Electronic transfer from aluminum into the core of gold nanoparticles capped with conjugated 2-naphthalenethiol

Jianyong Ouyang

Department of Materials Science and Engineering, National University of Singapore, Singapore 117576, Singapore

ABSTRACT

The electronic contact between a bulk metal and metal nanoparticles can be significantly different from that between two bulk metals due to the unique electronic structure in the nanometer size. In this work, the electronic contact between Au nanoparticles and Al is studied by X-ray photoelectron spectroscopy. Al is deposited on a layer of Au nanoparticles capped with conjugated 2-naphthalenethiol (Au-2NT NPs) in high vacuum by e-beam deposition at room temperature. The Au 4f X-ray photoelectron spectrum (XPS) significantly changes after the Al deposition. New XPS bands with higher binding energy appear. The angle dependence of the Au 4f XPS bands indicates that the electron transfer takes place at the contact between Al and Au-2NT NPs. In contrast, the Al deposition hardly changes the Au 4f XPS spectrum for Au nanoparticles capped with saturated 1-dodecanethiol. The effect of the Al deposition on the Au 4f XPS spectrum of Au nanoparticles capped with 2-naphthalenethiol is attributed to the electron transfer from Al through the conjugated 2-naphthalenehiol into the core of Au nanoparticles, as the Fermi energy of Al is higher than Au. This understanding on the contact between metal and metal nanoparticles provides guidance for the development of novel electronic devices.

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1. Introduction

Materials in nanometer size can have structure and properties significantly different from bulk materials [1–4]. A striking example is metal nanoparticles. The energy levels become discrete at the quantum size, whereas a bulk metal has continuous energy band structure. The metal nanoparticles can be charged or discharged like a molecule. To charge a metal nanoparticle must overcome the Coulombic blockade, which depends on the particle size. The unique electronic structure suggests important application of metal nanoparticles in electronic devices. Effort has been made in developing novel electronic devices with metal or semiconductor nanoparticles, such as light-emitting diodes, resistive switching memories and thermoelectric devices [5–14]. These devices exploit the intrinsic properties of the nanoparticles, including the charge trapping, the optoelectronic properties, the Coulombic blockade and the processability. For electronic devices with bulk electronic materials, the electronic behavior depends on not only the intrinsic structure and properties of the electronic materials but also the interfaces between the active materials and the electrodes [15–20]. When two electronic materials with different work functions are put in contact, electron transfer can take place at

the contact. For example, electron transfer takes place at the contact between metal and semiconductor for the Schottky junction, which gives rise to rectified current–voltage curves along the two polarities of the junction. The contact becomes different for two metals. Electrons transfer from the metal with lower work function to the one with higher work function. The electron transfer leads to the formation of an internal electric field at the metal–metal contact. But the internal electric field at the contact of two bulk metals has no effect on the charge transport along the two polarities, since metals have a high density of free electrons and the electron transfer only occurs at a very thin layer at the metal–metal contact.

The metal–metal contact can become significantly different when one of the metals is nanoparticles capped with organic ligand. The organic ligand is needed to stabilize the metal nanoparticles. The electron transfer has to overcome the Coulombic blockade due to the quantum effect. In addition, the capping organic ligand of the metal nanoparticles increases the separation between the positive and negative charges of the two materials. The separation is significantly larger than that for the contact of two metals. The capping organic ligand also constructs an energy barrier for charge transfer into or from the core of the metal nanoparticles. All these factors suggest that the electrical behavior for an interface between a bulk metal and metal nanoparticles can be significantly different from that between two bulk metals. Therefore,

E-mail address: mseoj@nus.edu.sg

the interface between a bulk metal and metal nanoparticle can be exploited for the development of novel electronic devices. However, the interface between metal nanoparticle and metal has been rarely exploited. Although the preparation, structure and properties of metal nanoparticles have been hot research topics, there are few reports on the electronic interface between bulk metals and metal nanoparticles. Only recently, resistive switching devices that exploit the interface between a bulk metal like Al and Au nanoparticles capped with conjugated organic ligand like 2-naphthalenethiol (2NT) were demonstrated [21]. These devices exhibit asymmetrical switching behavior along the two polarities. The resistive switching mechanism is attributed to the electron transfer between a bulk metal electrode and metal nanoparticles [22–26]. The asymmetrical switching behavior is sensitive to the organic ligands capped on the metal nanoparticles. When metal nanoparticles capped with saturated alkanethiol, the electrical behavior is independent of the interfaces between the metal electrode and the active layer with the metal nanoparticles [11,27–33]. However, no direct evidence for the electron transfer between bulk metal and metal nanoparticles was reported.

In this work, X-ray photoelectron spectroscopy (XPS) was used to study the interface between bulk Al and Au nanoparticle. The Au 4f XPS spectrum of Au nanoparticles capped with conjugated 2NT significantly changes after the deposition of Al on them. The XPS results indicate the electron transfer from Al through 2NT into the core of the Au nanoparticles.

2. Experimental

2.1. Materials and chemicals

All the chemicals, including 2NT, were purchased from Sigma–Aldrich. The chemical structure of 2NT is shown in the inset of Fig. 1. Gold nanoparticles capped with 2NT (Au-2NT NPs) were synthesized according to literature [34]. In a typical experiment, 0.62 g $HAuCl_4 \cdot 3H_2O$ was dissolved in 50 ml water. It was subsequently mixed with 160 ml p-xylene solution of 3 g tetraoctylammonium bromide. The organic phase was collected, and 0.267 g 2NT was added. 50 ml aqueous solution of 0.76 g $NaBH_4$ was then dropwise added under vigorous stirring at room temperature. The solution color changed to black, which indicated the conversion of $HAuCl_4$ into Au-2NT NPs. The Au-2NT NPs were rinsed with 300 ml methanol for at least 3 times. They had a size distribution of 1.6–4.4 nm in diameter and average size of 2.8 nm.

2.2. Materials characterization

The Au-2NT NPs were re-dispersed in 1,2-dichlorobenzene. They were then cast on silicon wafers coated with Au in a glove box filled with nitrogen and dried overnight. The Au-2NT NP layer had a thickness of about 10 μm. The samples were then transferred into a system equipped with XPS measurement and Al deposition. The pressure of the chamber for the XPS measurement is 10^{-10} Torr. Al was deposited on the Au-2NT NP layer by e-beam evaporation at a chamber of 10^{-9} Torr at room temperature. The Al deposition rate was 0.04 Å s^{-1}. The samples were transferred between the deposition chamber and the XPS measurement chamber without breaking the vacuum. The other samples were characterized by a similar procedure.

3. Results and discussion

XPS was carried out on Au-2NT NPs deposited on silicon. As shown in Fig. 1(a), there are two XPS bands with the peak positions at 84.0 and 87.7 eV. The former is stronger than the latter. The two
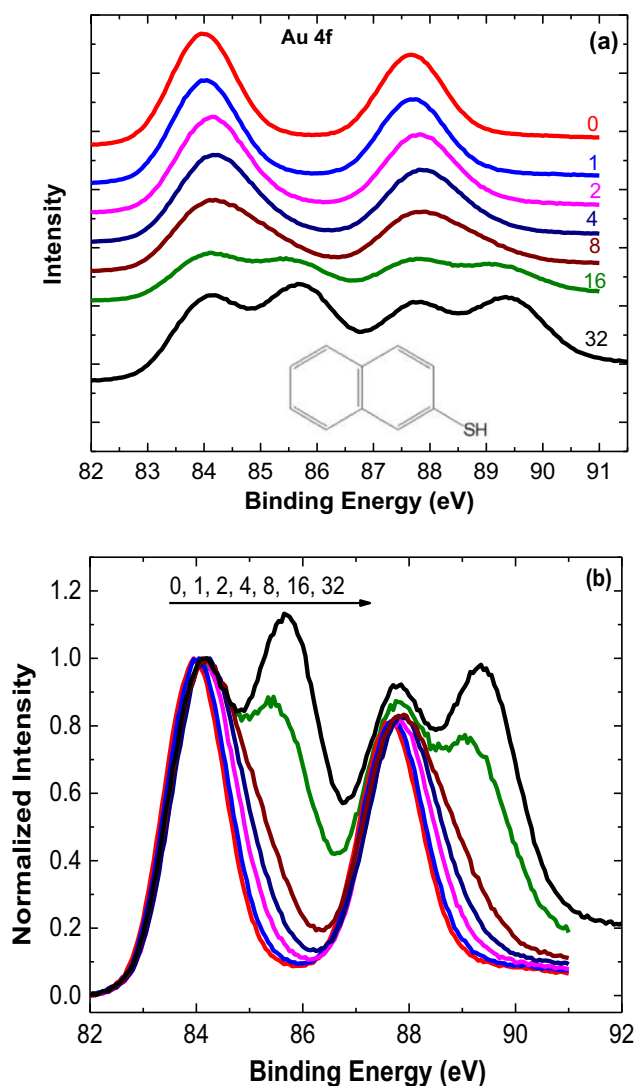

Fig. 1. (a) Au 4f XPS spectra of a Au-2NT NP layer deposited with Al of different thicknesses of 0, 1, 2, 4, 8, 16 and 32 Å. The inset is the chemical structure of 2-naphthalenethiol (2NT). (b) Replot of the Au 4f spectra with the intensities normalized to the peak intensity at around 84 eV.

XPS bands are assigned to Au 4f 7/2 and 5/2, respectively. They indicate the zero-valence Au. This Au 4f spectrum is similar to the Au 4f spectra of Au NPs capped with various organic ligands in literature [35–37]. Although Au NPs can have electronic structure and properties significantly different from bulk gold, the nanometer size has no effect on the XPS spectrum of Au. After the deposition of Al on Au-2NT NPs in high vacuum, the Au 4f XPS bands significantly change. The peak positions shift to higher binding energy after the deposition of 2 Å-thick Al. The two XPS bands become remarkably broader after the deposition of 2 Å-thick Al. Two new XPS bands appear when the Al thickness increases to 16 Å. Fig. 1(b) presents the XPS spectra by normalizing the intensity to the peak intensity at 84.0 eV. The broadening of the XPS bands and the appearance of the new XPS bands are readily observed.

The deconvolution of the Au 4f XPS spectra indicates that the binding energies for Au 4f 7/2 and 5/2 are 84.00 and 87.66 eV, respectively, for Au-2NT NPs before the Al deposition (Fig. S1). There are 4 XPS bands after the deposition of 32 Å Al on Au-2NT NPs. Their binding energies are 84.04, 85.69, 87.7 and 89.37 eV. The two XPS bands with the binding energies of 85.69 and