical and Transport Properties of Pristine and Alloyed Ultrathin Nanowires of Noble Metals

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1 Introduction

In the last two decades, nanoscience and nanotechnology have initiated much interest in fundamental research of the properties of nanomaterials and their industrial applications. As a result nanostructured materials as a foundation of nanoscience and nanotechnology, have become the hottest topics of research [2, 3, 49, 147]. Normally, nanostructures are defined as the structures with at least one dimension less than 100 nm. In this dimension, the number of atoms are countable, making the properties of nanostructures different from those of their bulk counterparts due to distinct density of states (DOS) and increased surface to volume ratio. According to the number of dimensions less than 100 nm, nanostructures can be classified into two-dimensional (2D, nanofilm), one-dimensional (1D, nanotube or nanowire), and zero-dimensional (0D, quantum dot) structures.

1.1 One-dimensional nanostructures

In a 1D nanostructure there is a confinement in two dimensions perpendicular to the longitudinal extent of the structure. This confinement is quantum mechanical in nature. Due to the combination of both quantum confinement in the nanoscaled dimensions and the bulk properties in the third dimension, many interesting properties and applications can be expected based on a wide variety of 1D nanostructures. Also it has been observed [1] that 1D nanostructures represent the smallest dimension structure that can efficiently transport electrical carriers and can be exploited as both the wiring and device elements in future architectures for functional nanosystems.

Depending on the topology and morphology, the 1D nanostructures can be classified into following main groups:

- Nanotubes [3].
- Nanowires [4, 5].
- Coaxial cable structures [6].
- Side-by-side biaxial nanowires [7].
- Nanobelts (or nanoribbons) [8].

The first three nanostructures listed above have a common characteristic of cylindrical cross section, biaxial nanowires have the stacking of two parallel nanowires of different materials and nanobelts have a rectangular cross section (belt like morphology). The distinctive geometrical shapes of these 1D nanostuctures are important as their mechanical, electrical, optical, and thermal transport properties are geometry dependent. To investigate the uniqueness offered by these shapes, new techniques have been developed to measure the properties of individual wire-like structures quantitatively and their structures are well characterized by electron microscopy techniques [2].

1.2 Review of Literature

The quantum confined nanowires have a wide range of applications in electronics [60–69], optoelectronics [10–13], thermoelectrics [70, 71], optics [62, 72, 73], chemo and bio-sensing [18, 21, 25–27, 74, 75, 77], magnetic media [78–85], photocatalysis [30–32] and piezoelectronics [33–39] **etc**. As a result of the rapid progression of modern nanoelectronics, nanowires (NWs) have begun to draw the attention of researchers in cross disciplinary areas of physics, chemistry and engineering. In nanoelectronics, nanowires can function as interconnects in the fabrication of integrated circuits [64, 65], resonators [66–69], diodes [9–13, 60], light emitting diodes (LED) [61], multifunctional devices [63], logic gates [18–23] using nanowire field-effect transistors (NW-FETs) [62] and single electron transistors [24]. Their small size and their high electrical conductivity makes them very attractive for applications in nanoelectronics [76].

Sensing is another area in which the application of nanowires is expected to have a great impact. Nanowire sensors have been reported, that can detect the presence of many gases like O_2, NO_2 and NH_3 [74] at very low concentrations. Nanowires also have been used for the detection of ultraviolet light [75] as well as highly sensitive biological and chemical species [77]. These sensors often function on the basis of changes in the electrical or physical properties of the nanowires when they come in contact of targeted chemical/biological [74–76] species. The sensing capabilities of nanowires can be controlled by selective doping that raises their affinities to certain substances. Also the nanowires of noble metals particularly have been used as barcode tags for optical read out [86, 87]. Single-crystalline NW have also been used in batteries [47], solar cells [48] and photoelectrochemcal cells [31] for effective charge separation and collection.

In these areas, NW structures exhibit unique and superior properties compared to their bulk counterparts, resulting from 1D confined transport of electrons or photons, large surface area, quantum confinement, and excellent mechanical properties [40–46].

In recent years, long metallic nanowires with well defined structures and a diameter of several nanometers have been fabricated using different methods [88–91]. For example, stable gold nanobridge with 0.8-3 nm in thickness and 5-10 nm in length has been produced by electron beam irradiation of gold (001) oriented thin film [88]. Also suspended gold nanowire with 6 nm in length

and diameter down to 0.6 nm have been made and the novel multishell structure were observed [91]. In 1998, Ohnishi *et. al.* [53] used scanning tunneling microscope and Yanson *et. al.* [54] through mechanically break-junction experiments produced atomically thin bridge of gold atoms and calculated the conductance equal to $G_o = 2e^2/h$ and the interatomic distance was reported as 2.6 $\mathring{A}$ [92]. The break-junction experiments have also been performed for Ag [55], Cu [52] and Pt [52] chains, with conductance nearly $1G_o$ ($G_o = \frac{2e^2}{h}$) for Cu, Ag and Au and $1.5G_o$ to $2.5G_o$ for Pt chains.

Noble metal nanowires, which is the subject matter of the proposed work, have been drawing a great deal of attention due to their significantly different structural, electronic, magnetic, optical and transport properties compared to their bulk manifestation [49, 50]. The increased surface to volume ratio and increased density of states (DOS) makes them different from their corresponding bulk materials. Also the DOS does not vanish at subband edges and remain finite. This makes these materials an interesting and exciting subject to explore optical properties. Noble metal nanowires, particularly, can also be used to create materials that exhibit negative index of refraction in the near-infrared region [51]. The finite monoatomic chains of noble metals can be produced by mechanical break junction experiments [52–55] for Cu, Ag, Au and Pt chains. Many innovative experimental studies on one dimensional systems [53,54,56,57], revealing their fascinating properties, have boosted related theoretical research. Depending upon the type of structure, the electronic, magnetic, optical and transport properties of these systems show interesting variations [58, 59].

Very few studies have been made of the properties of metal alloys at the atomic scale (alloyed metal nanowires) [93–98]. In 2002 and 2003, point contact studies were made of random alloys of a transition metal and a noble metal, namely gold and palladium [93], copper and nickel [94] and gold and platinum [96] for different concentration ratios. In these experiments peak has been found at $1G_o$, that is characteristic of the noble metals, survives for transition metal concentrations well over 50%. The interpretation for this observation requires further study. There is an evidence for segregation of the noble metals away from the contact under the application of a high bias current [98].

2 Theoretical Background

The universe around us is made of condensed matter *i.e.* matter whose energy is low enough that it gets condensed to form stable system of atoms and molecules usually in solid or liquid phases. These atoms and molecules are further made up of electrons and nuclei. The quantum mechanics has proven to be the best formulation to describe interacting system of electrons and nuclei. The Schrödinger equation is the fundamental quantum mechanical equation that describes a system of electrons and nuclei in terms of wave function ψ, which is fundamental entity in quantum mechanics.

The systems under study are indeed many electron systems and for a multi-electron system the Schrödinger wave equation can be written as:

$$\left(-\frac{\hbar^2}{2m_e}\sum_i \nabla_i^2 - \frac{\hbar^2}{2M_A}\sum_A \nabla_A^2 + \sum_{A>B}\frac{Z_A Z_B e^2}{4\pi\epsilon_o R_{AB}} + \sum_{i>j}\frac{e^2}{4\pi\epsilon_o r_{ij}} - \sum_{Ai}\frac{Z_A e^2}{4\pi\epsilon_o r_{Ai}}\right)\psi = E\psi$$

Here i and j are indices used for electrons and A and B are the indices used for nuclei. On the left hand side of above equation first two terms represent the kinetic energy of electrons and nuclei respectively and the following terms describe the inter-nuclear, electron-electron and electron-nuclear Coulomb interaction energies respectively. If we use atomic units *i.e.* ($e = m_e = \hbar = 4\pi\epsilon_o = 1$), the Schrödinger equation becomes

$$\left(-\frac{1}{2}\sum_i \nabla_i^2 - \frac{1}{2M_A}\sum_A \nabla_A^2 + \sum_{A>B}\frac{Z_A Z_B}{R_{AB}} + \sum_{i>j}\frac{1}{r_{ij}} - \sum_{Ai}\frac{Z_A}{r_{Ai}}\right)\psi = E\psi \quad (1)$$

The ultimate aim of any physicist or a chemist for a typical system is to solve this equation.

However, as Paul Dirac at the dawn of theoretical quantum mechanics has said that all the answers of chemistry could be calculated from schrödinger equation [103], but it is the most challenging task to solve this equation analytically. Unfortunately the schrödinger equation can be solved exactly for only a few systems such as hydrogen atom and even numerically to systems containing small number of electrons [102].

2.1 Approximations

To solve the equation (1) one uses various approximations, which do not significantly affect the involved physics of the system under study and facilitate meaningfully the study of variety of many body problems.

2.1.1 Born-Oppenheimer approximation

One of the most simplifying approximation is based upon the idea that mass of electron is much smaller than that of the nucleus and thus electrons move much more rapidly than nucleus. Thus for a given set of positions of nuclei, electrons adjust almost immediately to movement of nuclei. This is known as **Born-Oppenheimer approximation** [99]. In other words we can say that forces on both electrons and nuclei due to their charge are of same order of magnitude, so changes which occur in their momenta as a result of these forces must also be of the same magnitude. But since nuclei are much more massive than electrons so accordingly they have much smaller velocities. While solving the schrödinger equation given by equation (1), one can assume that nuclei are stationary and solve it for electronic ground state first and then calculate the energy of the system in that configuration and then later solve for nuclear motion. This helps to separate the electronic and nuclear motion. Furthermore, this allows us to separate the wavefunction as a product of nuclear and electronic terms. The electronic wave function $\phi_e(r, R)$ is solved for a given set of nuclear coordinates

$$\hat{H}_e\phi_e(r,R) = \{-\frac{1}{2}\sum_i \nabla_i^2 - \sum_{A,i}\frac{Z_A}{R_{Ai}} + \sum_{i>j}\frac{1}{r_{ij}}\}\phi_e(r,R)$$
$$= E_e(R)\phi_e(r,R) \quad (2)$$

and the electronic energy obtained contributes a potential term to the motion of nuclei described by the nuclear wave function $\phi_N(R)$.

$$\hat{H}_N\phi_N(R) = \{-\sum_A \frac{1}{2M_A}\nabla_A^2 + E_e(R) + \sum_{A>B}\frac{Z_A Z_B}{R_{AB}}\}\phi_N(R)$$
$$= E\phi_N(R) \quad (3)$$

2.1.2 Independent Electron Approximation

Another approximation called independent electron approximation [120] which assumes electrons to be non-interacting with each other has quantum manifestation because electrons obey Pauli's exclusion principle. This manifestation of Pauli's exclusion principle resulted in Hartree-Fock method and allows one to express total Hamiltonian for N-electron system (H) as summation of single electron Hamiltonian (H_i) i.e. $H = \sum_i H_i$ and total wave function as Slater determinant of single electron wave functions. The slater determinant approximation does not take into account Coulomb Correlation leading to a total electronic energy different from the exact solution of non-relativistic Schrödinger equation within Born-Oppenheimer Approximation. Therefore, Hartree-Fock Energy is always above the exact energy. This difference is called the *Correlation Energy*, a term coined by Löwdin [100].

2.2 Density Functional Theory: An *Ab initio* Approach

To overcome the difficulty of correlation energy and problem of 3N variables, a new approach **'Density Functional Theory (DFT)'** was adopted for electronic structure calculations. In 1964 Hohenberg and Kohn, showed in a conference paper [101] that schrödinger equation (for N electron system containing wave function of 3N variables) could be reformulated as an equation of electron density with only three variables. This theory gives approximate solutions to both Exchange and Correlation Energies. The main objective of DFT is to replace the many-particle electronic wavefunction with the electronic density as the basic quantity. Our interest is in solving Schrödinger's equation by means of *ab initio* Density Functional Theory (DFT) as described below.

The term *Ab initio* used here originates from Latin word which means 'from the beginning'. A method is said to be *Ab initio* or from first principles if it relies on basic and established laws of nature without additional assumptions or special models based upon particular material. Density functional theory (DFT) is an extremely successful *ab initio* approach to compute properties of matter at microscopic scales. DFT is a quantum mechanical modelling method used in physics to investigate the electronic structure (principally the ground state) of many-body systems, in particular atoms, molecules, and the condensed phases (bulk, surfaces, chains).

The fundamental pillars of density functional theory are two physical theorems proved by Kohn and Hohenberg [101,118,119]. The first Hohenberg Kohn (HK) theorem states that: The ground-state energy from Schrödingers equation is a unique functional of the electron density. This theorem provides one to one mapping between ground state wave function and ground state charge density. The first HK theorem is stated as: the ground state charge density can uniquely describe all the ground state properties of system. The fundamental concept behind density functional theory is that charge density (3-Dimensional) can correctly describe the ground state of N-particle instead of explicit usage of wave function (3N-Dimensional) [117]. Thus by using charge density instead of wave functions a 3N dimensional problem reduces to just a three dimensional problem.

The second HK theorem states that: The electron density that minimizes the energy of the overall functional is the true electron density corresponding to the full solution of the Schrödinger equation. If the true functional form of energy in terms of density gets known, then one could vary the electron density until the energy from the functional is minimized, giving us required ground state density. This is essentially a variational principle and is used in practice with approximate forms of the functional designed by quantum chemists/physicists to study different types of systems [120]. The simplest possible choice of a functional can be a constant electron density all over the space.

The total charge density can be written in terms of single particle wave functions as:

$$n(r) = \sum_{\mu} \psi_{\mu}^{*}(r)\psi_{\mu}(r) \tag{4}$$

An important step towards applying DFT to real systems was taken by Kohn and Sham in 1965 in the form of Kohn-Sham (KS) [119] equations. The Kohn-Sham equation reformulate the Schrödinger equation of interacting electrons moving in an external ion potential into a problem of non interacting electrons moving in an effective potential. The KS equations are defined by a local effective external potential (called Kohn-Sham potential) in which the non-interacting particles move. The Kohn-Sham equations have the form

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V_{\text{eff}}(\mathbf{r})\right)\psi_{\mu}(\mathbf{r}) = \varepsilon_{\mu}\psi_{\mu}(\mathbf{r}) \tag{5}$$

where

$$V_{\text{eff}}(\mathbf{r}) = V(\mathbf{r}) + V_{\text{H}}(\mathbf{r}) + V_{\text{XC}}(\mathbf{r}) \tag{6}$$

The contribution to the total energy here gets divided into two parts. The first part contains terms: the kinetic energy ($-\frac{\hbar^2}{2m}\nabla^2$), the hartree potential energy ($V_{\text{H}}(\mathbf{r})$) and classical Coulomb energy ($V(\mathbf{r})$) and second part contains the exchange correlation energy ($V_{\text{XC}}(\mathbf{r})$) which includes many body and quantum effects. It is customary to divide the exchange correlation into exchange part (for which there exists an exact expression although computationally expensive to calculate) and correlation part (which is unknown).

Kohn and Sham introduced a set of orbitals from which electron density can be calculated. These Kohn -Sham orbitals do not in general correspond to actual electron density. The only connection the Kohn-Sham orbitals have to the real electronic wave function is that they both give rise to the same charge density. To calculate the kinetic energy term, the Kohn-Sham orbitals are used as shown below:

$$T_s[\rho] = \sum_{i=1}^{N} \int d\mathbf{r}\ \psi_\mu^*(\mathbf{r}) \left(-\frac{\hbar^2}{2m} \nabla^2 \right) \psi_\mu(\mathbf{r}) \tag{7}$$

On the right-hand side of equation (6) there are three potentials, V, V_H, and V_{XC}. The first potential defines the interaction of an electron with different atomic nuclei present which is basically Coulomb potential. One takes care of this term with the help of a trick which replaces Coulomb potential by a *Pseudopotential* [120]. It is well known that since core electrons do not participate in bond formation, it was natural to assume that they can be replaced with a pseudo core. That means we have to deal with fewer number of electrons (valence electrons). Thus a pseudopotential is an approximation for the full core potential. How good a pseudopotential is, infact successful for the generated pseudopotential decided by how well it reproduce the results from all electron calculations. The effort in generating a pseudopotential lies in the fact that, all electron wave function must match with the pseudo wave function after a certain cut off radii.

The second potential is called the Hartree potential. This potential describes the Coulomb repulsion between the electron being considered in one of the Kohn-Sham equations and the total charge density defined by all electrons in the problem. The Hartree potential includes a so called self-interaction contribution because the electron we are describing in the Kohn-Sham equation is also part of the total electron density, so part of V_H involves a Coulomb interaction between the electron and itself. The self interaction is unphysical, and the correction for it is one of several effects that are lumped together into the final potential in the KS equations, V_{XC}, which defines exchange and correlation contributions to the single electron equations.

To solve KS equation we need Hartree potential which depends upon the charge density of the system and to know the charge density we need the single particle wave functions, which can be obtained only after solving KS equations. Thus the problem reduces to solving a set of self consistent equations. They are solved in an iterative way by starting with a trial set of single particle wave functions from which Hartree potential is obtained. The solution obtained in this way is called self consistent solution. The algorithm used to solve it is as given in figure 1.

2.3 Local Density Approximation(LDA)

The most important potential term in KS equations is V_{XC} [103] which is used to describe exchange and correlation effects. Unfortunately, exact form of the

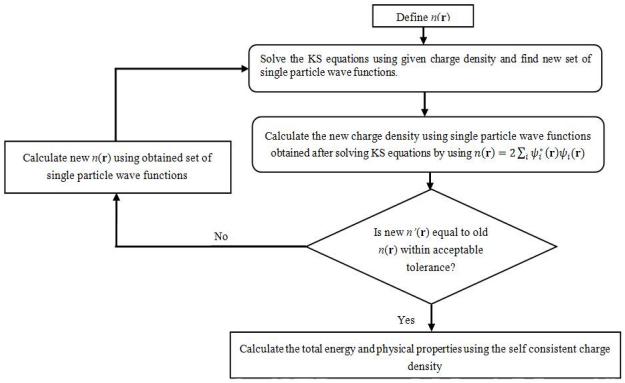

Figure 1: Algorithm to solve Kohn Sham equations in DFT Codes

exchange correlation functional whose existence is ensured by the Hohenberg-Kohn theorem is not known. There is only one case of uniform electron gas where this functional can be derived exactly as the electron density is constant at all points in space. Therefore, the exchange-correlation potential at each position is set to be obtained from the electron density observed at that position. Since this approximation uses only the local density to define the approximate exchange correlation functional, so it is called the local density approximation (LDA) [121]. Although, LDA gives a way to completely define the Kohn-Sham equations, but these equations do not exactly solve the true Schrödinger equation because the true exchange correlation functional are not being used rather are always approximately known.

2.3.1 Beyond LDA

Apart from LDA, many other functionals tailored to explain properties of particular systems have been tried for DFT calculations. After LDA, the best known class of functional that has been defined is generalized gradient correction (GGA). GGA uses information about the local electron density and also the local gradient in the electron density [122]. Though GGA includes more physical information than LDA, it is not necessary that it must be more accurate. There are a large number of distinct GGA functionals depending on the ways in which information from the gradient of the electron density can be included in a GGA functional.

2.3.2 Choosing a Functional

The choice of the functional is the main issue in DFT. The functionals which use LDA are CA (Ceperley-Alder) [123] and PW92 [121] (Perdew-Wang-92) and the functionals which use GGA are PBE [122] (Perdew-Burke-Ernzerhof), revPBE [124] (Revised Perdew-Burke-Ernzerhof), PBEsol [125] (Perdew-Burke-Ernzerhof for solids). The most popular functionals are pure density functionals and hybrid functionals. Altough LDA and GGA are very useful but have problems in certain applications. The main problems with LDA and GGA are the underestimation of band gaps, failure to describe localized electrons in both solids and molecules, absence of Vander Waals interactions, *etc.* [126].

2.3.3 Choosing a Wavefunction

There is another very important aspect of Kohn-Sham equation which lies in its solution described by wave function $\psi_\mu(\mathbf{r})$, which arises when one sets up a simulation. The important question is how does one represent the wavefunction inside the supercell. The wave function of the full macro-lattice is obtained by combining these via Bloch functions [127] (k-point sampling). This is known as basis set [120]. There are four main groups of basis sets used in literature namely: plane wave [120], Gaussian [128], augmented [129] and numerical basis set [130–132] and is the starting point of the solution of Kohn-sham equation. The choice of numerical basis sets makes DFT applicable for realistic large systems.

Atomic orbitals as a basis set have been used for a long time in the electronic structure calculations of molecules and bulks. Especially, in covalent molecular systems, one particle wave functions are well described by a linear combination of atomic orbitals (LCAO) [130] because of the nature of localization in the electronic states, which is a reason why chemists prefer to use the atomic orbitals. On the other hand, in the solid-state physics, LCAO has been regarded as a somewhat empirical method such as a tool for an interpolation of electronic structure calculations with a high degree of accuracy. However, during the last decade, LCAO has been attracting much interest from different points of view, since great efforts have been made not only for developing order N (O(N)) methods of the eigen value problem, but also for making efficient and accurate localized orbitals as a basis set being suitable for O(N) [130–132] methods to extend the applicability of density functional theories (DFT) to realistic large systems. Once atomic orbitals are chosen one can expand a Kohn-Sham (KS) orbital ψ_μ of a given system using these atomic orbitals $\phi_{i\alpha}$ in a form known as linear combination of atomic orbitals (LCAO) as:

$$\psi_\mu(\mathbf{r}) = \sum_{i\alpha} c_{\mu,i\alpha}\phi_{i\alpha}(\mathbf{r} - r_i) \tag{8}$$

where i is a site index, $\alpha \equiv (plm)$ is an organized orbital index, and $\phi_{i\alpha}(\mathbf{r}) \equiv Y_{lm}(\theta,\phi)R_{ipl}(\mathbf{r})$. Here R_{ipl} is the radial wave function, which depends on angular momentum quantum number l, site index i, and a multiplicity index p and Y_{lm} spherical wave function. The spherical wave function is well defined (fixed shape), also one can play with shape (number of atomic orbitals per atom), range (spatial extension of the orbitals) and shape of the radial part of wave function.

Density functional theory of electronic structure is widely and successfully applied in simulations throughout engineering and sciences. However, for many predicted properties, there are known failures [103] that can be traced to the delocalization error and static correlation error of commonly used approximations. A clear understanding of the errors from the most basic principles has enabled the development of functionals to open new frontiers for applications of DFT.

2.4 DFT and Structural Properties

The most basic type of DFT calculation is the computation of the structural properties of the system under study. One can begin with electron density, then use the trial density to define the effective potential. The Kohn-sham equations with this effctive potential are solved self consistently till self consistent solution for electron density is obtained as stated earlier. The electron density so obtained has been used to calculate the ground state energy for a given system. One can use various methods for structure optimization. Congugate gradient is one such structure optimization method. In these calculations one can allow the position of atoms to change keeping the shape of the supercell constant or can allow both atoms and supercell to change. The structure corresponding to minimum energy tell us about the structural parameters (for example lattice type, lattice constant, bond length, bond angle *etc.*).

2.5 DFT and Electronic Properies

One of the primary quantities used to describe the electronic state of a material is the electronic density of states (DOS):

$\rho(E)dE = number\ of\ electronic\ states\ with\ energies\ in\ the\ interval\ (E, E+dE)$

Once the DFT calculations have been performed, the electronic DOS can be determined by integrating the resulting electron density in k-space. There is another very important electronic property known as band structure, that can also be estimated using DFT. The DFT does not gives us exact band structure, but gives us Kohn-Sham band structure. The Kohn-Sham band structure is generally one-electron band structure and which is the dispersion of the energy levels n as a function of k in the Brillouin zone. The Kohn-Sham eigenvalues and eigenstates are not one-electron energy states for the electron in the solid. However, it is common to interpret the solutions of Kohn-Sham equations as one-electron states: the result is often a good representation, especially concerning band dispersion. The main problem with the band structure is the underestimation of band gap. Band gap error is not due to LDA, but can be attributed to the discontinuity in the exact Vxc [104–107]. DFT is, in principle, an exact theory to reproduce and predict ground state properties (*e.g.*, the total energy, the atomic structure, etc.). However, DFT is not a theory to address excited state properties, such as the band plot of a solid. Hence, in principle, Kohn-Sham based DFT is not a band theory, i.e., not a theory suitable for calculating bands and band-plots. In principle time-dependent DFT can be used to calculate the true band structure although in practice this is often difficult.

2.6 DFT and Dielectric Properties

DFT also have been used to perform dielectric properties calculations of materials. The formula used for calculating dielecric function [108, 110, 111] was given as:

$$\epsilon(\omega, q) = 1 + \frac{8\pi e^2}{\Omega q^2} \sum_{k,n,m} \frac{|\langle \mathbf{k+q}, n|e^{iqr}|\mathbf{k}, m\rangle|^2 (f_{\mathbf{k},m} - f_{\mathbf{k+q},n})}{E_{\mathbf{k},m} - E_{\mathbf{k+q},n} + \hbar\omega + i\delta} \tag{9}$$

where $E_{\mathbf{k},n}$, $f_{\mathbf{k},n}$ and $|\mathbf{k},n\rangle$ are the band energies, fermi distribution function and Kohn-Sham eigenfunctions. These are calculated via band structure calculations within density functional theory (DFT). For metals we split the dielectric function into two parts interaband contribution (taking $\mathbf{q} \to 0$) and interband contribution [109, 110]. Using this dielectric function becomes

$$\begin{aligned}\epsilon(\omega) &= \epsilon^{intra}(\omega) + \frac{8\pi e^2\hbar^2}{3m^2(2\pi)^3}\int d\mathbf{k}\sum_{n\neq m}\frac{2f_{\mathbf{k},n}(1-f_{\mathbf{k},m})|\langle\mathbf{k},n|\mathbf{p}|\mathbf{k},m\rangle|^2}{(E_{\mathbf{k},m}-E_{\mathbf{k},n})\left[(E_{\mathbf{k},m}-E_{\mathbf{k},n})^2-(\hbar\omega)^2+i\delta\right]} \\ &= 1-\frac{\omega_p^2}{\omega(\omega+i\tau^{-1})} \\ &+ \frac{8\pi e^2\hbar^2}{3m^2(2\pi)^3}\int d\mathbf{k}\sum_{n\neq m}\frac{2f_{\mathbf{k},n}(1-f_{\mathbf{k},m})|\langle\mathbf{k},n|\mathbf{p}|\mathbf{k},m\rangle|^2}{(E_{\mathbf{k},m}-E_{\mathbf{k},n})\left[(E_{\mathbf{k},m}-E_{\mathbf{k},n})^2-(\hbar\omega)^2+i\delta\right]} \qquad (10)\end{aligned}$$

Here $\mathbf{p}$ is the momentum operator, τ is the relaxation time and ω_p is the plasma frequency. Plasma frequency is related to the fermi velocity, integrated over the fermi surface

$$\omega_p^2 = \frac{8\pi e^2}{3\Omega}\sum_{\mathbf{k},n}|\frac{1}{\hbar}\frac{\partial E_{\mathbf{k},n}}{\partial\mathbf{k}}|^2\ \delta(E_{\mathbf{k},n}-E_F) \qquad (11)$$

The interband part of $\epsilon_2(\omega)$ is calculated from equation (10) and $\epsilon_1(\omega)$ follows using Kramers-Kroning transformations [146] as shown below.

$$\epsilon_1(\omega) = 1 + \frac{2}{\pi}P\int_0^\infty \frac{\omega'\epsilon_2(\omega')}{\omega'^2-\omega^2}d\omega' \qquad (12)$$

here P denotes the principal value.

2.7 DFT and Transport Properties

Density functional theory has found its application to study non equilibrium electron transport [112] also. DFT methods in transport study in general are limited to two aspects:

- the geometry is restricted to either finite or periodic systems and
- electronic system must be in equilibrium.

DFT also give us the information about the electron density and total energy of the system. To study the non equilibrium electron transport, one uses total electron density and Kohn-Sham wave functions as calculated using DFT. Also to study electron transport, the model must be able to describe the non equilibrium situation and also it must be capable of treating an infinite and non periodic system.

Consider a situation as shown in figure 2. Two semi infinite electrodes, left (L) and right (R) are coupled via contact region (C). The main challenge is that how to couple the finite contact to infinite electrodes. The solution is the green functions at zero bias voltage (*i.e.* equilibrium). In case when there is non-equilibrium situation *i.e.* when potential is applied or two electrodes at different chemical potentials, then non-equilibrium formulation of green functions [112–116] is used.

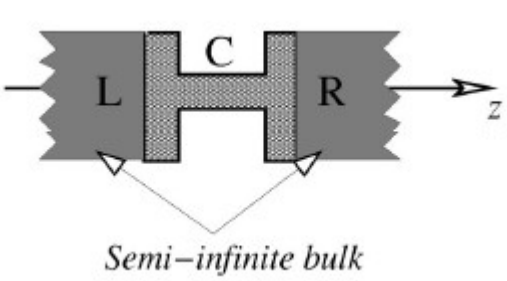

Figure 2: A model to study transport properties

3 Computational Method

Today many open source and proprietary computer codes are available which provide a way to calculate and study various properties of materials using density functional theory. These codes differ in terms of their implementations used to solve KS equations. Depending on how atomic electrons are treated they are termed as full potential (FP-Wien2k [133] and ELK [134]), pseudopotential (SIESTA [135], CASTEP [136]), atomic sphere approximation (ASA-SPRKKR [137]) or Muffin tin (LMTO [138]) based. They are also classified depending upon what basis set is used to expand wave function. Various methods use plane wave (PW: Quantum Essperso, ABINIT, VASP, CASTEP), augmented plane wave (APW: ELK, Wien2k, EXCITING) or localised atomic orbitals as basis sets (SIESTA, FPLO) [139]. We in our study of nanowires have decided to use SIESTA (*Spanish Initiative for Electronic Simulations on Thousands of Atoms*) code which is an open source code, using atomic orbitals and is very efficient, easy to run on a quad core machine in parallel mode. In the following, is given a brief description of SIESTA code which we are using to calculate the structural, electronic, optical and transport properties of Nanowires using DFT.

3.1 SIESTA Code

SIESTA (*Spanish Initiative for Electronic Simulations on Thousands of Atoms*) is a calculation method and computer code which solves problems of condensed matter using density functional theory (DFT). These problems are, generally, related to ground-state properties. Energy/volume curves, phase diagrams (e.g., magnetic ones), phonons are all related to ground-state structural properties and *ab initio* molecular dynamics. It uses norm-conserving pseudopotentials in their fully nonlocal (Kleinman-Bylander) form. As stated above atomic orbitals are used as a basis set, allowing inclusion of unlimited multiple-zeta and angular momenta, polarization and off-site orbitals. This is an efficient code to perform DFT calculations on systems containing large number of atoms.

SIESTA falls into category of methods with atom-centered basis sets. It means that it allows choice of big unit cell volumes. For doing calculations with large systems, we have to only optimize basis set.

3.2 Possibilities with SIESTA

SIESTA can be used to study the structural (lattice constant, bulk modulus, cohesive energy, phonon spectrum), electronic (band structure, DOS), magnetic (magnetic moment) and optical (real and imaginary part of dielectric function) properties of Bulk materials, surfaces, clusters, CNT, nanowires, liquids (radial distribution function), biomolecules. It can also be used to study the transport properties of nanosystems at zero bias voltage and at some finite bias voltage. In other words we can say that SIESTA is a very efficient method and a tool to study various properties of condensed matter.

3.3 Structural Properties using SIESTA

Several options for structural optimization have been implemented in SIESTA. CG [140](Coordinate optimization by conjugate gradients), Broyden [141] (Coordinate optimization by a modified Broyden scheme) and FIRE (Coordinate optimization by Fast Inertial Relaxation Engine (FIRE) [142]. These different relaxation methods moves the atoms (and optionally the cell vectors) trying to minimize the forces (and stresses) on them. One can calculate the structural parameters (lattice constant, bond length and bond angle with the help of visualization code known as Xcrysden [143]) of the relaxed structure

3.4 Electronic Properties using SIESTA

The band structure calculations have been performed after the geometry optimization. k-mesh is a very important parameter for doing band structure calculations. However one needs to check the convergence, in terms of gradually increasing the k-mesh density.

3.5 Dielectric Properties using SIESTA

Other important feature of SIESTA code is to study dielectric properties of the materials. The dielectric properties calculations in the code is performed by using first-order time-dependent perturbation theory [144, 145] to find the dipolar transition matrix elements between occupied and unoccupied single-electron eigenstates as implemented in SIESTA, in which the exchange and correlation effects are taken care of by plugging, the self consistent ground state DFT energies and eigenfunctions into the dipolar transition matrix elements. Thus the imaginary part of the dielectric function ϵ_2 is obtained, which can be further used to calculate real part ϵ_1 of dielectric function and reflectance spectra with the help of Kramers-Kronig transformations [146]. The electron energy loss spectra (EELS) can be calculated from real and imaginary parts of dielectric functions as

$$Im\left\{-\frac{1}{\varepsilon(\omega)}\right\} = \frac{\varepsilon_2(\omega)}{\varepsilon_1^2(\omega)+\varepsilon_2^2(\omega)} \tag{13}$$

.

Using real and imaginary part of dielectric function, other optical properties like refractive index (n), extinction coefficient(κ), reflectance (R) *etc.* can also be calculated using following relations:

$$n = \sqrt{\frac{\sqrt{\epsilon_1^2 + \epsilon_2^2} + \epsilon_1}{2}}$$
$$\kappa = \sqrt{\frac{\sqrt{\epsilon_1^2 + \epsilon_2^2} - \epsilon_1}{2}}$$
$$R = \frac{n + i\kappa - 1}{n + i\kappa + 1} \tag{14}$$

3.6 Transport Properties using SIESTA

One of the most interesting features of SIESTA is availability of a module to calculate transport properties particularly of nano-systems, known as TranSiesta. It is based on DFT and Non-equilibrium Green Function [112,114,115] (NEGF) method which can be used for both structure relaxation and conductance calculations. Using TranSiesta, one can calculate electronic transport properties such as, zero bias conductances and the I-V characteristics, of a nanoscale system in contact with two electrodes at different electrochemical potentials. Here density functional theory (DFT) is used for the electronic structure calculations and then combined with non-equilibrium Greens function (NEGF) theory for the quantum transport. Various steps used by TranSIESTA are as follows:

- Calculation of the bulk electrodes, to get H (hamiltonian), charge density (ρ), and Self-energies.
- Calculation for the open system
    1. Reads the electrode data.
    2. Builds H from ρ.
    3. Solves the open problem using Non-equilibrium Greens Functions.
    4. Builds new ρ.
    5. If ρ self consistent, then stop, otherwise go to step 2.
- Postprocessing tool, which computes T(E), I and V.

In other words we can say that this method is based on non equilibrium Greens functions (NEGF), that are constructed using the density functional theory Hamiltonian obtained from a given electron density. A new density is computed using the NEGF formalism, which closes the DFT-NEGF self consistent cycle.

4 Motivations and Research Objectives

The structural, electronic and magnetic properties of transition metals and noble metals NWs (free standing) with different topologies (linear, ladder, zigzag, double zigzag) [147–151] have been studied extensively in the past. But there is a dearth of reports on optical properties. These properties can prove to be a useful tool in analyzing the electronic properties of bulk and low-dimensional

structures. Also their study equips one with a better understanding of the electronic structure. Literature shows that the optical studies have mainly concentrated on NWs of semiconductor materials. We are particularly interested in the ultrathin NWs of the noble metals in pristine and alloyed form. Also the alloyed nanowires have many applications in electronics and optoelectronics [86,152]. But there is lack of theoretical/computational reports on electronic, optical and transport properties of alloyed ultrathin nanowires of noble metals.

Our main objective is to study the structural, electronic, optical and transport properties of pristine and alloyed free standing ultrathin nanowires of noble metals with different topologies and morphologies.

5 Work Done So Far

Till date we have studied the bulk properties (structural, electronic and dielectric) of FCC structured noble metal namely Cu, Ag, Au and Pt [58]. We have also studied the structural, electronic and dielectric properties of pristine free standing noble metal (Cu, Ag, Au and Pt) ultrathin nanowires in different topologies.

Dielectric functions of bulk noble metals is in good agreement with experimentally measured data. The binding energy has been found largest for Pt nanowires and smallest for Ag nanowires. Dimer topology of Ag wire and linear topology of the Ag and Cu wires are found nearly semi metallic in nature as compared to metallic nature of all other topologies of studied wires. The partial DOS of all the studied topologies of noble metals have been found to have contribution mainly from 'd'orbitals, however, significant contribution from 's'orbitals have been found to come from linear and dimer topologies of all the noble metals. The pronounced DOS has been found to increase in nanowires as compared to their bulk counterparts. Ballistic conductance increases for ladder and zigzag topology of Cu, Ag and Au as compared to other topologies, while it remains same for all the topologies of Pt wire. The reflectance edge for all the studied topologies of wires is found in infrared region except ladder topology of Pt for which reflectance edge has been found near visible region. The percentage decrease in the position of reflectance edge *w.r.t.* bulk has been found largest for Pt ultrathin nanowires among all the studied ultrathin nanowires of noble metals. Dielectric properties of nanowires has been found to change significantly with the topology, therefore, suggesting that the optical properties can be used as a tool for characterization of the nanowires.

6 Future Plan of Work

In future we will focus on structural, electronic and optical properties of free standing alloyed nanowires of noble metals with different topologies (linear, ladder, double zigzag). We will compare the results with the corresponding pristine nanowires. Further we will study the transport properties of of these free standing nanowires (both pristine and alloyed nanowire) using TRANSIESTA a module in SIESTA to study electron transport of nanowires.

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7 List of Publications

- *Ab initio study of structural, electronic and dielectric properties of free standing ultrathin nanowires of noble metals*, Arun Kumar, Ashok Kumar and P.K. Ahluwalia, Physica E, 46 (2012) 259269.

8 Papers Presented in Conferences/Symposia

- *Electronic and Optical Properties of Free Standing Pt Nanowires using Localized Basis-sets*, Arun Kumar, Ashok Kumar and P.K. Ahluwalia, AIP Conf. Proc. 1447 (2012) 831-832, 56th DAE Solid State Physics Symposium (DAE-SSPS 2011) at SRM University Kattankulathur, Tamilnadu, India.

- *Electronic and Optical Properties of Free Standing Au Nanowires using Density Functional Theory* Anil Thakur, Arun Kumar, P. K. Ahluwalia, 57th DAE Solid State Physics Symposium (DAE-SSPS 2012) at IIT Bombay, Powai, Mumbai, India.

9 Papers Under Preparation

- Electronic and Optical Properties of Free Standing Alloyed Nanowires of Noble metals.

- Transport Properties of Pristine and Alloyed Nanowires of Noble Metals.

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