A comparative analysis of electron spectroscopy and first-principles studies on Cu(Pd) adsorption on MgO

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Abstract

Ultrathin MgO films were grown on a W(110) substrate while metastable impact electron (MIES) and photoelectron (UPS) spectra were measured in situ; apart from the valence band emission, no additional spectral features were detected. The oxide surface was exposed to metal atoms (Cu, Pd) at RT. A comparison with the DOS extracted from first-principles DFT calculations shows that the metal-induced intensity developing above the top of the O 2p valence band in the UP spectra under Cu(Pd) exposure is caused by Cu 3d (Pd 4d) emission. The emission seen in the MIES spectra is attributed to the ionization of Cu 3d and 4s states of adsorbed neutral Cu atoms in an Auger process, Auger neutralization, involving two electrons from the surface, at least one of them from the metal adsorbate. The shape of the MIES spectra suggests metallic island growth even at the lowest studied exposures, which is supported by the first-principles calculations.
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1. Introduction

Metallic nanoparticles supported on metal oxide surfaces and, in general, metal/oxide interfaces represent a wide class of materials which play a fundamental role in many technologically important fields [1–5], including catalysis, microelectronics, metal–ceramic composites, gas sensors, coatings for corrosion protection etc.

First-principles computational studies on the metal/oxide interface, based either on periodic slab [6–11] or cluster models [12–17], are now standard for these systems. A comparison with experiment needs calculation of at least the adhesion energy and the electronic density of states (DOS). The former controls the growth mode of metal particles on the oxide surface (two- or three-dimensional) as well as the mobility of adsorbed species on the surface, while the latter allows the interpretation of valence band electron spectra obtained using the ultraviolet photoelectron spectroscopy (UPS) and metastable impact electron spectroscopy (MIES).

As suggested in Refs. [18,19], we use ultrathin oxide (several nm) films rather than bulk oxides. These films are thin enough to avoid charging, but thick enough to exhibit the electronic structure of the bulk oxide. Still, spectral features from the DOS of the underlying supporting substrate often obscure the electronic structure of small metallic islands. Consequently, we combine UPS with MIES in order to analyze changes of the electronic structure occurring during the early stage of island formation. MIES is sensitive only to the DOS of the film and the charge density of the species adsorbed on the outermost layer; it is not sensitive to the DOS of the underlying substrate supporting the oxide film.

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In our previous work on Cu(Pd)/MgO we have suggested a qualitative interpretation of our MIES/UPS (HeI) data for the growth of metallic ad layers [20]. It was concluded that at room temperature (RT) metallic island formation takes place from the very beginning of the Cu(Pd) exposure. In the present paper, our interpretation will be put on a more sound basis by adding the UPS (HeII) data and making a detailed comparison with first-principles DFT calculations.

2. Experimental and theoretical details

With respect to its application for a study of the growth of metallic aggregates and films on metal oxides, the apparatus has been described previously [20–22]. Briefly, it is equipped with a cold-cathode gas discharge source for the production of metastable He*(^{3}S/^{1}S) ($E^* = 19.8/20.6$ eV) atoms with thermal kinetic energy and HeI photons ($E^* = 21.2$ eV) for UPS. A second photon source provides HeII photons. The characterization of both the oxide film, deposited onto W(1 1 0) substrate, and the deposition of the metal atoms onto the MgO film are done under the in situ control of these electron spectroscopies. The procedure for the preparation of the MgO films (2 nm thick, typically) and the deposition of the metal species onto these films at RT is described in Refs. [20,21]. The chosen oxide film thickness guarantees a negligible influence of the tungsten substrate onto the metal adsorption process.

First-principles calculations have been performed for Cu using the CRYSTAL-2003 computer code [10,23]. In these periodic DFT calculations a localized (atomic) basis set is combined with the hybrid B3LYP exchange-correlation functional. We used the slab model periodic in two dimensions with Cu atoms adsorbed on the perfect MgO(0 0 1) surface. The regular coverage by Cu adsorbates was varied from 0.25 monolayer (ML) up to 2 ML (Fig. 1). The Cu positions above the O ions on the MgO surface were optimized for each surface coverage, and adsorption energies, effective atomic charges, total and projected DOS were calculated. The nature of interfacial bonding at all coverages is physisorption. With increasing Cu atom fraction, a decrease of the substrate-induced polarization of Cu adatoms, accompanied by the increase of both in-plane metallic bonding and the interfacial distance are observed. We observe no appreciable charge transfer across the modelled perfect interface. In Ref. [10] we discussed mostly the Cu/MgO interface energetics whereas the preliminary analysis of the DOS (the total density of states and the densities projected (PDOS) onto the Cu 3d and O 2p states as well as the states of the pure magnesia substrate) was performed only for the two (0.25 ML and 1 ML) adsorbate coverages. In this paper, we focus on the electronic structure on the basis of the detailed DOS analysis for all the coverages mentioned above, paying more attention to the analysis of Cu(4s) PDOS which falls into the magnesia band gap. Note that Pd is more strongly bound on the regular MgO(0 0 1) substrate than Cu (1.35 eV as compared to 0.8 eV per ad atom [24]).
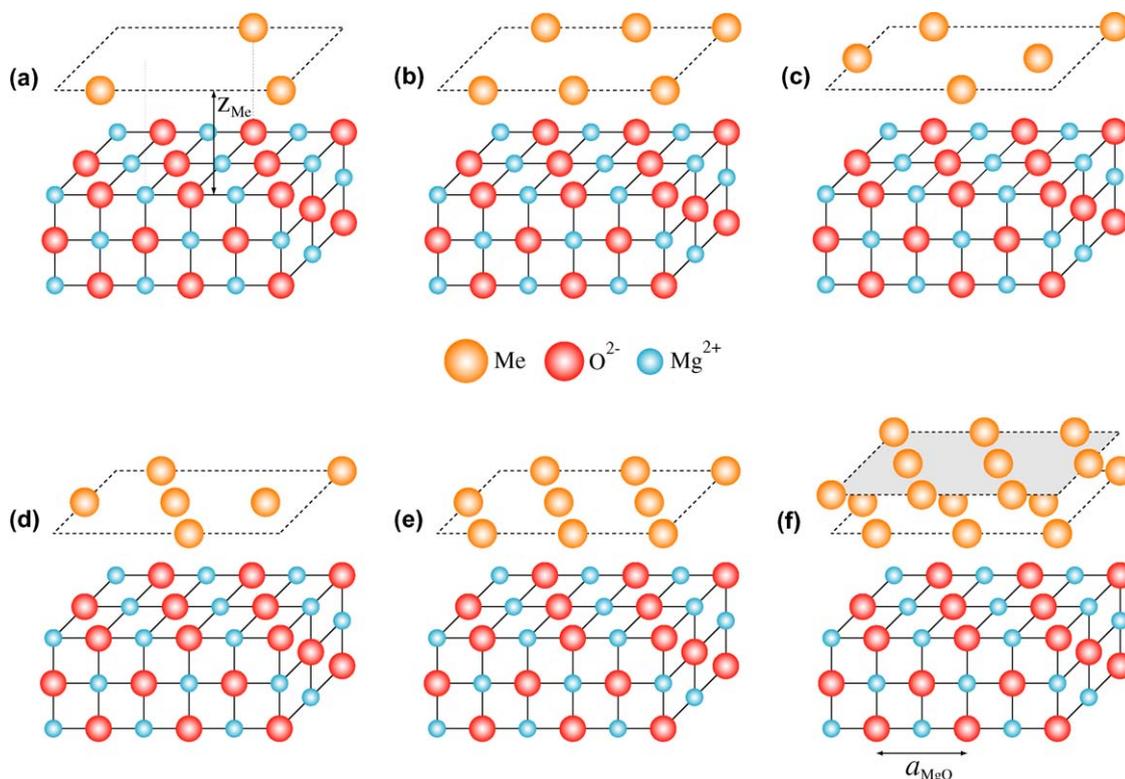

Fig. 1. Models of calculated interfaces with different coverages (in ML): 1/4 (a), 1/2 (b,c), 3/4 (d), 1 (e) and 2 (f).

3. Results and interpretation

The UPS (HeII) results are shown in Fig. 2 for Cu/MgO (a) and Pd/MgO (b), respectively, as a function of the metal atom exposure. The uppermost spectra are for the clean MgO film; no spectral features from the underlying W(110) substrate can be seen. During the preparation of the MgO film (by means of Mg deposition in an oxygen atmosphere) the work function (WF) of the surface decreases from that of the clean W(110) (5.1 eV) to about 3.3 eV whereby most of the observed decrease takes already place during the formation of the first MgO ad layer. A decrease by the work function of about 1 eV has been observed by us during the preparation of a MgO film on clean Mo(100) under the in situ control of MIES and UPS (not shown). As for HeI, the emission from the O 2p valence band consists of two peaks [20], and suggests well-ordered MgO(100) surfaces [25]; in contrast to the UPS spectra, the corresponding O 2p emission in MIES does not show the peak at the higher binding energy very clearly [20,21]. During the metal (Cu, Pd) exposure, the Cu 3d and Pd 4d structures emerge in HeII (as in HeI) at the binding energy $E_B \approx 2.5$ eV and directly at E_F, respectively; they are due to photoionization of the Cu 3d and Pd 4d bands. The d-emission partly overlaps with the O 2p valence band emission of MgO.

In Fig. 3 the calculated total DOS (a) and its projection onto the Cu 4s states (b) are displayed as a function of the Cu coverage of the MgO slab between 0.25 and 2 ML. The adsorption sites are described in Refs. [10,11]. Assuming that the shape of the HeII spectra corresponds mainly to the initial DOS of the Cu and Pd/ MgO systems, we can compare experimental results for clean MgO and Cu/MgO with the DOS derived from the first-principles calculations. Both the two-peak structure of the O 2p band of MgO and the "pseudo-gap" between the O 2p and Cu 3d contributions, developing during the Cu deposition, are well reflected in the calculations. Cu 4s states lie inside the band gap of the bulk MgO right below E_F (see Fig. 3(b) for more details). Only for low coverages a single Cu 4s peak is observed. As Cu coverage increases, the DOS projected onto Cu 4s becomes increasingly complicated, consisting of several peaks of different intensity; however, the dominant structure remains located right below E_F. For Pd/MgO theory also predicts that the O 2p and Pd 4d contributions are rather well separated, even for Pd monolayer coverage [8].
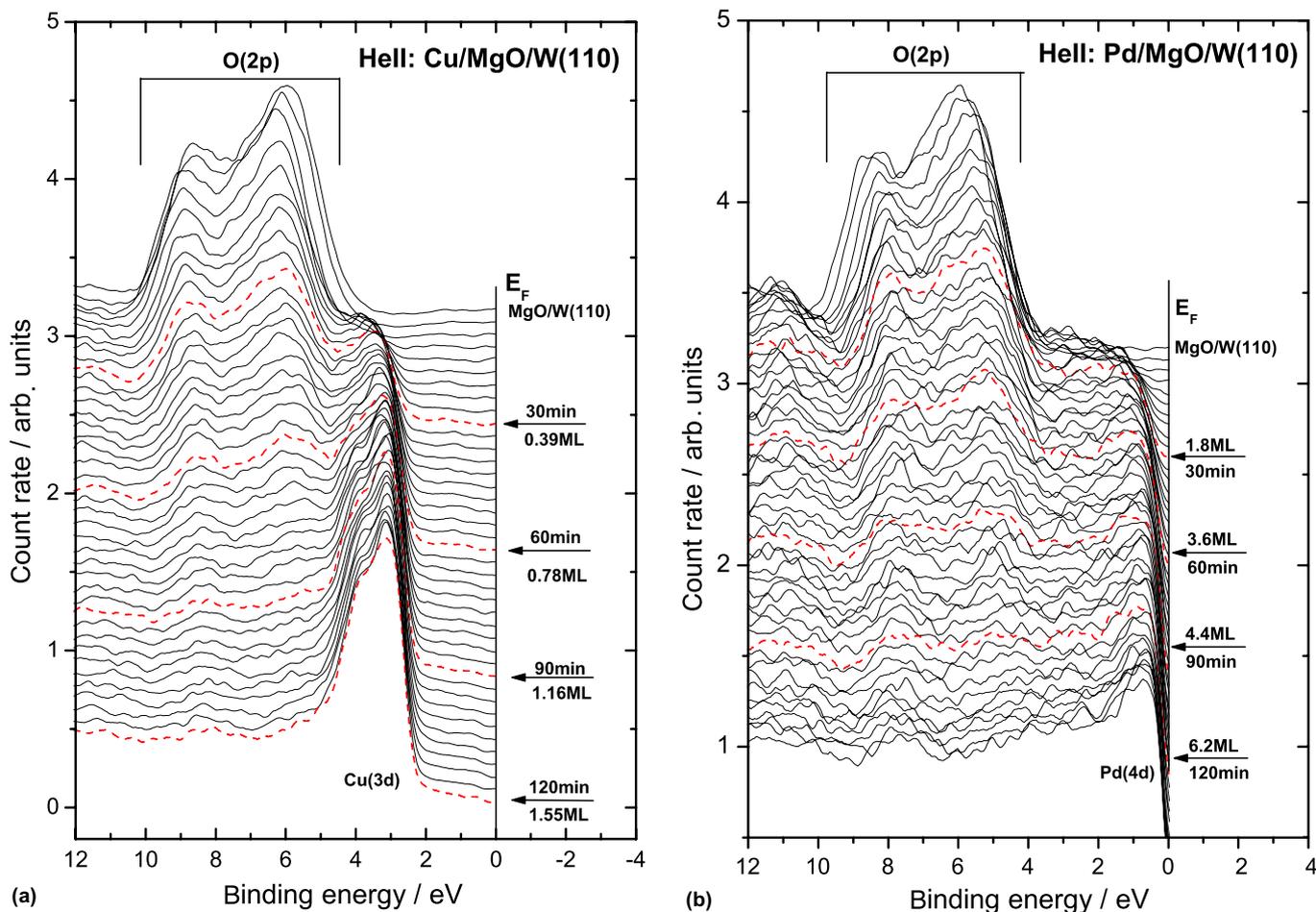

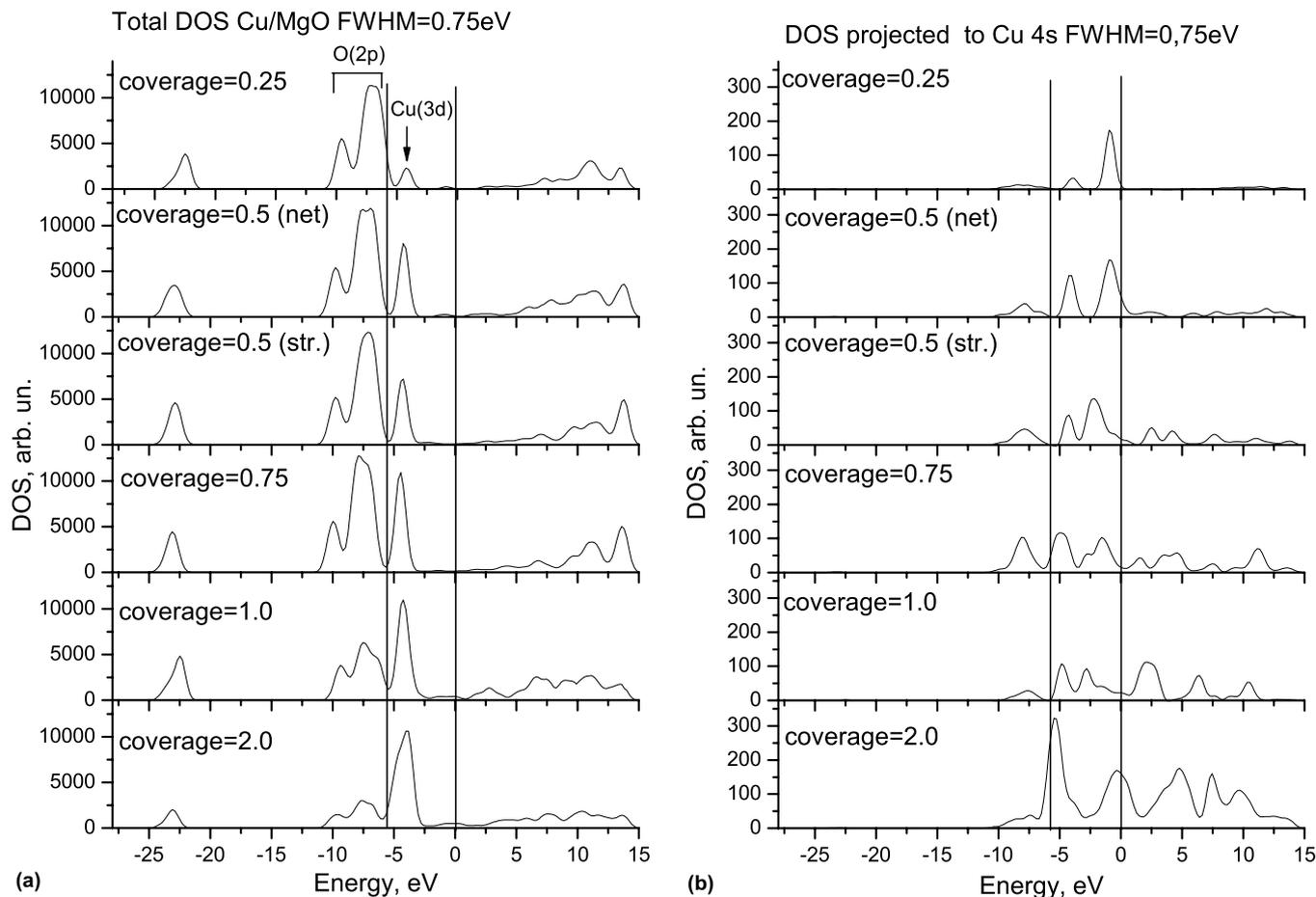Fig. 2. UPS(HeII)-spectra for (a) Cu and (b) Pd on MgO as a function of the metal exposure.

Fig. 3. Total DOS for Cu interacting with MgO films (a) Total DOS, (b) Cu4s part of the DOS.

We exclude very small coverages (<0.1 ML for Cu) from the discussion because no detailed information comes from the present results. In this regime, adsorption may be defect-dominated. The defective part of the MgO(0 0 1) substrate usually contains surface F_s centers (oxygen vacancies with two trapped electrons). According to our calculations, the Cu 4s band overlaps with the defect level band resulting in both substantial charge transfer from oxygen vacancies towards the Cu adsorbates (up to 0.4e) and the formation of a strong ionic bonding (2.36 eV versus 0.62 eV adsorption energies per ad atom for the position over surface oxygen ion).

The MIES spectra for the deposition of Cu(Pd) onto MgO have been presented and analyzed previously [20]. We have already pointed out that, even at the lowest studied coverages (0.1 ML for Cu), the metal-induced part of the MIES spectra is not due to the Auger de-excitation (AD) process (which would yield MIES spectra rather similar to those found in UPS), but is caused by the Auger neutralization (AN) process involving two electrons from the metal adsorbates [20]. This indicates that already at 0.1 ML physisorption of Cu takes place at terraces.

Would it be for the adsorption of well-isolated atoms, the transition of the He 2s electron into unoccupied states is energetically unfavorable. Thus, resonance ionization of

the He* projectile would not take place, and its interaction will be AD. Consequently, the Cu 3d-induced emission should resemble that found for HeI [20] and HeII (Fig. 2), i.e., should reflect the DOS of the Cu 3d states, which is obviously not the case. As far as the Cu 4s-induced emission is concerned, the DOS for 0.25 ML suggests that the spectra should reflect the narrow peak found in the DOS just below the Fermi energy. Such an emission is definitely not observed in MIES. Obviously, as already pointed out [20], thermal Cu evaporation onto the MgO substrate held at RT leads to metallic island formation, right from the beginning of the metal deposition.

For Ag and Au atoms interacting with a thin MgO film, the possibility was discussed [26] that the electron affinity (EA) level of the metal adsorbate could come into a resonance with filled states of the underlying metal substrate onto which the MgO film is deposited, i.e., it moves below the Fermi level, thus leading to negatively charged Ag and Au species. The EA of a free Cu atom is 1.23 eV. The dominant contribution to its increase during the adsorption onto the MgO film can be expected to come from the interaction of the surface-adsorbed Cu^- ion with its image in the W substrate. Assuming that the Cu atoms sit about 4 a.u. above the MgO film of 6 a.u. thickness and the image plane is at the surface of the W substrate, the increase of

EA could be estimated as 0.7 eV. Since we found that the WF of MgO/W is 3.3 eV, the affinity level would be located about 1.4 eV above the Fermi level. Thus, accurate considerations are required to check whether the affinity level could come into the resonance with filled metal states, and charge transfer from the W substrate to the Cu adsorbate could indeed take place. However, even if the formation of Cu^- would take place, again a narrow feature would be produced in the MIES spectra near the Fermi level, due to the Auger processes involving the 4s electrons from the narrow, atomic-like doubly-filled Cu 4s level, which is not seen in the experiment.

We can also exclude the formation of few atoms (molecular) clusters which do not yet display metallic-like properties: the transition of the He 2s electron into unoccupied states would still be energetically unfavorable and AD-like spectra should still be seen. Instead, a comparison with theory should be done with the DOS obtained for coverages beyond 1 ML Cu where the Cu 3d and 4s bands are formed; this situation is also found for clusters containing 100 and more Cu atoms. In particular, the Cu 4s-induced part of the DOS spreads out here over the entire O 2p band gap of the MgO film. Under these conditions, a transfer of the Cu 4s electron will take place into unoccupied states above the Fermi level, followed by AN of the He^+ ion formed in this way.

A more detailed comparison of the MIES results for Cu(Pd) deposition on MgO films with the Cu(Pd)-induced DOS requires the simulation of MIES spectra on the basis of the DOS results. The procedure to model MIES spectra was described in Refs. [27–29]. Simulations carried out on the basis of a DOS similar to that in Fig. 3 for 1 ML gives indeed qualitative agreement with the experimental MIES spectra [20]. Hereby, it was assumed that the spectra are caused by AN and an "effective" surface density of states (SDOS) as seen by the He probe atoms in front of the surface was employed; this is the distance around which the Auger processes take place with high probability in a rather narrow distance interval. The high sensitivity of the MIES technique to s-states (as compared to the compact, localized d-states) is reflected in the enhanced s-contribution (as compared to the d-contribution) to the "effective" SDOS as seen by the He^* probe atoms. It reflects the fact that the overlap of He 2s is larger with s- than with d-states [30].

Similarly, we have modelled the Pd/MgO spectra [29] where we do not see a contribution above the O 2p valence band because the Pd 5s states remain unoccupied during Pd adsorption on MgO. As for Cu/MgO, the Pd-induced part of the spectra is found to be caused by AN; the agreement with experiment is reasonable. We conclude that for coverages larger than 0.44 ML for Cu and 1.8 ML for Pd the MIES spectra for Cu(Pd)/MgO (at least for $E_{kin} > 10$ eV), although not the UPS spectra, have become practically identical with those for the respective metallic films.

Our findings agree well with AFM results on the growth of Cu on MgO(1 0 0) [5]: for deposition at RT, islands are formed across the terraces of the surface. Only isolated islands are observed below 0.6 ML. The average island diameter is 6 nm between 0.1 and 0.6 ML; the island height ranges from 0.08 to 0.8 nm with an average of 0.15 nm. It could be estimated that these islands consist of 300–450 atoms. Detailed theoretical considerations concerning the initial stage of the growth of metal films, Cu and Ag in particular, on MgO can be found in Refs. [10,31]. In these papers we presented the first-principle thermodynamic theory of the metallic film growth mode. The analysis presented in these papers confirm that for Cu/MgO the island growth mode is predominant starting with the initial stage of the exposure to Cu.

4. Summary

Two-nanometer-thin MgO films were grown on W(1 1 0) substrate and in situ characterized by means of the metastable impact electron and ultraviolet photoelectron (HeI and II) spectroscopy. The interpretation of the results, both for the clean MgO film and those obtained during the deposition of Cu and Pd, are made on the basis of first-principle calculations. Apart from the O 2p valence band emission no additional spectral features can be seen which excludes formation of a large number of oxygen vacancies at the surface. Both theory and experiment predict formation of 3D metallic clusters beginning with surface coverages as small as 0.15 ML. A possible scenario of such aggregation discussed in Ref. [32]. Our considerations made beforehand let us expect that a controlled reduction of the island size down to 1 nm clusters will give rise to the change of the interaction process between He^* and the adsorbate from AN to AD as soon as the transition from metallic-like to molecular behavior of the cluster takes place. Such experiments, employing size-selected laser deposition of very small clusters, are in progress (U. Heiz, TU München).

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