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Two photon photoemission of deposited silver clusters

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Abstract. We use time resolved two photon photoemission to study the stability of size selected silver clusters deposited onto highly oriented pyrolytic graphite (HOPG) substrates. Size-selected Ag_n^+ clusters ($n = 2 - 9$) are deposited at low coverage onto HOPG surfaces at liquid nitrogen temperatures. After deposition, the samples are irradiated by a series of ultrashort laser pulse pairs. Photoelectrons created by two photon photoemission are collected in a magnetic bottle type time-of-flight photoelectron spectrometer. Their kinetic energy distribution is recorded as a function of the delay time between subsequent light pulses. With the exception of Ag_3 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 deposited clusters retain their size and identity on the sample. The lifetime of the photoexcitation rises with cluster size. This is attributed to an increasing electronic density of states for larger clusters.

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1 Introduction

Time resolved two photon photoemission (2PPE) is a powerful tool for the investigation of electronic and molecular dynamics on pure and adsorbate covered surfaces. It probes not only the density of states of the occupied and unoccupied levels in the substrate-adsorbate complex, but allows 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.

Bulk photoemission experiments require the absorption of a photon that excites an electron, which is transported to the surface and finally coupled to a vacuum plane-wave state. 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. There are two possible excitation pathways: In a substrate mediated process the first photon might transfer an electron from the substrate into an unoccupied state of the adsorbate. In a direct photoexcitation of the adsorbate however, the first photon might be absorbed by the cluster. The second photon excites the electron from the intermediate state into an 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.

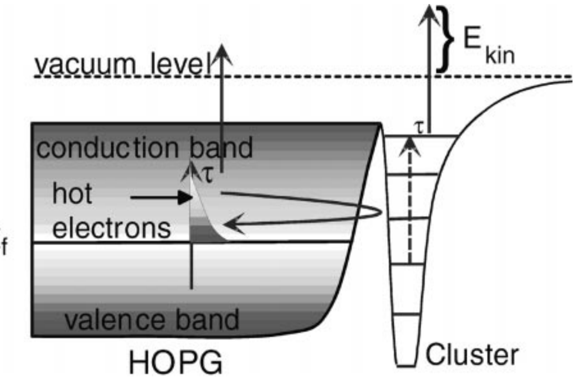

Fig. 1. Scheme of the two photon photoemission process from adsorbate covered surfaces. The first laser pulse creates hot electrons in the substrate which eventually transfer into unoccupied levels of the adsorbate. From there they are photodetached by the second laser pulse.

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 charge transfer [16, 17] and electron dynamics of image-potential states [13, 18–20].

HOPG combines a low density of states at the Fermi level [21] with a sufficient electrical conductivity to avoid sample charging during photoemission experiments. It is therefore an ideal substrate to observe moderately perturbed clusters with only weak coupling to the surface. It is well known from scanning tunneling microscopy, that silver clusters on HOPG diffuse easily and tend to aggregate

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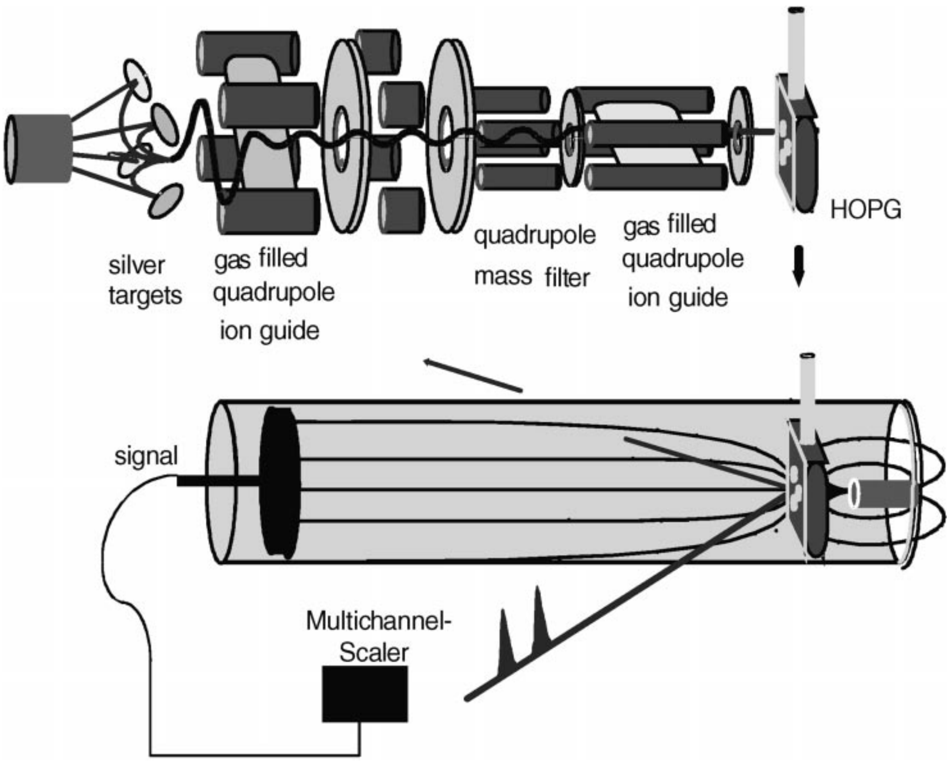

Fig. 2. Schematic diagram of the experimental setup. (For details see main text)

at room temperatures. Moreover this effect depends on the deposition energy of the clusters [22]. Therefore our experiments have been conducted at the temperature of liquid nitrogen.

2 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 ion source and extracted into a helium-filled quadrupole ion guide, where they are thermalized by collisions with the purified background gas. The silver clusters are transferred to a quadrupole mass filter, where the cluster size of interest is selected. The size selected clusters are guided into another helium-filled quadrupole where their kinetic energy is further reduced. With this setup it is possible to achieve real soft landing conditions with deposition energies of $1\,\mathrm{eV} - 2\,\mathrm{eV}$/cluster. 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 up to 1400 K. The substrate is then cooled to liquid nitrogen temperatures within 2 h. The temperature is measured at the sample holder near the sample. Electrical isolation of the sample holder by means of sapphire crystals 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 16 mm^2.

After cooling of the sample, the deposition of 8% of a monolayer of silver clusters takes between 5 and 45 min corresponding to the above mentioned cluster beam current. After the deposition, the sample is moved into the photoelectron spectrometer. Generally 15 series of measurements are made with the same cluster size until the sample is again cleaned by heating with the electron gun.

We use a magnetic bottle type time-of-flight spectrometer which was introduced some years ago by Kruit and Read for gas-phase applications [23]. 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 a electron multiplier (microsphere plate [24]). 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

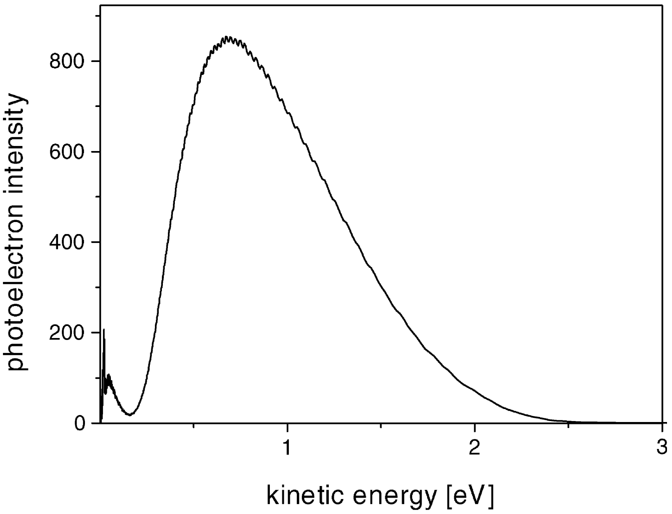

Fig. 3. 2PPE spectrum for Ag_5 deposited on a HOPG substrate. The spectrum is summed over 10^5 shots with a background signal negligible on the scale shown.

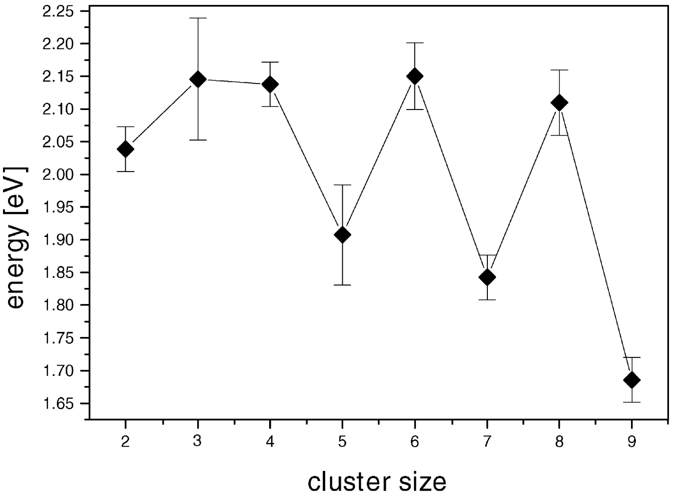

Fig. 4. Position of the Fermi level of the photoelectron spectra plotted as a function of the cluster size.

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 μJ/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 slightly focussed beam, a pulse energy of 500 nJ and a peak intensity of about 10^8 watt/cm^2. Both beams were *p*-polarized, i. e. with the electric field vector being parallel to the plane of incidence.

3 Results and discussion

Figure 3 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, its form is similar for all cluster sizes ($n = 2 - 9$), but it shifts along the energy axis for the different sizes. This is equivalent to a shift of the Fermi level in the spectra as it has been found for small silver islands on an amorphous carbon substrate by DiCenzo and Wertheim [25]. Therefore we show the size dependence of the Fermi level in Fig. 4. With the exception of Ag_3, it reveals an odd/even alternation that is well known from gas phase photoelectron spectroscopy of small silver clusters [26, 27]. The odd/even effect was found for the ionization potential (IP) of neutral gas phase silver clusters [28, 29] as well as for the electron affinity or the vertical detachment energy (VDE) of negatively charged gas phase silver clusters [27, 30]. The IP and the VDE were also theoretically calculated with ab-initio methods [31] and correspond well with the experimental results.

First of all, the observation of size dependent variations of the Fermi level in our experiments indicate, that the larger 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 a high Fermi level shift for the odd numbered clusters. The Fermi level shift is due to the charge remaining on the cluster after the photoexcitation process. This suggests, that the even numbered clusters have a shorter recombination time than the odd numbered clusters, because they profit from paired *d*-electrons upon neutralization by charge transfer from the substrate.

In the case of the Ag_3, it might be possible that fragmentation occurs even at low deposition energies or alternatively the small clusters might be more mobile on the surface, so that diffusion takes place even at liquid nitrogen temperatures.

We estimate the relaxation dynamics of the photoexcitation, 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_8 and HOPG is given in Fig. 5. 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 as shown in Fig. 6. Taking into account the finite laser pulse width, which is estimated to be about 150 fs, the measured autocorrelation width translates in a relaxation time which rises from about 240 fs ± 60 fs for Ag_4 to 500 fs ± 130 fs for Ag_9. This result might be due to a higher density of states in larger clusters which favours the stabilization of the cluster. The relaxation times also depend on the coupling between cluster and substrate. A sys-

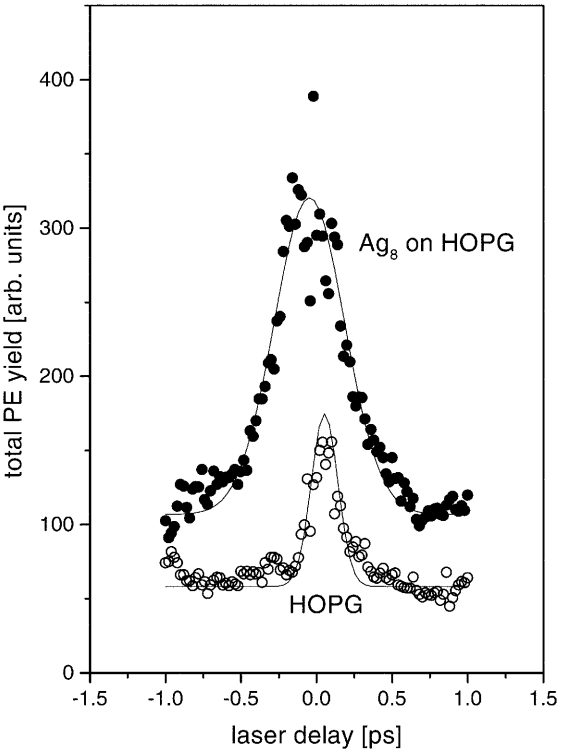

Fig. 5. Delay spectrum: correlation traces obtained from the 2PPE of the HOPG substrate covered with Ag_8 (upper curve, solid circles) and of the pure HOPG substrate (lower curve, hollow circles). The solid line reproduces the gaussian fit to the correlation.

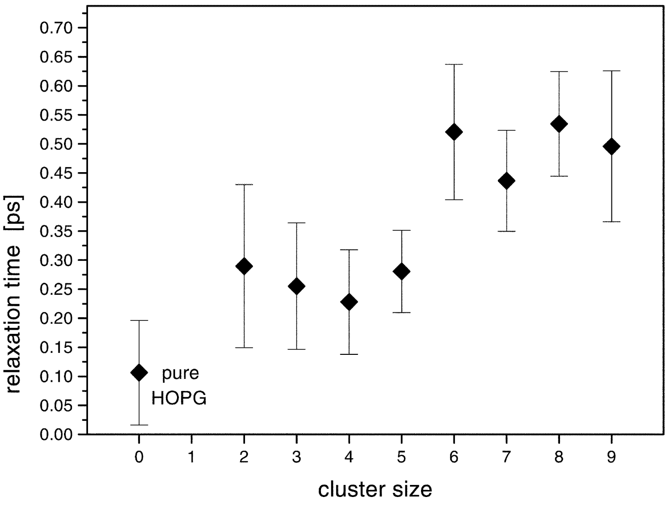

Fig. 6. FWHM of the measured delay spectra plotted as a function of the cluster sizes.

tematic study for different cluster materials and substrates should therefore provide valuable information on the cluster-surface interaction. The value for the pure HOPG substrate characterizes the lifetime of the hot electrons and is about 70 fs ± 50 fs. Considering our laser pulse width this is in correspondence with the literature value [32].

Upon warming of the sample, the photoelectron yield and kinetic energy changes dramatically within a narrow temperature range. This indicates the onset of a structural rearrangement of the clusters on the surface. As these investigations are still under way, a detailed account will be given in a subsequent publication.

4 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 deposited clusters retain their size and identity on the substrate at liquid nitrogen temperatures. These odd/even effects are correlated to the neutralization dynamics after the photoexcitation process. The FWHM of the delay spectrum might be related to the lifetime of the photoexcitation. 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.

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