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Topology dependent electronic and dielectric properties of free standing alloyed ultrathin nanowires of noble metals

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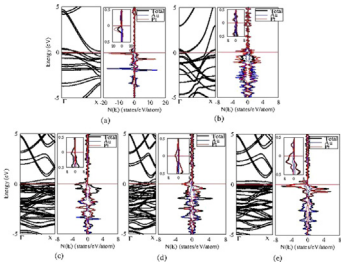
HIGHLIGHTS

- This paper analyzes structural, electronic and dielectric properties of alloyed ultrathin nanowires of noble metals.
- The studied topologies containing Pt are found to be ferromagnetic in nature.
- Linear and double zigzag topologies without Pt are found to be semiconducting in nature.
- Optical properties are different than the corresponding pristine nanowires due to change in band structure on alloying.

GRAPHICAL ABSTRACT

We present electronic and dielectric response of free standing alloyed ultrathin nanowires of noble metals with different topologies namely linear, ladder and double zigzag. Illustartion 1: Electronic band structure and corresponding total and partial DOS for both spin up and spin down for (a) linear (b) ladder (c) DZZI (d) DZZ2 and (e) DZZ3 topologies of ultrathin alloyed nanowires of AuPt. The Fermi energy has been set at 0 eV. In inset we have shown the PDOS in the vicinity of Fermi level for the systems which are magnetic in nature. From these we conclude that Pt is contributing for magnetism with more DOS at Fermi energy for Pt than Au.



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ABSTRACT

Structural, electronic and dielectric properties of free standing ultrathin alloyed nanowires of noble metals (AgAu, AgCu, AgPt, AuCu, AuPt and CuPt) in various topologies (linear, ladder and double zigzag) have been studied by using *ab initio* density functional theory. Among the different topologies of alloyed ultrathin nanowires of noble metals, double zigzag (DZZ) topology has been found to be most stable and the linear topology the least stable. Also the binding energy of alloyed nanowires of AgAu and AuCu for all the studied topologies is found to be larger than the average binding energy of the corresponding pristine nanowires, indicating a strong alloying effect for these topologies. Among electronic properties, the alloyed nanowires of different topologies containing Pt (AgPt, AuPt and AuCu) are found to be ferromagnetic in nature, a result of d charge depletion in Ag, Au and Cu sites and d charge gain at Pt sites. On the other hand, all the topologies (except ladder topology) of alloyed nanowires *viz.* AgAu, AgCu and AuCu are found to be semiconducting in nature.

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The optical properties of the studied alloyed nanowires have been found to be different from their corresponding pristine nanowires due to change in the band structure on alloying. The linear topology of AgAu, AgCu and AuCu and DZZ topologies (DZZ1, DZZ2 and DZZ3) of Ag, Au, Cu, AgAu, AgCu and AuCu are semiconducting in nature with band gap lying in the infrared region, causing absorption of photons from a visible spectrum leading to blackish appearance. Whereas, remaining topologies are found to be metallic in nature, with plasmon frequency lying in the energy range of 0.35 eV to 1.62 eV, which is in the infrared region and hence these nanowires shall appear to be transparent to the visible region.

1. Introduction

In the last few years, investigations on metallic nanowires [1–10] have increased largely because of various potential applications, such as their usage as interconnects in nanoelectronic systems [11], optical nanometallic communication channels [12] and biological spectroscopic enhancers [13] and as sensors [14–16]. Nanowire sensors have been used to detect many gases like O_2, NO_2 and NH_3, at very low concentrations [14]. They also have been used for the detection of ultraviolet (UV) light [15], as well as light sensitive biological and chemical species [16]. The usage of noble metals' nanowire is well known as barcode tags [17,18] for optical read out and lithium ion batteries [19]. These can also be used to create the materials with negative refractive index in the near infrared region [20].

The electronic, magnetic, optical and transport properties of these one dimensional (1D) systems are found to be topology dependent [1,2]. Increased surface-to-volume ratio and increased density of states (DOS) of nanowires at the Fermi level make their properties different from the corresponding bulk materials. The quantum confinement effects lead to formation of sub-bands. As a consequence, there are more transitions near the sub-band edges [21], which contribute to band edge emission.

Along with the experiments on pristine noble metal nanowires, many experiments have also been performed to study the properties of the alloyed metal nanowires [22–27]. In the first decade of 2000, point contact studies were made to study random alloys of transition metal and noble metal, namely gold and palladium [22], copper and nickel [23] and gold and platinum [25] for different concentration ratios. Pan et al. [10] have studied the optical properties of the Au–Ag alloy nanowire coated with a radially dielectric anisotropic shell on the basis of quasi-static theory. It has been observed that surface plasmon resonance (SPR) peak undergoes redshift with the increasing component ratio of Au in the alloy, while increasing the component ratio of Ag in the alloy shows an increase in the intensity of extinction section at SPR. Also 1D ultrathin nanowires ($Au_{25}Pt_{75}$ and $Au_{48}Pt_{52}$) have been synthesized *via* a wet chemistry approach at room temperature by Teng et al. [28] and they have observed ferromagnetism in $Au_{48}Pt_{52}$ nanowire. In 2011, Kundu and Liang [29] have synthesized the alloyed nanowire of Au–Ag with diameter 4–12 nm with length few micron long which is found to be semiconducting in nature. The noble metal alloyed nanowires ($Au_{0.5}Ag_{0.5}$, $Au_{0.67}$ $Ag_{0.33}$, $Au_{0.9}$ $Ag_{0.1}$) with diameter below 50 nm have also been synthesized and used in the lithium ion battery [19]. Experimentally, the one dimensional alloyed nanoporous nanotubes of Au–Ag have also been fabricated by Chae et al. [30] which have been found to possess distinct optical properties, such as tunable absorption in the near infrared region. These alloyed porous nanotubes of Ag–Au show higher molecular sensing activity than solid 1D wire of Au and comparable to that of porous 1D Au nanotube.

Despite many experimental investigations, there is lack of systematic theoretical study of ultrathin alloyed nanowires. However structural and electronic properties of alloyed nanowires of AgPt, AgAu and PdAu have also been studied theoretically [31–34]. In 2010 Fioravante and Nunes [31] have studied the free standing alloyed nanowires of Ag and Au with different topologies *viz.* ladder, zigzag and double zigzag (DZZ) using density functional theory (DFT) and reported semiconducting nature of nanowires of DZZ topology and nanowires of other topologies (ladder and zigzag) are found to be metallic in nature. It has also been observed using DFT that linear monoatomic wire of Au also gets stabilized by alloying with Zn and Mg [35]. Studies have also been conducted on pristine nanowires of noble metals (Ag, Au, Cu and Pt) with linear, dimer, ladder and zigzag topologies and compared their electronic and optical properties with the corresponding bulk [36].

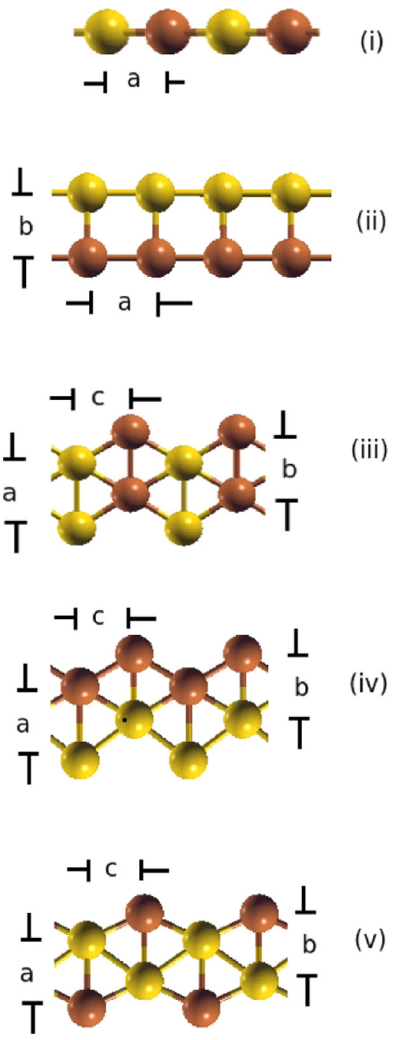

Fig. 1. Optimized structures of different topologies of ultrathin alloyed nanowires, (i) linear, (ii) ladder, (iii) DZZ1, (iv) DZZ2 and (v) DZZ3. For alloyed nanowires light (yellow colored) and dark (brown colored) circles represents the different atoms. Various structural parameters are represented by a, b and c. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this paper.)