The Electronic Properties and L_3 XANES of Au and Nano-Au

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ABSTRACT

The electronic properties of Au crystal and nano Au have been investigated by theory and experiment. Molecularly capped nano-Au was synthesized using the two-phase method. Gold nano-particles have been characterized by X-Ray Diffraction (XRD) and Transmission Electron Microscopy (TEM). They retain the face center cubic (fcc) crystal structure. Their sizes have been determined to be in a range from 5.5 nm to 1.7 nm. The L_3 X-ray Absorption Near Edge Structure (XANES) spectra of nano-Au and Au foil have been recorded using synchrotron radiation, and examined by theoretical calculation [1] based on the first principles [2,3]. Both theory and experiment show that the molecular capped nano-Au particles have essentially all the Au L_3 XANES features of bulk Au in the near edge region with less pronounced resonance peaks. It is also shown that nano Au exhibits slightly deeper 4f binding energy than bulk Au in good agreement with quantum confined Au systems reported previously [4].

Keywords: Nano Gold, Au, XANES, DFT, and GGA.

1 INTRODUCTION

The development of high performance computer and nano electronics require downsizing of devices to the ultimate quantum sizes where quantum size effect plays an important role in the designs of these quantum devices [5].

Nano clusters and crystals of semiconductors and metals which are isolated from interfaces show anomalies and are influenced by quantum confinement effect [6]. We are investigating the properties of nano metals, in particular the noble metals, and exploring the nano regime where the quantum confinement first occurs and above which the precious metals still ensure the bulk properties, i.e. the conductivity and resistivity [7].

The small size of nano crystals and solids requires quantum mechanical consideration. The classical models, e.g. classical molecular dynamics and Monte Carlo simulation using semi-empirical potentials, do not render adequate information. Thus, quantum mechanical model for nano crystals and solids is crucial for the consideration of their properties, e.g. quantum confinement and tunneling [8].

2 THORY AND COMPUTATION METHOD

The complicated many body problems of the crystal system of heavy metals become solvable using Density Functional Theory (DFT) [2].

Nano-crystals of gold have been modeled using supercells with unit cells large enough for the crystallites to interact. The crystallites have face center cubic (fcc) symmetry. The unit cube is a crystallite of one basis unit cell of fcc Au atoms (14 atoms) centered at the cube's center and separated by multiple (N) of a, where a is the lattice constant of fcc Au. The nano wire model is a bunch of wires with basic cube of fcc crystal (5ML) with [100] along z direction. The distance between these wires is far apart for the interaction between atoms on the wire surface. The nano plane model is a set of crystal planes (5ML) of fcc symmetry, parallel with each others, and separated by aN. To simply the many body problems, these nano structures are made to fulfill periodic boundary conditions.

Nano structures can be classified in two cases. Case 1: electrons are allowed to enter the interstitial region between atoms. Case 2: electrons are confined at the atomic sites, where muffin tin potential dominates.

Case 1. These are the cases where nano structures are closely packed together so that electrons can tunnel through. This model can describe nano gates and nano devices where nano Au crystallites are fabricated in narrow separation and small current are allowed to pass through.

Case 2. In the confined electron model, electrons are restricted to be present inside the muffin tin potential around the atomic sites within a cut-off distance slightly smaller than half of the distance between nearest neighbors of the crystals. This is the case where electrons are strongly bound to nucleus in the nano crystallites.

We are using the first case to probe the gold systems, since gold is a heavy metal with free electrons permeating inside the metal.

Self-consistent full potential linear augmented plane wave method (FPLAPW) [1] using Density Functional Theory (DFT) [2] together with Generalized Gradient Approximation (GGA) [3] has been used to investigate nano structures where electrons are allowed to "leak out" from the atomic area. Full potential linear augmented plane wave method (FPLAPW) is a method that use bases as spherical harmonics inside the atomic spheres and plane waves in the interstitial regions. At the atomic boundary, the Dirichlet boundary condition is satisfied.

3 RESULTS AND DISCUSSION

Self-consistent Functional Density calculation using GGA was performed employing the Wien code [1]. The calculated electronic densities of states of fcc bulk gold, quantum-cube, sub nano-wire, and sub naon-plane, as calculated using the above-mentioned model 1, are shown in Fig. 1. The quantum-cube is made of 14 gold atoms that are arranged at the perfect fcc positions. The number of gold atoms is not large enough to produce a band like feature, and in stead discrete levels below the Fermi level is present. In particular, there are quantum states present about 1eV below the Fermi Energy.

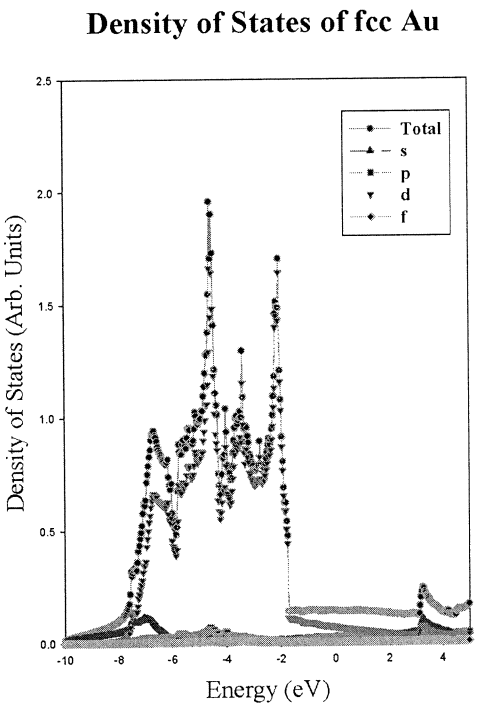

Figure 1: Theoretical (DFT) Electron Density of fcc Au using GGA.

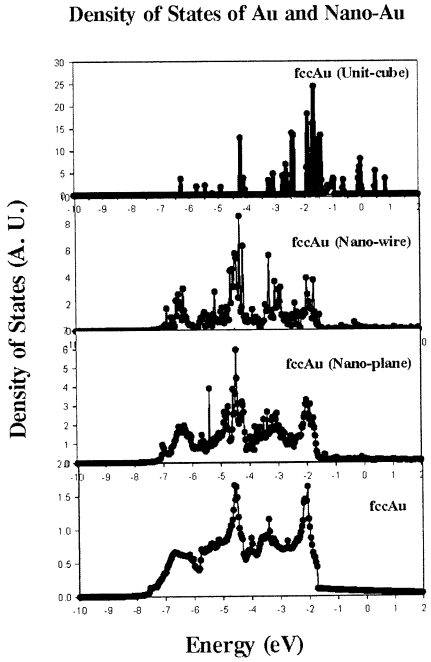

Figure 2: Theoretical (DFT) Electron Density of Au and Nano-Au using GGA.

Experimentally, nano particle can be prepared using either the hard or soft templates. For the hard template, we have used porous silicon as the template substrate and grew nano gold or platinum on top [9]. Soft templates are molecules like dendrimer or thiol. Combining chemical and electro methods, we make molecularly capped nano gold crystallites. Their sizes have been determined by Transmission Electron Microscope (TEM) to be ranging from 5.5nm to 1.6 nm. The crystallines are examined by X-Ray Diffraction (XRD).

The core levels and valence bands have been probed using XPS (X-ray Photoelectron Spectroscopy) of Surface Science Western of the University of Western Ontario. The 4f peaks of bulk Au, 4.2nm, 2.4nm, and 1.6nm Au are 87.7, 87.9, 88.0, and 88.1eV (peak 1), and 84.1, 84.2, 84.3, and 84.4eV(peak 2), respectively. The smaller the size of the thiol capped nano-gold crystalite, the deeper is the binding energy of the 4f core levels.

The valence band spectra are shown in Fig. 3, where a slight narrowing of the d band is observed in the same direction as calculated.

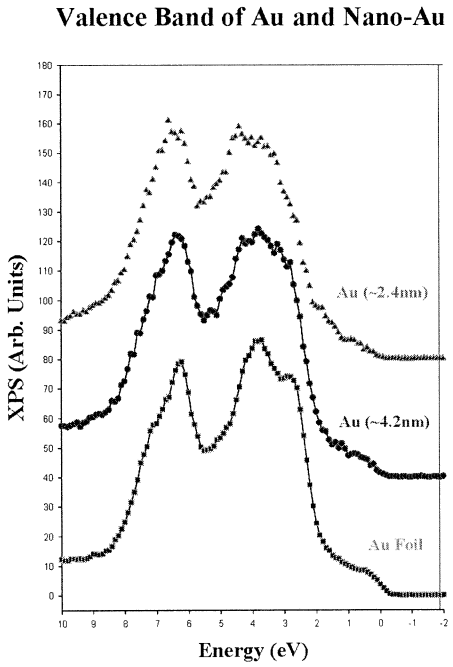

Figure 3: Experimental XPS of Au and Nano-Au.

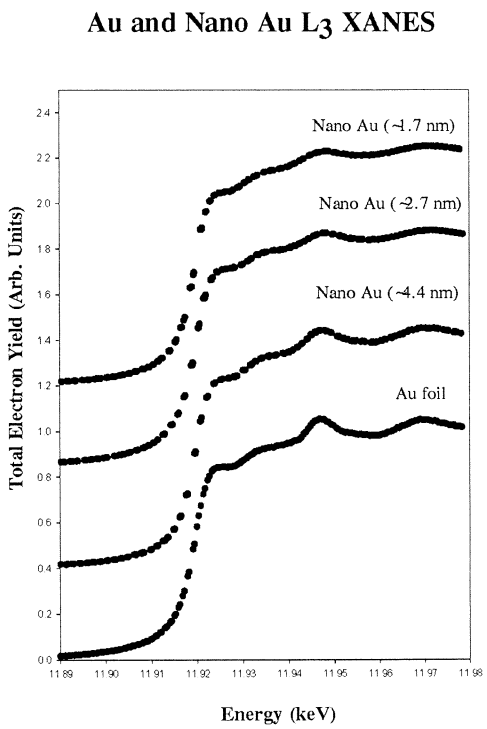

Figure 4: Experimental L_3 XANES of Au and Nano-Au.

The Au XANES (X-ray Absorption Near Edge Structure) spectra were obtained at the Advanced Photon Source (APS) at Argonne National Laboratory. We show the L_3 XANES of gold foil, and the molecular capped nano gold in the sizes of 4.2, 2.4, and 1.6 nm in Fig. 4. To compare the experimental data with the calculated L_3 XANES edge, we plot the corresponding fcc bulk, and nano structures of gold in Fig. 5. The theoretical XANES spectra of fcc gold and nano gold crystals have been calculated using dipole transitions between the orbital states [10]. The XANES spectra have been convoluted with a Lorentzian line-width broadening of 6 to 7eV.

The gold foil shows distinguishable three peaks about 40 eV above the L_3 XANES edge. The molecularly capped nano gold particles show less pronounced peaks in this spectral region. The nano gold crystals resemble the L_3 XANES edge of the bulk fcc gold with relaxed peaks, but do not show quantum confined sharp peak.

Quantum well states have not been observed with our Nano gold prepared either by molecularly capped method or on porous silicon [4]. These states were reported to be present around 1 eV below the Fermi level in the Valence Band region of Ag on Au foil but not for Au on Ag foil [11].

Finally, it should be noted that the porosity and uniformity of nano structure play an important role, in addition to the crystallite size, in the existence of the observed quantum size effects.

The beam size of the X-ray beam in the XPS and XANES experiment is of the order of about a few mm, and the observed XPS and XANES are thus an average value of the gold crystallites.

It is also noted that one has to apply the Local Density Approximation and the Generalized Gradient Approximation within the Density Functional Theory cautiously. LDA and GGA require the condition of the system to have slowly varying density functional. For a quantum confined system with soft boundary, GGA or meta GGA (inclusion of more gradient terms to the density functional) must be used, and not LDA. It cannot be applied to hard wall quantum well where the boundary has discontinuity.

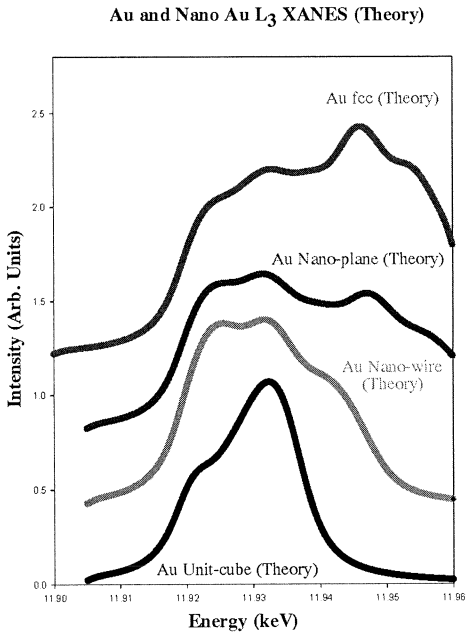

Figure 5: Theoretical (DFT) L_3 edge XANES of Au and Nano-Au using GGA.

4 CONCLUSION

We have conducted calculations of the Density of States and L_3 XANES spectra of Au and nano Au. The method we used is the Full Potential Augmented Plane Wave Method and Generalized Gradient Approximation within the Density Functional Theory. Qualitatively, the results compare favorably with experiment of the trend of downsizing.

Experimentally, molecularly capped nano gold crystals and nano gold crystals prepared on porous silicon resemble the bulk properties, e.g. the electron density of states and XANES. The quantum size effect is washed out by the inclusion of capped molecules and substrates.

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