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Dynamic final-state nanoparticle-substrate interaction in the photoemission of dodecanethiolate-passivated Ag nanoparticles on graphite substrates

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We have carried out a photoemission study of dodecanethiolate- (DT-) passivated Ag nanoparticles supported on the highly oriented pyrolytic graphite (HOPG) substrates. From detailed photoemission measurements, it is found that the Fermi-level onsets in the photoemission spectra of DT-passivated Ag nanoparticles on the HOPG substrates are not the metallic Fermi edge, with the steep slope being away from the Fermi level. We attribute the unusual spectral features in the vicinity of Fermi level to the dynamic final-state effect in photoemission, indicative of the interaction between the nanoparticle and substrate through the surface passivants on a femtosecond time scale.

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Metallic nanoparticles are attracting much interest from the viewpoint of both fundamental and device physics, since they show the distinctive physical and chemical properties found in neither bulk nor molecular-atomic systems, such as high catalytic activity[1] and Coulomb blockades.[2] The detailed study of these size-dependent properties of metallic nanoparticles should require a systematic synthesis of monodisperse samples. Recently, surface-passivated metallic nanoparticles have been chemically synthesized in a solution including surfactants.[3,4] These surface-passivated nanoparticles are monodisperse and very stable at room temperature: therefore, these are suitable to characterize their fundamental size-dependent properties. Furthermore, these surface-passivated nanoparticles exhibit closed-packed nanoparticle self-assemblies on single-crystalline substrates,[5,6] and therefore, it is considered that they could be important constituents of future nanostructured devices, such as single-electron devices, catalysts, and ultrahigh-density memory. In order to elucidate their detailed intriguing properties and to develop future devices, it is indispensable to understand the interactions with the substrates supporting the nanoparticles as well as their electronic structures.

In this work, we have carried out a photoemission study of dodecanethiolate- (DT-) passivated Ag nanoparticles supported on highly oriented pyrolytic graphite (HOPG) substrates. Photoemission spectroscopy, especially x-ray photoemission spectroscopy (XPS), has been used to study the electronic structures of free nanoparticles[7] (clusters) and nanoparticles evaporated on substrates,[8–11] but to our knowledge there is no report of an *ultraviolet* photoemission study with high energy resolution to date that highlights *surface-passivated* metallic nanoparticles synthesized by the chemical method. On the other hand, the final-state effect in the photoemission spectrum due to the photohole created by photoionization has been reported in previous photoemission studies.[7–11] The Coulomb interaction between the photoelectron and positive charge (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, although the nanoparticles are limited to having only positive charge in the case of photoemission. Knowledge of these quantum effects 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 ultraviolet photoelectron spectroscopy (UPS) for DT-passivated Ag nanoparticles supported on the HOPG substrates. From the discussions regarding the final-state effect on the photoemission spectra, especially we will discuss nanoparticle-substrate interactions through the surface passivants of DT-passivated Ag nanoparticles on the HOPG substrates.

The DT-passivated Ag nanoparticles were synthesized by a two-phase (water-toluene) reduction method.[3] An aqueous silver-ion solution ($AgNO_3$) was mixed with a toluene solution of phase transfer catalyst, tertraoctylammonium bromide $[(C_8H_{17})_4NBr]$, and consequently the silver salt is transferred into the toluene phase. This toluene phase was subsequently corrected, and a dodecanethiol ($C_{12}H_{25}SH$) and an aqueous sodium borohydride ($NaBH_4$) were added as a surface passivants and reducing catalyst, respectively. After stirring, the toluene-nanoparticle-rich phase was corrected and was evaporated in a rotary evaporator, and then was washed 3 times with ethanol to remove the phase transfer catalyst, excess dodecanethiol, and reaction by-products. This crude product was redispersed in toluene and was annealed at 353 K with dodecanethiol, and then was washed 3 times again with ethanol to remove the excess dodecanethiol. After that, the product was redispersed in toluene, and finally size-selective precipitation using the toluene-ethanol as the solvent-nonsolvent pair was performed by a centrifugation to improve the nanoparticle size distribution. In this method, the nanoparticle size can be controlled by the ratio of initial Ag ($AgNO_3$) and dodecanethiol. The size distributions in diameter and shapes of the synthesized DT-passivated Ag nanoparticles were characterized by *ex situ* observations with a JEM-2000EXII (JEOL Co.) transmission electron microscope (TEM). The samples for TEM observations were prepared by drying the toluene dispersions of DT-passivated Ag nanoparticles on the amorphous carbon-coated copper TEM grids. As a further characterization, the optical measurements were performed using the V-570 (Jasco Co.) spectrometer.

The thus-synthesized DT-passivated Ag nanoparticles were supported on HOPG substrates by evaporating the solvent (toluene) from the dispersion of DT-passivated Ag nanoparticles on the single-crystalline HOPG cleaved surface in a nitrogen-filled glove bag directly connected to the

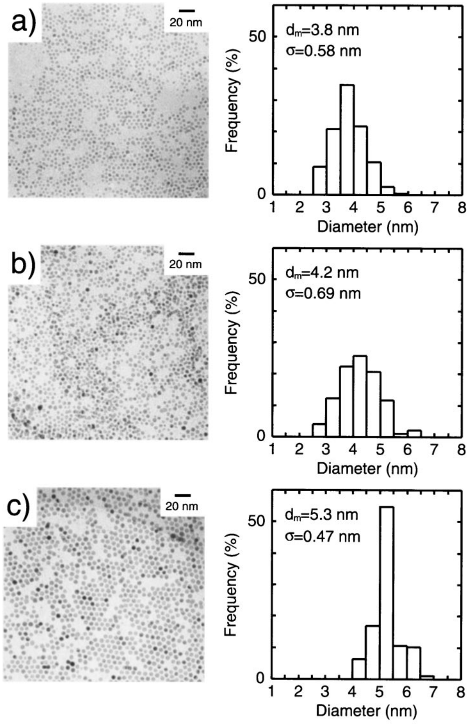

FIG. 1. TEM micrographs and size distributions in the diameter of dodecanethiolate-passivated Ag nanoparticles with mean diameters d_m and standard deviations σ of (a) $d_m = 3.8$ nm, $\sigma = 0.58$ nm, (b) $d_m = 4.2$ nm, $\sigma = 0.69$ nm, and (c) $d_m = 5.3$ nm, $\sigma = 0.47$ nm.

ultrahigh-vacuum photoelectron spectrometer. Then the samples were transferred into the photoemission analysis chamber without exposure to air. The cleanliness was checked by *in situ* Auger electron spectroscopy (AES) and *in situ* XPS. The thus-prepared samples show no AES and XPS signals from the contaminants. UPS measurements were performed using a ARUPS10 (VG Microtech Co.) photoelectron spectrometer with the He I resonance line ($h\nu = 21.2$ eV) as the excitation source. The base pressure of the photoelectron spectrometer was in the 10^{-9} Pa range. The total energy resolution was about 70 meV, and all measurements were performed at 40 K using a closed-cycle He refrigerator in order to minimize the thermal broadening effects. The photoemission spectra showed no change in the course of the measurements.

Figure 1 shows the TEM micrographs and the corresponding size distributions in diameter obtained by TEM observations for the DT-passivated Ag nanoparticles used in this work. The obtained mean diameters d_m are 3.8, 4.2, and 5.3 nm, and the standard deviations σ are 0.58, 0.69, and 0.47 nm, respectively. As shown in the TEM micrographs of Fig. 1, the present DT-passivated Ag nanoparticles show a homogeneous and spherical shape. An important point to note is that each nanoparticle is well separated from its neighboring nanoparticles, indicating that the present Ag nanoparticles are well surface passivated by the dodecanethiol molecules. Furthermore, the Ag nanoparticle sample with a mean diameter of 5.3 nm [Fig. 1(c)] has an extremely narrow size distribution in diameter ($\sigma < 9\%$) and locally forms the hexagonally ordered two-dimensional assemblies of Ag nanoparticles.

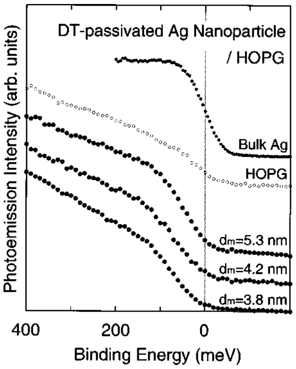

FIG. 2. Photoemission spectra in the vicinity of the Fermi level of dodecanethiolate-passivated Ag nanoparticles supported on the HOPG substrates at 40 K measured with the He I resonance line ($h\nu = 21.2$ eV). The mean diameter d_m is indicated on each spectrum. The top spectrum shows the Fermi-level onset observed for bulk Ag polycrystalline evaporated film for a comparison. The spectrum denoted by open circles shows the photoemission spectrum of the HOPG substrate.

Figure 2 shows the photoemission spectra in the vicinity of Fermi level of the DT-passivated Ag nanoparticles with various diameters on the HOPG substrates at 40 K using the He I resonance line ($h\nu = 21.2$ eV), compared with those of a bulk Ag polycrystalline evaporated film and HOPG substrate. As shown in Fig. 2, 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 similar spectral features: however, these photoemission spectra show distinct deviations from that of bulk Ag. That is, 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 the metallic Fermi edge observed for bulk Ag. Since the photoemission spectrum in the vicinity of the Fermi level of the HOPG substrate exhibits the featureless shape reflecting the vanishing semimetallic density of states toward the Fermi level as shown in Fig. 2, 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. In general, the photoemission spectra directly reflect the change in the electronic structure of the samples (initial-state effect) and are also affected by the final-state effect originating from the positively charged photohole created by the photoionization.[7–11] Therefore, first of all, these photoemission spectra seem to indicate that the electronic structures of the present DT-passivated Ag nanoparticles change with the nanoparticle size and exhibit the nonmetallic ones in this diameter regime. However, from the Kubo criterion,[12] this discussion is not reasonable for the relevant diameter regime. Of course, we cannot recognize the size-dependent spectral features originating from the quantum size effects on the *sp* and *d* states in the overall valence-band photoemission spectra of the present DT-passivated Ag nanoparticles. 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, indicative of a collective motion of valence electrons typical for a metallic material. These discussions mean that the observed spectral features in the vicinity of Fermi level are not due to the initial-state effect originating from the change in the electronic structure. Therefore, it is considered that these spectral features in the vicinity of the Fermi level of the present DT-passivated Ag nanoparticles originate from the final-state effect due to the photohole left behind in the nanoparticles during the photoemission process. When the vacuum ultraviolet light excites a photoelectron, the photohole left behind in the nanoparticles during the time scale relevant to the photoemission process will lower the kinetic energy of photoelectrons through the Coulomb interaction. Thus, although the relaxation response within the nanoparticle may otherwise proceed normally, an excess positive charge left behind in the nanoparticle significantly induces the final-state effect in the photoemission. In fact, these final-state effects on the photoemission spectra have been reported for the free nanoparticles[7] and even for nanoparticles on the substrates.[8–11] This final-state effect would play a more important role in the present surface-passivated Ag 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 of photoelectrons due to the photohole left behind in the nanoparticle is given by $\Delta E = e^2/2C$, where $C = 4\pi\varepsilon_0 R_N$ is the self-capacitance of the nanoparticle with a radius of 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 nanoparticles.[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 the photoemission process should be same as that of single-electron tunneling. Therefore, investigations of the final-state effect on the photoemission process will provide information about the single-electron tunneling.

In order to theoretically describe these observations, we analyzed the photoemission spectra in the vicinity of the Fermi level of DT-passivated Ag nanoparticles using a dynamic final-state effect model[9,10] that takes into account the Coulomb interaction between the photoelectron and photohole with a finite lifetime during the photoemission process. In this model, the probability of photohole neutralization during the time interval $[t, t+dt]$ is described by $P(t)dt = (1/\tau)\exp(-t/\tau)dt$, with a charactertic time τ determined by the coupling strength between the nanoparticle and substrate. While the photohole created by photoionization remains in the nanoparticle, the Coulomb interaction between the photoelectron and photohole induces energy shifts of the photoelectrons. The Coulomb potential acting on the photoelectron due to the photohole from the nanoparticle to infinity 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 the nanoparticle. Since the present Ag nanoparticles have 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 described by $W(R_N + vt)$. The observed photoemission spectra are averaged over a large number of photoelectrons at different times t: therefore, this leads to a distribution of the energy shifts 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 $C_N = R_N/v\tau$ and $W_{\max} = \alpha e^2/4\pi\varepsilon_0 R_N$ with $\alpha = 0.41$ for Ag. This means that this dynamic final-state effect induces an energy-shift distribution of photoelectrons even if all nanoparticles are monodisperse and identically interact with the substrates. In Eq. (1), $W_{\max}$ corresponds to the maximum energy shift of the photoelectron due to the dynamic final-state effect and is identical to the energy shift for a free nanoparticle with an infinite photohole lifetime. The photoemission spectrum in the vicinity of the Fermi level for a nanoparticle with a radius of R_N, $S(E_B, R_N)$, can be described by the convolution of the Fermi-Dirac function at a relevant temperature and the 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 a 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 a 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 photoemission spectra in the vicinity of the Fermi level observed for DT-passivated Ag nanoparticles on the HOPG substrates originates from the dynamic final-state effect on the photoemission process.

In addition to the intrinsic spectral feature as described above, 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 contributions from a finite instrumental width and the photoemission intensity from uncovered region of the HOPG substrate. Therefore, the observed photoemission spectra 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 determined from the TEM observation as show in Fig. 1, $B(E_B)$ is the photoemission intensity from the HOPG substrate, and $G(E_B)$ is an instrumental Gaussian function derived from a fit to the experimental Fermi edge of bulk Ag. Using Eq. (2) with $S(E_B, R_N)$, we have carried out a fit to the experimental spectra of the DT-passivated Ag nanoparticles by the least-squares method. The fitting lines to the experimental spectra are shown by solid lines in Fig. 3. As shown in Fig. 3, these fitting lines, which take into account the dynamic final-state

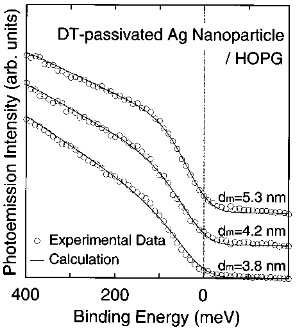

FIG. 3. Comparison of the calculated results based on the dynamic final-state effect model (see text) with the experimental photoemission spectra at 40 K of dodecanethiolate-passivated Ag nanoparticles with mean diameters of 3.8, 4.2, and 5.3 nm. Open circles and solid lines show the experimental photoemission spectra and the fits to the experimental spectra, respectively.

effect, reproduce the experimental spectra for all diameters fairly well. From these calculations, the obtained parameters τ of the DT-passivated Ag nanoparticles supported on the HOPG substrates are 0.20×10^{-15}, 0.21×10^{-15}, and 0.25×10^{-15} sec for the mean nanoparticle diameters of 3.8, 4.2, and 5.3 nm, respectively. It is concluded that the observed spectral features for DT-passivated Ag 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 (DT) on a femtosecond time scale. In the previous analyses for the photoemission spectra of evaporated Ag clusters by Hövel *et al.*,[9,10] they need a modified value of $W_{\max}$ compared to that with $\alpha=0.41$, given in the work for free Ag nanoparticles,[7] in order to reproduce their experimental data. On the other hand, in our analyses, we can reproduce the experimental spectra fairly well by the calculations using $\alpha=0.41$ in $W_{\max}$, within the theoretical framework of the above dynamic final-state model. The present model, as described above, treats the case of perfectly spherical particles. As shown in Fig. 1, our DT-passivated Ag nanoparticles have spherical shapes, but the previous evaporated Ag clusters have 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 nanoparticles.[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 nanoparticles 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 DT. From the analogy of single-electron tunneling, these photohole lifetimes τ can be estimated to be $\tau=RC$, 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 discussions will provide 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 detailed comparison with the tunneling microscopic experiments would be necessary. Furthermore, synthesis of the noble-metal nanoparticles passivated by other alkanethiolates and other organic molecules[13] has been reported to date: therefore, it would be possible to more systematically investigate the nanoparticle-substrate interaction by controlling the nanoparticle-substrate configurations with the surface passivants.

In summary, we have performed a photoemission study of DT-passivated Ag nanoparticles with various diameters supported on HOPG substrates. It is found that the photoemission spectra in the vicinity of the Fermi level of DT-passivated Ag nanoparticles on HOPG substrates are not the metallic Fermi edge, with the steep slope being away from the Fermi level. From comparison with a theoretical calculation 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 the nanoparticle-substrate interaction, it is found that the calculated results reproduce fairly well the experimental ones for the present DT-passivated Ag nanoparticles on HOPG substrates. This suggests that the observed photoemission spectra give direct evidence of the nanoparticle-substrate interaction through the surface DT's on a femtosecond time scale and provide knowledge of single-electron phenomena.

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