Femtosecond Nanoparticle-Substrate Interaction in the Photoemission Final-State of Surface-Passivated Metallic Nanopaticles on Graphite Substrates

Akinori Tanaka, Yuitsu Takeda, Masaki Imamura, and Shigeru Sato

Department of Physics, Graduate School of Science, Tohoku University, Aoba-ku, Sendai 980-8578, Japan
Fax: 81-22-217-6419, e-mail: a-tanaka@srpe.phys.tohoku.ac.jp

We have carried out a photoemission study of dodecanethiolate- (DT-) passivated metallic (Ag and Au) nanoparticles supported on the highly oriented pyrolytic graphite (HOPG) substrates. From the detailed photoemission measurements, it is found that the Fermi-level onsets in the photoemission spectra of DT-passivated metallic nanoparticles on the HOPG substrates are not the usual metallic Fermi-edge, with steep slope being away from the Fermi-level. The observed photoemission spectra are well characterized by the theoretical calculations based on the dynamic final-state effect model that takes into account the Coulomb interaction between the photoelectron and photohole during the photoemission process and nanoparticle-substrate interaction. This suggests that the observed photoemission spectra give a direct evidence of nanoparticle-substrate interaction through the surface-passivants on a femtosecond timescale and provide the knowledge of single electron phenomena.
Key words: Surface-passivated nanoparticle, Photoemission spectroscopy, Nanoparticle-substrate interaction

1. INTRODUCTION

Metallic nanoparticles have attracted much interest from the viewpoints of both fundamental and device physics, since they show the distinctive properties found in neither bulk nor molecular/atomic systems, such as high catalytic activity[1] and Coulomb blockade.[2] Recently, the surface-passivated metallic nanoparticles have been chemically synthesized in the solution including surfactants.[3,4] These surface-passivated metallic nanoparticles are monodisperse and very stable even at room temperature, and exhibit the closed-packed nanoparticle self-assemblies on the single-crystalline substrates.[5,6] Therefore, it is considered that they could be important constituents of future nanostructured devices, such as single electron device. In order to elucidate their detailed intriguing properties and to develop the future devices, it is indispensable to understand the interactions with the substrates supporting the nanoparticles as well as their electronic structures.

On the other hand, the final-state effect in the photoemission spectrum due to the photohole created by photoionization has been reported in the previous photoemission studies of nanoparticles.[7-10] The Coulomb interaction between the photoelectron and positively charged photohole left behind in the nanoparticle during the photoemission process influences the observed photoemission spectra. This charging effect is a similar quantum phenomenon to the single electron tunneling effect. The knowledge of this quantum phenomenon observed when the nanoparticle and substrate interact through a tunneling gap, might be important for future nanoelectronic devices. In this work, we report the results of photoelectron spectroscopies for dodecanethiolate- (DT-) passivated metallic (Ag and Au) nanoparticles supported on the highly oriented pyrolytic graphite (HOPG) substrates. From the considerations regarding the final-state effects on the photoemission spectra, we will discuss the nanoparticle-substrate interactions through the surface-passivants of DT-passivated metallic nanoparticles on the HOPG substrates.

2. EXPERIMENT

The DT-passivated Ag and Au nanoparticles were synthesized by two-phase reduction method.[3] The detailed procedure is described elsewhere.[11,12] The size distributions and shapes of synthesized nanoparticles were characterized by observations with a transmission electron microscope (TEM). As a further characterization, we also performed the optical measurements. For the photoemission measurements, the synthesized DT-passivated metallic nanoparticles were supported on the HOPG substrates by evaporating the solvent from the dispersion of DT-passivated nanoparticles on the single-crystalline HOPG cleaved-surface in a nitrogen-filled glove bag directly connected to the ultrahigh-vacuum photoelectron spectrometer. The cleanliness was checked by Auger electron and x-ray photoelectron spectroscopies. The photoemission measurements were performed at 40 K with a He I resonance line ($h\nu$=21.2 eV) as the excitation source.

3. RESULTS AND DISCUSSION

Figure 1 shows the TEM micrographs and size distributions obtained by TEM observations for DT-passivated Ag nanoparticles used in this work. The obtained mean diameters are 3.8, 4.2, and 5.3 nm, and the standard deviations are 0.58, 0.69, and 0.47 nm, respectively. As shown in Fig. 1, the present DT-passivated Ag nanoparticles show

the homogeneous and spherical shape. An important point to note is that each Ag nanoparticle is well separated from its neighboring nanoparticles, indicating that the present Ag nanoparticles are well surface-passivated by the dodecanethiol molecules.

Figure 2 shows the photoemission spectra in the vicinity of Fermi-level of the DT-passivated Ag nanoparticles with the various diameters on the HOPG substrates at 40 K using the He I resonance line as an excitation source, compared with that of bulk Ag. The photoemission spectrum of bulk Ag shows the usual metallic Fermi-edge, with the midpoint of the steep slope just at the Fermi-level. On the other hand, all the DT-passivated Ag nanoparticles exhibit the similar spectral features, however, the Fermi-level onsets in the photoemission spectra are not the usual metallic Fermi-edge observed for bulk Ag, with the steep slope being away from the Fermi-level. Furthermore, it is found that the slopes of the leading edges are different from that of metallic Fermi-edge observed for bulk Ag. Since the photoemission spectrum in the vicinity of Fermi-level of HOPG substrate exhibits the featureless shape reflecting the vanishing semimetallic density of states toward the Fermi-level (not given here), the observed spectral features of DT-passivated Ag nanoparticles on the HOPG substrates are not caused by the HOPG substrates but are characteristic of Ag nanoparticles. The DT-passivated Au nanoparticles with the same size regime on the HOPG substrates (not given here) also exhibit the same spectral features as the DT-passivated Ag nanoparticles described

above.[11] In general, the photoemission spectra directly reflect the change in the electronic structure of the samples (that is, initial-state effect), and are also affected by the final-state effect originating from positively charged photohole created by the photoionization.[7-10] Therefore, these photoemission spectra are seemed to indicate that the electronic structures of the present DT-passivated Ag nanoparticles exhibit the non-metallic ones in this diameter regime. However, from the Kubo criterion,[13] this discussion is not reasonable for the relevant diameter regime. Furthermore, the optical extinction spectra of the present DT-passivated Ag nanoparticles exhibit the distinctive size-dependent Mie plasmon resonance around 3 eV photon energy for all diameters, i.e. an indicative of a collective motion of valence-electrons typical for a metallic material. These discussions mean that the observed spectral features are not due to the initial-state effect originating from the change in the electronic structure. Therefore, these spectral features of the present DT-passivated metallic nanoparticles are considered to originate from the final-state effect due to the photohole left behind in the nanoparticles during the photoemission process. In the case that the vacuum ultraviolet photon excites a photoelectron, the photohole left behind in the nanoparticles during the time scale relevant to photoemission process will lower the kinetic energy of photoelectrons through the Coulomb interaction. Although the relaxation response within the metallic nanoparticle may otherwise proceed normally, an excess positive charge left behind in the nanoparticle significantly induces
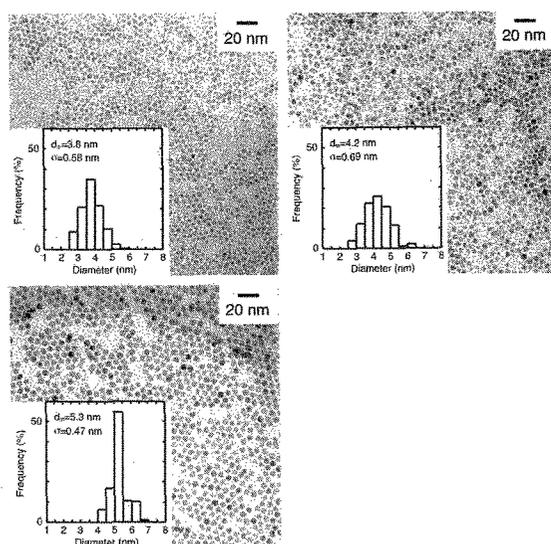
Fig. 1. TEM micrographs and size distribution in diameter of DT-passivated Ag nanoparticles with mean diameters d_m and standard deviations σ of d_m=3.8 nm and σ=0.58 nm, d_m=4.2 nm and σ=0.69 nm, and d_m=5.3 nm and σ=0.47 nm.
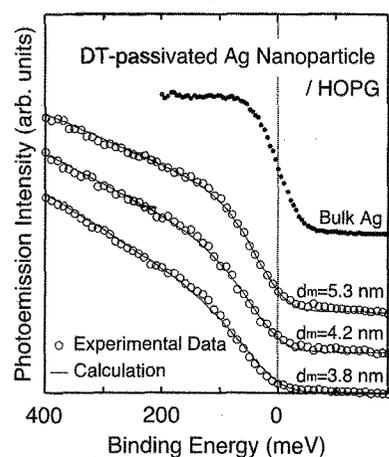
Fig. 2. Comparison of the experimental photoemission spectra in the vicinity of Fermi-level of DT-passivated Ag nanoparticles supported on the HOPG substrates at 40 K measured with the He I resonance line ($h\nu$=21.2 eV) with the calculated results based on the dynamic final-state effect model (see text). The mean diameter d_m is indicated on each spectrum. The top spectrum shows the Fermi-level onset observed for bulk Ag for a comparison.

the final-state effect in the photoemission. In fact, these final-state effects on the photoemission spectra have been reported for free nanoparticles[7] and even for the nanoparticles on the substrates.[8-10] This final-state effect would play a more important role in the present surface-passivated metallic nanoparticles supported on the substrates, since the surface-passivated nanoparticles weakly couple with the substrates through the surface-passivants. From the static viewpoint, the kinetic energy shift ΔE of photoelectrons due to the photohole left behind in the nanoparticle is give by $\Delta E = e^2/2C$, where $C = 4\pi\varepsilon_0 R_N$ is the self-capacitance of the nanoparticle with a radius R_N. On the other hand, an exact calculation shows that this energy-shift is given by $\Delta E = \alpha e^2/4\pi\varepsilon_0 R_N$ with $\alpha = 0.41$ for Ag nanoparticle.[7] In the case of photoemission, the nanoparticles are limited to have only positive charge (photohole), but the origin of this final-state effect on photoemission process should be same as that of single electron tunneling. Therefore, the investigations of the final-state effect in the photoemission process will provide information about the single electron tunneling.

In order to theoretically describe these observations, we analyzed the photoemission spectra using a dynamic final-state effect model[8,9] that takes into account the Coulomb interaction between the photoelectron and photohole with a finite lifetime during the photoemission process. The probability of photohole neutralization is described by $P(t)dt = (1/\tau)\exp(-t/\tau)dt$, with a charactertic time τ that is determined by the coupling strength between the nanoparticle and substrate. While the photohole created by photoionization is remaining in the nanoparticle, the Coulomb interaction between the photoelectron and photohole induces the energy-shifts of photoelectrons. The Coulomb potential acting on the photoelectron due to the photohole is expressed by $W(r) = \alpha e^2/4\pi\varepsilon_0 (1/R_N - 1/r)$, where r is the distance from the center of nanoparticle. Since the present Ag nanoparticles have the spherical shapes as shown in Fig. 1, this expression is considered to be reasonable. When the photohole left behind in the nanoparticle is neutralized after a time t, the energy-shift for the photoelectron with a velocity v is expressed by $W(R_N + vt)$. Since the observed photoemission spectra are averaged over a large number of photoelectrons at the different times t, this leads to the distribution $P(W)$ of energy-shifts W of photoelectrons given by,

$$P(W)dW = \frac{C_N W_{max}}{(W_{max} - W)^2} \exp\left(-\frac{C_N W}{W_{max} - W}\right) dW, \quad (1)$$

with $C_N = R_N/vt$ and $W_{max} = \alpha e^2/4\pi\varepsilon_0 R_N$. This means that this dynamic final-state effect induces to an energy-shift distribution of photoelectron even if all nanoparticles are monodisperse and identically interact with the substrates. In Eq. (1), the parameters of W_{max} corresponds to the maximum

energy-shift due to the final-state effect, and is identical to the energy-shift for a free nanoparticle with an infinite photohole lifetime. As a result, the photoemission spectrum in the vicinity of Fermi-level for nanoparticle with a radius R_N, $S(E_B, R_N)$, can be described by the convolution of Fermi-Dirac function at relevant temperature and energy-shift distribution function $P(W)$ in Eq. (1), as a function of binding energy E_B. In the case of $C_N \ll 1$, the photoemission spectrum $S(E_B, R_N)$ is the Fermi-edge shifted by W_{max}. This corresponds to the case of free nanoparticle with an infinite photohole lifetime, i.e. the case of static charging. On the other hand, the case of $C_N \gg 1$ means that the photohole is immediately neutralized, therefore, the photoemission spectrum $S(E_B, R_N)$ shows no energy shift and is almost identical to the Fermi-edge observed for usual bulk metal. In the case of the intermediate regime of C_N, the Fermi-level onset in the photoemission spectrum is not the usual metallic Fermi-edge, with the steep slope being away from the Fermi-level, and the slope of leading edge depends on the values of C_N. Therefore, it is considered that the present photoemission spectra in the vicinity of Fermi-level originate from the dynamic final-state effect on the photoemission process. In addition to the intrinsic spectral feature $S(E_B, R_N)$, the experimental photoemission spectra $I(E_B)$ include the contribution from the inhomogeneous width due to the size distribution as shown in Fig. 1, since the photoemission spectrum $S(E_B, R_N)$ depends on a nanoparticle radius R_N. Furthermore, the observed photoemission spectra in the present experiments also include the contributions from a finite instrumental function and the photoemission intensity from the uncovered region of HOPG substrate. Therefore, the observed spectra $I(E_B)$ in the present experiments are expressed by,

$$I(E_B) \propto [S(E_B, R_N) \otimes D(R_N)] \otimes G(E_B) + B(E_B), \quad (2)$$

where $D(R_N)$ is a Gaussian size-distribution function in radius determined from the TEM observation, $B(E_B)$ is the photoemission intensity from the HOPG substrate determined by the experimental spectrum of HOPG, and $G(E_B)$ is an instrumental Gaussian function derived from a fit to experimental Fermi-edge of bulk Ag and Au. Using Eq. (2) with $S(E_B, R_N)$, we have carried out a fit to the experimental spectra by the least-squares method. The fitting lines to the experimental spectra are shown by solid lines in Fig. 2. As shown in Fig. 2, these fitting lines reproduce the experimental spectra for all diameters fairly well. Moreover, the spectral features of DT-passivated Au nanoparticles are also reproduced by the above theoretical calculations. From these calculations, the obtained parameters τ of the DT-passivated Ag nanoparticles on the HOPG substrates are 0.20×10^{-15}, 0.21×10^{-15}, 0.25×10^{-15} sec for the

mean diameters of 3.8, 4.2, and 5.3 nm, respectively. It is concluded that the observed spectral features for DT-passivated metallic nanoparticles on the HOPG substrates can be explained with the dynamic final-state effect model and reflect the nanoparticle and substrate interactions through the surface-passivants (DTs) on a femtosecond timescale. In the previous analyses for the photoemission spectra of evaporated Ag clusters by Hovel et al.,[9,10] they need a modified value of W_{max} compared to that with literal value $\alpha=0.41$, in order to reproduce their experimental data. On the other hand, we can reproduce the experimental spectra fairly well by the calculations using $\alpha=0.41$ in W_{max}, within the above theoretical framework. The present model treats the case of perfectly spherical particle. As shown in Fig. 1, our DT-passivated Ag nanoparticles have the spherical shapes, but the previous evaporated Ag clusters have the nonspherical shapes. Therefore, the effect due to the nonspherical particle shape might contribute to the deviation of W_{max} in the previous analyses. Furthermore, the obtained parameters of τ for the present DT-passivated Ag nanoparticles supported on the HOPG substrates is very close to those obtained for the evaporated Ag clusters.[9,10] This seems in contradiction to the expected weaker nanoparticle-substrate interaction through the surface-passivants in the present cases. However, the derivation of τ for the previous evaporated Ag clusters includes the additional modification of W_{max}. Therefore, it is difficult to quantitatively discuss the comparison of the both cases, and these comparisons are not conclusive. The lifetimes τ of the photohole directly correspond to the tunneling times through the surface-passivants of DTs. From the analogy of the single electron tunneling, these photohole lifetimes τ can be estimated to $\tau=RC$, where R is the tunnel resistance between the nanoparticle and substrate through the surface-passivants, and C is the self-capacitance of the nanoparticle as described above. Therefore, the present discussion will provide the knowledge about the single electron tunneling in the nanoparticle/tunneling-gap (surface-passivant) /substrate system. However, in order to quantitatively discuss the single electron phenomena from these final-state effects on photoemission, a more rigorous calculation, detailed size-dependence, and the detailed comparison with the tunneling microscopic experiments would be necessary. Furthermore, the synthesis of noble-metal nanoparticles passivated by other alkanethiolates and other organic molecules[14] have been reported to date, therefore, it would be possible to more systematically investigate the nanoparticle and substrate interaction by controlling nanoparticle-substrate configurations with the surface-passivants.

4. SUMMARY

We have performed a photoemission study for DT-passivated metallic nanoparticles supported on the HOPG substrates. It is found that the photoemission spectra in the vicinity of Fermi-level of DT-passivated metallic nanoparticles on the HOPG substrates are not the metallic Fermi-edge, with the steep slope being away from the Fermi-level. From a comparison with the theoretical calculation based on the dynamic final-state effect model that take into account the Coulomb interaction between the photoelectron and photohole during the photoemission process and the nanoparticle-substrate interaction, it is found that the calculated results reproduce fairy well the experimental ones for the present DT-passivated metallic nanoparticles on HOPG substrates. This suggests that the observed photoemission spectra give a direct evidence of nanoparticle-substrate interaction through the surface DTs on a femtosecond timescale and provide the knowledge of single electron phenomena.

REFERENCE

[1] M. P. A. Viegers and J. M. Trooster, *Phys. Rev. B*, **15**, 72 (1977).
[2] G. Medeiros-Ribeiro, D. A. A. Ohlberg, R. S. Williams, and J. R. Heath, *Phys. Rev. B*, **59**, 1633 (1999).
[3] M. Brust, M. Walker, D. Bethell, D. J. Schiffrin, and R. Whyman, *J. Chem. Soc., Chem. Commun.*, **1994**, 801 (1994).
[4] M. M. Alvarez, J. T. Khoury, T. G. Schaaff, M. Shafigullin, I. Vezmar, and R. L. Whetten, *Chem. Phys. Lett.*, **266**, 91 (1997).
[5] A. Taleb, V. Russier, A. Courty, and M. P. Pileni, *Phys. Rev. B*, **59**, 13350 (1999).
[6] W. D. Luedtke and U. Landman, *J. Phys. Chem.*, **100**, 13323 (1996).
[7] M. Seidl, K.-H. Meiwes-Broer, and M. Brack, *J. Chem. Phys.*, **95**, 1295 (1991).
[8] H. Hovel, B. Grimm, M. Pollmann, and B. Reihl, *Phys. Rev. Lett.*, **81**, 4608 (1998).
[9] H. Hovel, B. Grimm, M. Pollmann, and B. Reihl, *Eur. Phys. J. D*, **9**, 595 (1999).
[10] M. G. Mason, *Phys. Rev. B*, **27**, 748 (1983).
[11] T. Nagasawa, A. Tanaka, H. Sasaki, Y. Kuriyama, S. Suzuki, S. Sato, and T. Sekine, *Mat. Res. Soc. Symp. Proc.*, **704**, 319 (2002).
[12] A. Tanaka, Y. Takeda, T. Nagasawa, and S. Sato, *Phys. Rev. B*, **67** 033101 (2003).
[13] R. Kubo, A. Kawabata, and S. Kobayashi, *Annu. Rev. Mater. Sci.*, **14**, 49 (1984).
[14] T. Teranishi, M. Haga, Y. Shiozawa and M. Miyake, *J. Am. Chem. Soc.*, **122**, 4237 (2000).