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Two-photon photoemission from silver nanoparticles on thin alumina films: Role of plasmon excitation

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Abstract

Two-photon photoemission (2PPE) from silver nanoparticles on a thin Al_2O_3 film on NiAl(1 1 0) has been investigated using femtosecond lasers. The 2PPE spectra show a feature similar to the surface state of Ag(1 1 1). The total 2PPE yield possesses a maximum at about 3.6 eV which corresponds to the surface plasmon resonance of the silver particles. For particle sizes of about 10 nm an enhancement by a factor 450 compared to Ag(1 1 1) is found. Up to this diameter the photoemission yield increases but levels off for larger sizes due to interactions between the particles. It is inferred that the 2PPE process is a direct transition via a virtual state, and that the enhanced 2PPE yield results from the enhancement of the electromagnetic field at the surface of nanoparticles.

Keywords: Surface photochemistry; Photoelectron spectroscopy; Plasmon; Silver; Cluster

1. Introduction

Electron dynamics at metal surfaces has been the focus of intense studies in the last decade. Especially, the dynamics of electrons in the image potential state and secondary electrons have been successfully investigated by time-resolved two-photon photoemission spectroscopy (2PPE) [1,2]. In photo-induced processes of adsorbates on metal surfaces, the surface electron dynamics play a crucial role especially in the substrate mediated mechanism [3] where adsorbates are excited by hot electrons (or holes) from the substrate.

On surfaces of nanometer-sized metal particles, electron dynamics and photo-induced processes are expected to differ significantly from those on bulk metal surfaces due to the confinement effects when the particle size is reduced to nanometer order. The tunability of particle size will provide a way to control photochemistry of adsorbed

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molecules on nanoparticles. For example, the cross section and branching ratio of photochemistry of methane and photodesorption of NO on palladium nanoparticles were shown to depend on the particle size [4,5]. Another unique property for metal nanoparticles is the excitation of surface plasmons. It is well known that small particles and surface corrugations of gold and silver show plasmon resonances at around 2 and 3 eV. Surface enhanced Raman Spectroscopy (SERS) utilizes the plasmon enhanced surface electric field up to 10^6 times.

Meech et al. have shown that the surface plasmon enhances photochemistry of small molecules adsorbed on ion bombardment roughened silver surfaces [6]. The photoreaction cross sections of OCS, NO, and SO_2 were found enhanced at about 3.5 eV irrespective to the type of molecules, which corresponds to the typical surface plasmon resonance of silver. They proposed that the plasmon enhanced surface electric field enhances the excitation of electron–hole pairs which trigger photochemistry of adsorbates.

The enhancement of the electron–hole pair yield by plasmon excitation can be probed by two-photon photoemission spectroscopy. Gerber et al. investigated 2PPE from silver nanoparticles (3.6 nm diameter) on HOPG [7]. The 2PPE yield was enhanced by two orders of magnitude compared to the bare HOPG substrate at 3.2 eV (400 nm). This led them to propose coherent multiple excitation of surface plasmons.

In addition to the excitation mechanism, the size dependence of the 2PPE process from silver nanoparticles with photon energies near the plasmon resonance is of particular interest in connection with the surface photochemistry. The particle size can be controlled by the amount of deposited silver [8]. In this work, we investigate the photon energy and particle size dependences of two-photon photoemission from size-controlled silver nanoparticles on thin alumina films.

2. Experimental

A two-chamber ultrahigh vacuum system (base pressure $<1 \times 10^{-10}$ mbar) was used [9]. An oxidized NiAl(1 1 0) crystal, coolable to 83 K, is used as support for the Ag nanoparticles. After cleaning by argon bombardment and annealing an epitaxial film of Al_2O_3 of 0.5 nm thickness is obtained by two cycles of oxidizing the clean NiAl at an oxygen pressure of 4×10^{-6} mbar at 540 K and annealing at 1200 K [10]. Prior to each measurement the sample is sputtered again and re-oxidized.

Silver atoms are evaporated from an evaporation oven onto the oxide film at room temperature; the average thickness is monitored by a microbalance. The particle sizes and island densities have been obtained from separate STM measurement [8]. Under the experimental conditions ordered Ag nanoparticles between 2 and 12 nm, located preferentially at atomic steps, are produced at a constant density of 4×10^{11} cm^{-2}.

The measuring principle of 2PPE and photodesorption is illustrated in Fig. 1. For 2PPE either the 390 nm radiation of the femtosecond laser at 1 kHz (pulse length 100 fs) is used or the tunable light from an optical parametric amplifier (TOPAS, Light Conversion) at a typical fluence

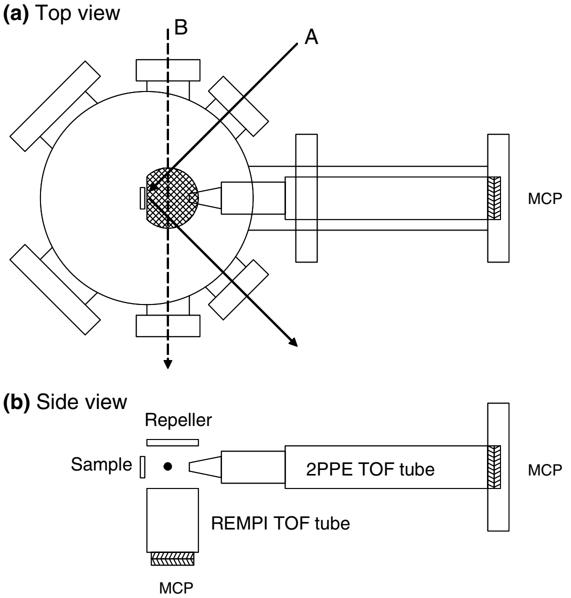

Fig. 1. Experimental setup for 2PPE and REMPI photodesorption measurements: arrow A indicates the femtosecond laser beam for 2PPE and arrow B the probe laser beam for REMPI.

of 30 nJ/cm^2. For polarization dependent measurements a $\lambda/2$ plate is positioned in front of the entrance view port. The energy-resolved electron spectra have been obtained with a time of flight (TOF) spectrometer (tube length of 60 cm, resolution 2 ns). For comparison a (1 1 1) oriented Ag crystal is also mounted on the cooling stage. Each crystal can be heated separately by radiation or additionally by electron impact from a tungsten filament.

3. Results and discussion

Fig. 2 displays a series of 2PPE spectra measured at $h\nu = 3.2$ eV with p-polarization from Ag(1 1 1) and Ag nanoparticles on Al_2O_3/NiAl(1 1 0) for various silver depositions (0–0.9 nm mean thickness). The 2PPE spectrum from Ag(1 1 1) shows the Shockley surface state peak near the Fermi energy, E_F (at about 2.0 eV), and the sp-band peak [11] at 1.0 eV. The 2PPE intensity of silver nanoparticles initially increases with silver deposition and levels off at about 0.9 nm. The total photoelectron yield is then about 100 times larger than that from the bulk Ag(1 1 1). The broad feature near the Fermi edge becomes more pronounced with increasing deposition, and its maximum shifts to higher kinetic energy. A similar behavior has been observed by ultraviolet photoemission spectroscopy (UPS) for the surface states of Ag(1 1 1) thin films on graphite which approach the position of the bulk Ag(1 1 1) surface state peak with increasing film thickness [12]. Also, we confirmed that this feature is quenched by adsorption of NO accompanied by the reduction of 2PPE intensity. Therefore it can be attributed to surface states on Ag nanoparticles. Even though silver on alumina grows at 300 K in the Volmer–Weber mode forming 3D particles [10], there might exist small (1 1 1) facets on the particle surface which produce occupied Shockley surface states near the Fermi level. The feature appeared only with p-polarized light in accord with the selection rule at Ag(1 1 1). In contrast to the compact crystal, however, the total 2PPE yield with p-polarized light was 8.5 times higher compared to s-polarized light, for silver deposition of 0.4 nm and more. This could be due to the enhancement of the surface electric field by plasmon excitation as will be discussed later.

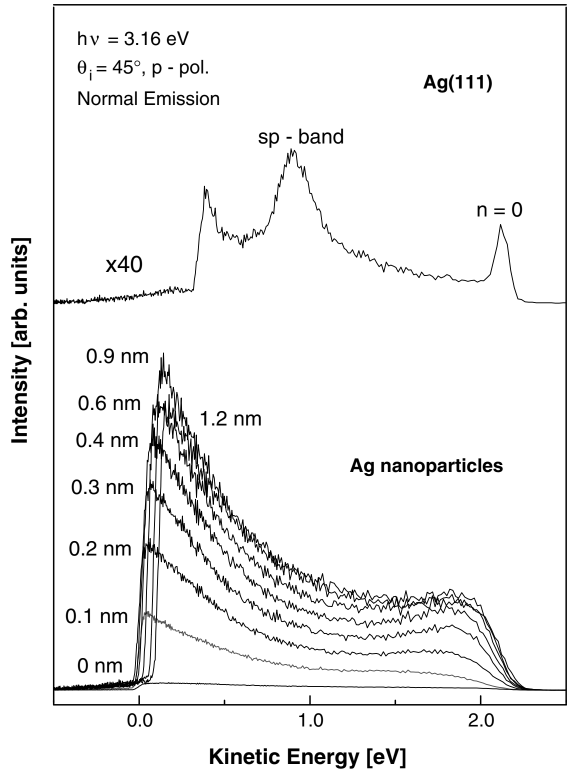

Fig. 2. 2PPE spectra from Ag(1 1 1) and Ag nanoparticles on Al_2O_3/NiAl(1 1 0). The corresponding silver deposition is shown in nm units.

We confirmed that the total 2PPE yield is proportional to the square of laser intensity. The quadratic dependence was checked also by measuring the photocurrent for higher laser intensities ($\leqslant 9\ \mu J/cm^2$) for 0.9-nm silver deposition at $h\nu = 3.6$ eV for which the photocurrent was the highest (~80 pA). Therefore it is concluded that the photoemission from silver nanoparticles with photon energies near the plasmon resonance is a two-photon process in the range of our measurements.

The photon energy dependence of the 2PPE yield is shown in Fig. 3. The total 2PPE yield from 0.9-nm deposited silver nanoparticles, obtained by integration of the spectrum from zero to E_F is

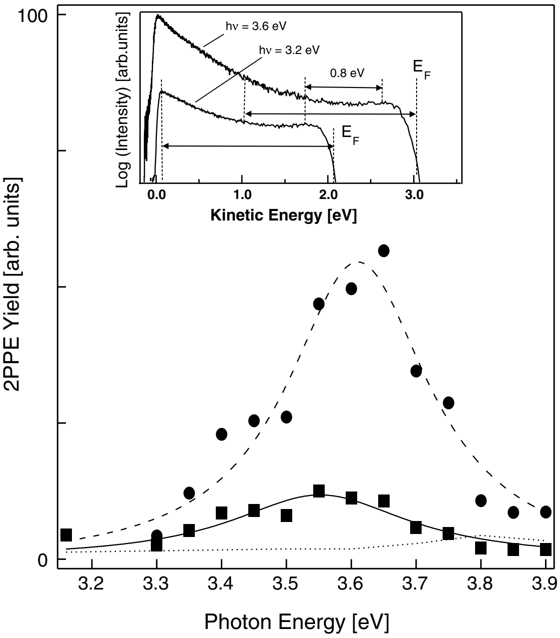

Fig. 3. Photon energy dependence of the 2PPE yield of Ag nanoparticles. The solid circles and the solid squares represent the total and the partial integrations of the 2PPE yield, respectively. The solid and the dashed curves indicate Lorentzian fits. The dotted curve shows the total 2PPE yield of Ag(1 1 1). The inset displays 2PPE spectra of 0.9-nm deposited silver nanoparticles at $h\nu = 3.2$ and 3.6 eV. The arrows indicate the width of integration and the peak shift.

plotted by solid circles. The fit by a Lorentzian shown by the dashed curve gives a peak at 3.61 eV with a width of 0.27 eV, which corresponds to the surface plasmon resonance of silver. In the inset, the 2PPE spectra of silver nanoparticles measured at $h\nu = 3.2$ and 3.6 eV are shown. We notice that the signal intensity is much larger at 3.6 eV than at 3.2 eV, and that the contribution of secondary electrons increases with increasing photon energy. In order to compare the photoemission cross section, the same energy window of the initial state is used. The solid squares correspond to integration from E_F to E_F-2 eV. The Lorentzian fit shown by the solid curve gives a peak at 3.55 eV and a width of 0.34 eV. For both cases, the peak position agrees with the results from photon STM [8] and cathodoluminescence [13] measurements, where the peak was attributed to the surface plasmon resonance. In contrast, the total 2PPE yield for Ag(1 1 1), shown by the dotted line, is much lower than that of the silver nanoparticles. The peak at about 3.8 eV is due to interband transitions [14]. At $h\nu = 3.6$ eV the ratio of the total 2PPE yields of Ag(1 1 1) and 0.9-nm deposited silver nanoparticles is 450 (135) with (without) correction for the coverage of silver nanoparticles (about 0.3). With increasing silver deposition to 2.0 nm, the peak shifted to 3.67 eV. Compared to the shift, the peak broadening was more evident (0.40 eV), suggesting inhomogeneity in the particle sizes and structures.

It is of interest to see how the total 2PPE yield changes with the volume of a particle V. Note that V is proportional to the silver deposition because the density of small silver nanoparticles is nearly constant at 4×10^{11} cm^{-2} [8]. Fig. 4(a) is a plot of the total 2PPE yield measured at $h\nu = 3.2$ and 3.6 eV as a function of silver deposition. The 2PPE yield at $h\nu = 3.2$ eV monotonically increases up to 0.4-nm deposition, then levels off for larger deposition. At $h\nu = 3.6$ eV, the 2PPE yield initially increases with V, i.e., as the number of silver atoms, but grows more weakly from 0.6 nm. After a peak at 0.9 nm, the yield decreases for larger deposition.

We ascribe the saturation of the 2PPE yield to coalescence of nanoparticles that begins at about 0.6-nm deposition [15]. For larger depositions, the particles start to form elongated wires decorating substrate steps, because the majority of the particles grow on step edges. This should lead to changes in the size evolution. Both particle shape and interaction between particles influence the plasmon oscillation [16]. This manifests itself in the irregular change of the 2PPE yield for $h\nu = 3.6$ eV. The 2PPE yield should be most sensitive to shape changes at the resonant photon energy, i.e., at $h\nu = 3.6$ eV. On the other hand, it is less sensitive at photon energies far from the resonance, e.g., at $h\nu = 3.2$ eV. The saturation and decrease of the 2PPE yield is explained by the decrease of particle number and the change in optical properties of the nanoparticles by further coalescence.

Fig. 4(b) is a plot of the total 2PPE yield data in Fig. 4(a) as a function of mean particle diameter

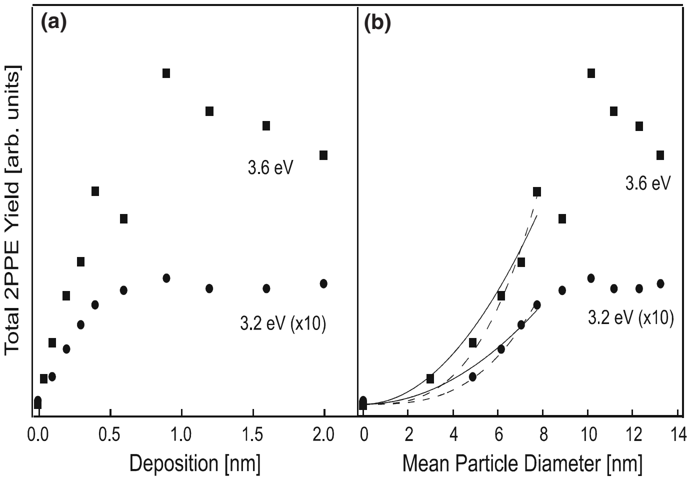

Fig. 4. Total 2PPE yield of Ag nanoparticles at $h\nu = 3.2$ and 3.6 eV as functions of (a) silver deposition and (b) mean particle diameter. The solid curves and the dashed curves indicate fits by quadratic and cubic functions, respectively.

($D \propto V^{1/3}$). Here, we used an experimental calibration curve from STM observations of silver nanoparticles [17], $D = ax^{1/3}$, where D is particle diameter (nm), x silver deposition (nm), and a a scaling factor. The solid and dashed curves are the best fits to a quadratic and a cubic function for small particle sizes, respectively. It is seen from these plots that the 2PPE yield at $h\nu = 3.6$ eV scales as $V^{2/3}$, i.e., as the surface area of particles, and that the 2PPE yield at $h\nu = 3.2$ eV scales as V, i.e., the volume of particles. However, the difference between the quadratic and the cubic fits is too small to determine the size dependence. For both cases, the 2PPE yield is expressed by a simple function form of V. Therefore, intrinsic size effects on electron dynamics are not recognizable for the smaller size region where the interaction between particles is not significant.

Now we discuss the mechanism of 2PPE from the silver nanoparticles. Because there is no unoccupied state at about 3.6 eV above E_F, the 2PPE process is likely a direct transition. Then the question arises as to the nature of the intermediate state. In the 2PPE of Ag(1 1 1), the intermediate state is a virtual state. Here, we consider the single-particle state created by plasmon decay (Landau damping) as the intermediate state. The energy transferred to an electron by plasmon decay should be peaked at the plasmon resonance energy [18], i.e., at about 3.6 eV, because the decay time of these electron is short enough compared to the pulse duration used in this study (~100 fs). Because the excitation of this electron by the second photon is incoherent, the resulting electron kinetic energy should be $h\nu + 3.6 + E_B - \phi$, where E_B is the binding energy of the initial state and ϕ the work function. This disagrees with our 2PPE results: As shown in the inset of Fig. 3, the shift of the feature near E_F is about 0.8 eV, i.e., twice the photon energy difference, $2\Delta h\nu$. The Fermi edge also shifts by $2\Delta h\nu$. This photon energy dependence, $2h\nu + E_B - \phi$, indicates that the 2PPE is a direct (coherent) excitation without scattering processes [19]. This criterion is not applicable to the structureless distribution of the hot electrons dominating the major part of the 2PPE spectrum. Therefore single-particle states created by plasmon decay with lower energies than $h\nu$ cannot be excluded completely. Importantly, our results clearly show that the direct 2PPE process via a virtual state, which was ruled out by Gerber et al. [7], is not a minor process.

The observed enhancement of the direct two-photon excitation can be explained by the enhancement of the surface electric field at the particle surfaces. Recently, Geshev et al. reported calculated field enhancement factors (FEF) on a metal particle near a metal surface [20]. The FEF on the top of a 16-nm silver particle 1 nm above a gold substrate is estimated to be about 4 at $h\nu = 3.6$ eV, and the FEF without the substrate is to about 5. These values result in enhancement factors of 256–625 for a two-photon process. It should be noted that the FEF calculations are based on an axial ratio of 3–5 and a particle–substrate distance of 1 nm which are different from our case (axial ratio = 0.6 and distance = 0.5 nm separated by an Al_2O_3 film from a NiAl substrate). However, these values agree reasonably with the range of the observed enhancement of 2PPE yield.

Another interpretation for the 2PPE yield which is resonantly enhanced at the surface plasmon energy is the Beutler–Fano effect. In this case, 2PPE can be regarded as a transition to continuum states and the surface plasmon as a discrete state. The asymmetrical shape characteristic for the Beutler–Fano effect is not seen in the photon energy dependence data shown in Fig. 3. However, this data is the sum of two-photon photoemissions from different initial states including hot electrons. The possible contribution of this effect will be investigated in future studies.

4. Conclusion

We have investigated the role of plasmon excitation in the 2PPE processes of silver nanoparticles on thin alumina films. An enhancement of the 2PPE yield by a factor 450 compared to Ag(1 1 1) was found. The 2PPE yield scales almost to the volume of silver particles, suggesting the lack of an intrinsic size effect. The observed 2PPE process is a direct transition via a virtual state. We suggest that the enhancement is due to the surface electric field enhancement. The 2PPE spectra suggest the presence of surface states similar to that of Ag(1 1 1).

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