

Cluster–surface interaction studied by time-resolved two-photon photoemission

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Abstract. We use time-resolved two-photon photoemission to study the stability of size selected Ag_n^+ clusters ($n = 2 - 9$) deposited onto highly oriented pyrolytic graphite (HOPG) substrates at liquid nitrogen temperatures. The deposition was carried out with variable kinetic energies of the clusters. Clusters deposited with high kinetic energy (up to 60 eV/cluster) become fragmented upon impact. For low deposition energies (1–4 eV/cluster) the size dependence of the photoelectron spectra reveals a pronounced odd/even effect, which is well known for gas phase silver clusters. This indicates that the soft deposited clusters retain their size and identity on the sample. The phase of the odd/even effect suggests that transient negatively charged cluster ions serve as an intermediate step in the two-photon photoemission process. The lifetime of the anions rises with cluster size. This is attributed to an increasing electronic density of states for larger clusters.

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Time-resolved two-photon photoemission (2PPE) not only probes the density of states of the occupied and unoccupied levels in the substrate–adsorbate complex, but also allows one to access the dynamics of charge and energy transfer processes [1–6]. The method is used here for the first time to probe surfaces covered with mass selected clusters. 2PPE experiments are especially suited to study substrate–adsorbate complexes, because an empty state or resonance of the adsorbate can serve as an intermediate state. This is schematically illustrated in Fig. 1. The first photon transfers an electron from the substrate into an unoccupied state of the adsorbate. The second photon excites the electron from the intermediate state into a continuum state above the vacuum level. With short pulse lasers it is therefore possible to study the dynamic behavior of electrons which cross the interface between substrate and adsorbate.

Time-resolved pump–probe techniques of this kind combined with 2PPE spectroscopy using ultrashort laser pulses have been applied to study carrier dynamics in semiconductors [7–10] and metals [11–15], adsorbate–substrate

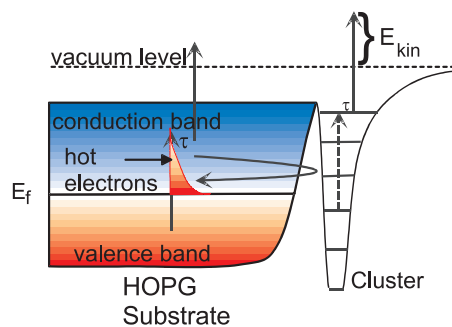


Fig. 1. Scheme of the two-photon photoemission process from adsorbate covered surfaces. The first laser pulse creates hot electrons in the substrate which eventually transfer into unoccupied levels of the adsorbate. From there they are photodetached by the second laser pulse

charge transfer [14, 16–18] and electron dynamics of image-potential states [13, 19–21].

It is well known from scanning tunneling microscopy, that silver clusters on HOPG diffuse easily and tend to aggregate into larger particles at room temperatures [22, 23]. Therefore our experiments have been conducted at the temperature of liquid nitrogen. Moreover diffusion depends on the deposition energy of the clusters [24]. The impact of clusters on surfaces might result in a variety of possible deformations of the cluster or the surface. Ag_n^+ ($n = 50 - 400$) was found to flatten after deposition with 10 eV per atom on graphite [25]. Ag_7^+ fragments upon impact on a Pd(100) surface with a deposition energy of 2.85 eV per atom [25]. It was modelled by Cheng and Landman that a Cu_{147} cluster deposited with 2 eV per atom on a copper surface undergoes internal melting [26].

1 Experiment

The experiments were performed in a ultra-high-vacuum system with a base pressure of 5×10^{-10} mbar. Figure 2 shows a scheme of the experimental setup. The silver clusters are produced in a sputtering arrangement and they are mass-filtered in a quadrupole mass filter. Our setup allows cooling of the clusters in a gas-filled quadrupole ion guide, which

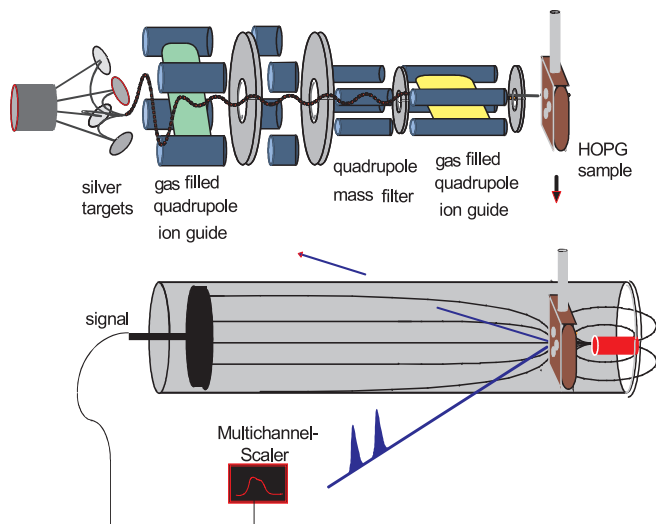


Fig. 2. Schematic diagram of the experimental setup. (For details see main text)

is located between the sputtering source and the mass filter. We thereby can perform a soft-landing experiment with mass-selected cluster ions with a deposition energy considerably lower than the binding energy per atom of the cluster. A cold-reflex discharge ion source (CORDIS) [27, 28] was modified to yield four primary Xe^+ -ion beams of typically 15 kV and about 5 mA each. They are directed onto four water-cooled silver targets. The emerging clusters are collected by electrostatic fields and they are deflected into a large gas-filled ion guide, which serves to moderate and cool the ions by collision with He gas. The cluster ions are mass selected by a quadrupole mass filter and are guided into the UHV deposition chamber by another quadrupole ion guide where their kinetic energy is further reduced. Adjustable electrostatic lenses and a retarding potential at the sample serve to determine the kinetic energy distribution in the cluster beam. With this setup it is possible to achieve real soft landing conditions with deposition energies of 1–2 eV/cluster (Fig. 3, below). It is possible as well to deposit clusters with preselected high deposition energies and a narrow energy distribution. The cluster source provides a cluster beam between 700 pA for Ag_4 and 3 nA for Ag_3 .

The HOPG substrate is cleaved before insertion into the vacuum chamber. Under UHV conditions it is cleaned by an electron gun which allows rapid flashing of the sample to 1400 K. The substrate is then cooled to liquid nitrogen temperatures within 2 hours. The temperature is measured near the sample at the lower part of the sample holder which is electrically isolated against the upper part of the sample holder by means of sapphire crystals. This allows to monitor the deposition rates by measuring the cluster current on the sample as the spot size of the cluster beam was measured to be 15.7 mm^2 . The distribution of the kinetic energy of the deposited clusters is controlled by monitoring the current of the deposited ions as a function of the retarding potential applied to the substrate. Typical curves obtained with and without buffer gas are displayed in Fig. 3. The width of the distribution of the kinetic energy of the clusters is obtained by taking the FWHM of the negative derivative of the curves shown in Fig. 3. Without buffer gas it amounts to 18.13 eV, which is

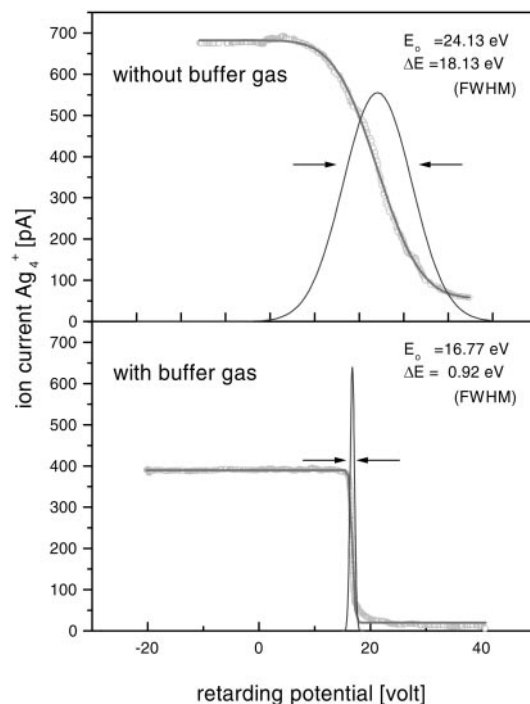


Fig. 3. Deposition current as a function of retarding voltage and corresponding energy distribution of silver tetramer anions with and without buffer gas (see text)

a typical value for sputtering ion sources. With buffer gas in both ion guides, the width decreases to 0.92 eV while the total intensity remains about 60% of the initial value. By adjusting the retarding voltage of the substrate, we are therefore able to control the kinetic energy of the deposited clusters.

The coverage of the sample was chosen to lie below 8% of a monolayer. The duration of the deposition is depending on the cluster size. Corresponding to the above mentioned cluster beam current it takes between 5 and 45 minutes. After the deposition, the sample is moved into the photoelectron spectrometer.

We use a magnetic bottle type time-of-flight spectrometer which was introduced some years ago by Kruit and Read for gas-phase applications [29]. The instrument makes use of a strong diverging magnetic field to collect the photoelectrons and a weak guiding magnetic field, which directs the electrons through a flight tube to an electron multiplier (microsphere plate [30]). The strong field is produced by a small bakeable permanent magnet (1 T) which is placed directly behind the HOPG substrate. The guiding field (1 mT) is produced by a long coil. The whole electron spectrometer is surrounded by four Helmholtz coils for the compensation of the magnetic field of the earth. The interior of the spectrometer is coated with graphite to ensure a homogeneous work function. An electron acceptance angle of about 2π is theoretically possible. For these experiments the magnetic bottle design was indispensable because of the efficient increase of the signal compared to a conventional time-of-flight spectrometer. The time-of-flight of the electrons is measured by a time-to-digital converter and later converted into the kinetic energy of the electrons. The calibration of the spectrometer is carried out by taking a series of photoelectron spectra of the pure graphite sample with different voltages applied to the sample.

The sample is irradiated under 45° by two subsequent laser pulses of 390 nm ($h\nu = 3.17$ eV) with adjustable time delay. The laser system consists of a titanium sapphire oscillator which is pumped by a 9 W argon ion laser and of a Nd:YLF-pumped regenerative amplifier to produce ultrashort ($\tau < 100$ fs, $400 \mu\text{J}/\text{pulse}$) laser pulses with a repetition rate of 1 kHz. The pulses are frequency doubled in a BBO crystal. The beam is separated into two pulses and one of them is delayed by a computer controlled delay line. The intensity of the light on the sample must be controlled carefully in order to avoid multiphoton processes and space charge broadening. Therefore the experiments were carried out with a pulse energy of below 500 nJ and a peak intensity of about 10^8 watt/cm 2 as the spot size on the sample is about 1 mm 2 . Both beams were *p*-polarized, i. e. with the electric field vector being parallel to the plane of incidence.

2 Results and discussion

Figure 4 shows a typical 2PPE spectrum. The photoelectron yield is plotted as a function of the kinetic energy of the photoelectrons. The spectrum has a broad and asymmetric shape. At liquid nitrogen temperatures, the form is similar for all cluster sizes ($n = 2 - 9$), but it shifts along the energy axis for the different sizes. Therefore we show the size dependence of the mean kinetic energy of the photoelectrons in Fig. 5. It reveals an odd/even alternation that is well known from gas phase photoelectron spectroscopy of small silver clusters [31, 32]. The odd/even effect was found for the ionization potential (IP) of neutral gas phase silver clusters [33, 34] as well as for the electron affinity or the vertical detachment energy (VDE) of negatively charged gas phase silver clusters [32, 35]. The IP and the VDE were also theoretically calculated with ab-initio methods [36] and correspond well with the experimental results.

First of all, the observation of size dependent variations of the mean photoelectron energies in our experiments indicate, that the clusters retain their size and identity on the sample. This holds true especially at low sample temperatures, low deposition energies and low coverage. In our experiment, we find high photoelectron energies which correspond to low electron binding energies for the even numbered clusters. This suggests, that the transient species which is probed by

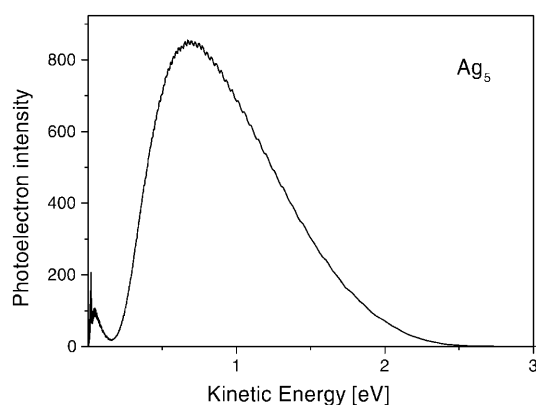


Fig. 4. 2PPE spectrum for Ag_5 deposited on a HOPG substrate. The spectrum is summed over 10^5 shots with a background signal negligible on the scale shown

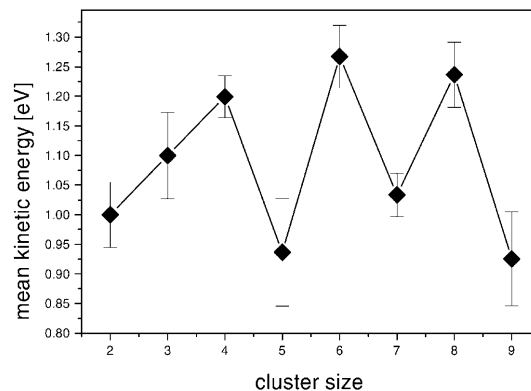


Fig. 5. The mean kinetic energy of the photoelectrons, defined as the center of gravity of the photoelectron spectra, plotted as a function of the cluster size

the second laser pulse is a cluster anion, as for Ag_n^- , the electron affinity is high for odd n but low for n even. This picture is also in agreement with the classical picture of substrate-adsorbate photochemistry [37].

Our tentative understanding of the 2PPE process is therefore as follows: The first photon excites an electron from an occupied state of the substrate to an unoccupied intermediate state of the cluster forming a transient cluster anion. A second photon of the same energy photodetaches the excess electron from the cluster which returns to be neutral in the final state.

We estimate the relaxation dynamics of the transient cluster anion, i. e. the lifetime of the transiently populated state, by varying the delay time between the laser pulses. A typical 2PPE signal obtained for Ag_5 is given in Fig. 6. The shape of the curve is roughly gaussian both for clean and cluster covered substrates, but the full-width at half-maximum (FWHM) of the curve is increasing with the cluster size. The signal is a convolution of the physical relaxation time of the system and the laser pulse autocorrelation width. The latter can be obtained with reasonable accuracy from two photon photoemission spectra of gold foils, as the relaxation times here are known to be on the order of some femtoseconds. From this we obtain a relaxation time which rises from about $210 \text{ fs} \pm 30 \text{ fs}$ for Ag_4 to $510 \text{ fs} \pm 70 \text{ fs}$ for Ag_9 as shown in Fig. 7. The relaxation times are a property of the whole cluster substrate system. At the present time the reason for the increasing life-

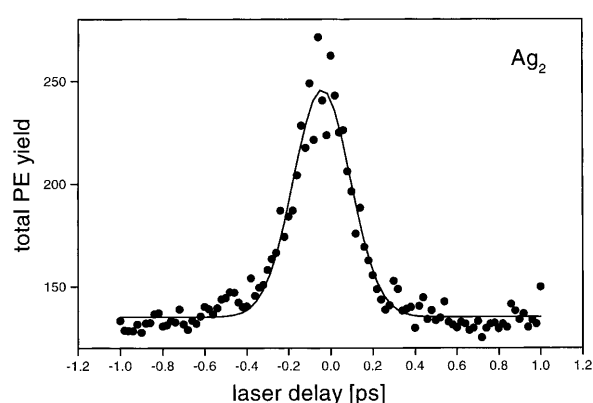


Fig. 6. Delay spectrum: correlation trace obtained from the 2PPE of the HOPG substrate covered with Ag_2 . The solid line reproduces the gaussian fit to the correlation

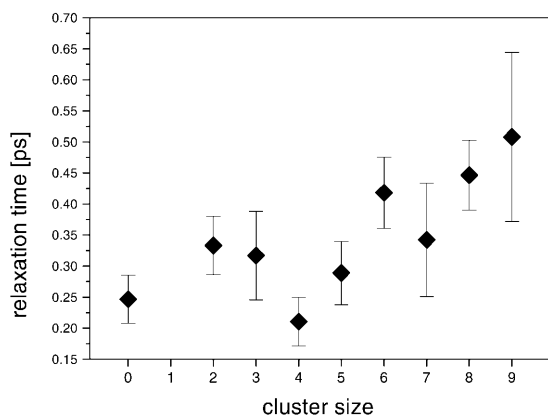


Fig. 7. Measured relaxation time as a function of the cluster size (definition see text)

time of the anionic state with cluster size is not clear, and we can only speculate, that in larger clusters the anionic state might be stabilized by intracluster energy transfer. A systematic study for different cluster materials and substrates should in future provide valuable information on the cluster-surface interaction.

By variation of the deposition energy it is possible to investigate the stability of the clusters during the deposition process. A series of measurements are carried out with Ag_9^+ , deposited with 10 eV, 20 eV, 50 eV and 60 eV per cluster and compared to the results obtained under soft landing conditions (3 eV per cluster). The energy distribution of the cluster beam is between 2 eV and 3 eV for all experiments. Again we concentrate on the mean kinetic energy of the photoelectrons (Fig. 8) and on the relaxation time (Fig. 9) as a function of the deposition energy. The mean kinetic energy rises abruptly from 0.9 eV at soft landing conditions to about 1.3 eV at a deposition energy of 10 eV and then stays constant to higher deposition energies. This behavior clearly indicates a change in the topology of the cluster/surface complex already at moderate deposition energies of 10 eV.

The relaxation time as defined above is first decreasing with increasing deposition energy and then increasing for 50 eV and 60 eV deposition energy per cluster. Fragmentation of Ag_9^+ would result in smaller fragments on the HOPG surface. As our measurements with smaller silver clusters reveal

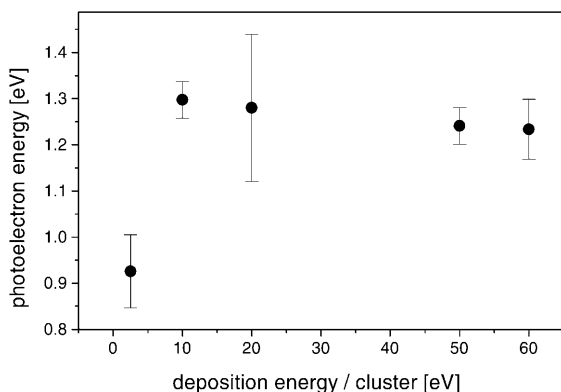


Fig. 8. The mean kinetic energy of the photoelectrons, defined as the center of gravity of the photoelectron spectra, plotted as a function of the deposition energy of Ag_9^+

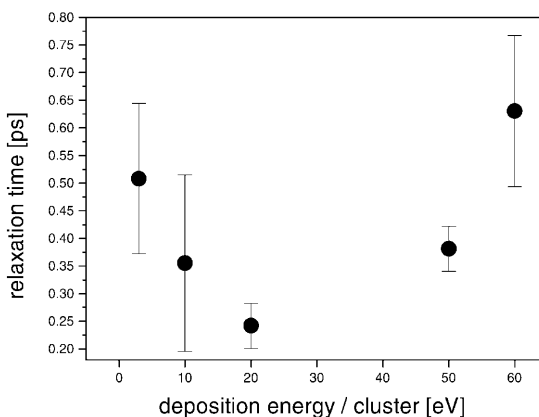


Fig. 9. Measured relaxation time of Ag_9^+ , plotted as a function of the deposition energy (see text)

a shorter relaxation time, the result for 20 eV deposition energy is easily explained. The increase of the FWHM at 50 eV and at 60 eV deposition energy might be due to some kinetic energy of the fragments that cause surface diffusion ending up in the accumulations of fragments in larger aggregates.

Though the scenario is rather speculative, our results indicate that it is important to deposit clusters with low deposition energies in order to avoid fragmentation.

3 Summary

As the size dependence of the photoelectron spectra reveals a pronounced odd/even effect which is well known for gas phase silver clusters, we assume that the soft deposited clusters retain their size and identity on the substrate at liquid nitrogen temperatures. These odd/even effects are correlated to the vertical detachment energies of the clusters. This indicates that the second photon probes a transient negatively charged cluster, which was created by the pump pulse. The FWHM of the delay spectrum might be related to the lifetime of the transient anion. The experiments show a broadening of the FWHM for larger cluster sizes. This effect might be related to a higher density of states for the larger clusters. Deposition with high kinetic energies results in fragmentation of the cluster during impact. This underlines the importance of soft landing conditions.

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