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Auger neutralization spectroscopy of clean and adsorbate-covered transition-metal surfaces by deexcitation of metastable noble-gas atoms

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The extreme surface sensitivity of metastable noble-gas atom deexcitation spectroscopy is demonstrated with clean Pd(111), Cu(110), and W(polycrystalline) surfaces as well as for the adsorption systems Pd(111)/H, W(polycr.)/H, Pd(111)/O, Cu(110)/O, and W(polycr.)/O. Proper analysis of the data leads to information on the electronic surface density of states not available with spectroscopic techniques of finite sampling depth such as uv photoelectron spectroscopy. The results are compared with calculated electronic surface densities of states if available. Chemisorption of hydrogen and oxygen strongly affects the electronic surface density of states because surface states and resonances are shifted to higher binding energies or lose their surface state character due to the formation of the adsorbate—metal bond. In addition, occupied bonding as well as antibonding adsorbate-metal states are observed. Based on the specific sensitivity of this spectroscopic technique for the outermost atomic layer, it can be shown that H on Pd(111) and O on Cu(110) adsorb at 300 K above the first metal layer, in contrast to earlier conclusions which favored subsurface sites.

I. INTRODUCTION

Deexcitation of metastable noble-gas atoms at transition-metal surfaces which are either clean or covered by atomic adsorbates occurs by resonance ionization (RI) of the metastable atom and subsequent Auger neutralization (AN) of the ion formed by RI at the surface.[1-4] The RI and AN processes have been discussed in detail in Ref. 1. AN takes place at a distance of a few angstroms in front of the surface and, therefore, involves two electrons from the electronic surface density of states (SDOS) of the outermost atomic layer. The energy distribution of the electrons emitted by AN transitions is governed by the self-convolution of the SDOS and by the Auger transition matrix elements. Experimental information on the SDOS is so far rather limited, because with other spectroscopic techniques, e.g., uv photoelectron spectroscopy (UPS), electron emission from the surface is usually superimposed by contributions from the bulk electron density of states (BDOS).[5]

The electron energy distribution due to the AN process does not directly reflect the SDOS. In Ref. 1 we have discussed how information related to the SDOS can be deduced from experimental AN spectra by a deconvolution technique. Here, we will present results for clean Pd(111), Cu(110), and W(polycrystalline) surfaces as well as on the adsorption of hydrogen on Pd and W and oxygen on Pd, Cu, and W surfaces.

II. EXPERIMENT

A detailed description of the experimental setup can be found in Refs. 1 and 6. In this work metastable ^1S He*, $^3P_2$ Ne*, and $^3P_2$ Ar* atoms are used which are created in an atomic beam connected to an ultra high vacuum (UHV) chamber equipped with low-energy electron diffraction (LEED), Auger electron spectroscopy (AES), thermal desorption spectroscopy (TDS), and UPS (21.2 eV) facilities. The electron energy analyzer has an energy resolution of about 0.3 eV. Electron energy distributions from deexcitation of the metastable atoms are compared with the 21.2-eV photoelectron spectra recorded *in situ*, The surface work function is determined from the total width of the photoelectron spectra. The samples can be cooled to 140 K, but the majority of the spectra is recorded at 300 K. The samples are cleaned by usual standard procedures including several sputter-anneal cycles. The cleanness of the surfaces is controlled by LEED, AES, and UPS. As will be discussed further, the AN spectra are the most sensitive probe for surface cleanness. The base pressure of the UHV system is in the 5×10^{-11} Torr range and increases to about 2×10^{-9} Torr by noble-gas atoms when the valve to the atomic beam system is opened. No contamination of the sample surface by the atomic beam is detected.

All AN spectra shown in this work are recorded at a 45° angle of incidence of the metastable atoms and normal electron emission. It is shown in Ref. 1 that these parameters have some influence on the measured intensities but the energetic positions of the spectral features are not affected. UP spectra are shown integrated over all emission angles in the plane defined by the surface normal and the incident photon beam (45° angle of incidence) to minimize angular dependent effects in the spectra due to **k** conservation rules. Since the AN process is governed by the overlap of localized atomic wave functions with the metal wave functions no **k** conservation rules come into play as with UPS.[1] Therefore, deconvoluted AN spectra are compared with angular integrated UP spectra.

III. RESULTS

A. Clean surfaces

AN spectra of a clean Pd(111) surface are shown in Fig. 1 for He*, Ne*, and Ar* atoms. Since the ionization energy decreases from He to Ar the maximum kinetic energy of the emitted electrons, i.e., the onset of the spectra, shifts to lower values on the kinetic energy scale (E_{kin}).[1,2] According to the AN process discussed in Ref. 1, the high kinetic energy part of the spectra originates from electrons emitted from the metal valence band region. At low kinetic energies a background contribution from secondary electrons as in UPS is present. $E_{\text{kin}}=0$ is defined by the low energy cutoff in the spectra. The deconvolution of the experimental spectra according to Ref. 1 is also shown in Fig. 1 The very intense maximum close to the Fermi energy (E_F, defined by the onset of the spectra[1]) in the deconvoluted spectra is caused by the strong intensity increase of the experimental spectra at high kinetic energies. This becomes very obvious by considering that the first derivative of the original experimental spectrum is a good approximation to the deconvolution (see discussion in Ref. 1). This intense maximum is followed by two weak maxima at higher binding energies (E_B). Because of the lower ionization energies of Ne and Ar with respect to He, electron emission due to AN transitions occurs there only from a smaller part of the SDOS. This is, of course, also reflected in the deconvolution. Over the common E_B range all three deconvoluted spectra are in excellent agreement which is an indication of the good reliability of the deconvolution method. Outside the Pd *d*-band range at $E_B=6.2$ eV and, therefore, detectable only by He* atoms, an additional peak is observed. This peak is not a deconvolution artifact but is caused by the maximum at $E_{\text{kin}}=4$ eV in the experimental He* spectrum. This can be shown either by the first derivative of the He* spectrum or by a backconvolution of the deconvoluted spectrum without this additional peak. Additionally, in Fig. 1 a UP spectrum of the clean Pd(111) surface is shown.

The AN spectra of the Cu(110) surface (Fig. 2) exhibit a distinct difference compared with the spectra of the Pd(111) surface. At the high kinetic energy onset a pronounced shoulder is observed which causes in the deconvolution a very intense peak at about $E_B=1$ eV. The broad maximum in the He* and Ne* spectra is as for the Pd surface due to emission from the *d*-band region of the Cu SDOS and produces the features in the deconvolution between $E_B=2$ eV and $E_B=5$ eV. Again, outside the *d*-band range at $E_B=7.0$ eV an additional peak is present. In the UP spectrum at $E_B=1$ eV only a very weak maximum occurs compared with the strong emission features of the Cu *d* band below $E_B=2$ eV.

Figure 3 shows the He* spectrum of a polycrystalline W surface together with an UP spectrum and the deconvolution. The deconvolution exhibits maximum intensity at E_F whereas in the UP spectrum the intensity is maximum at about $E_B=2$ eV. Once more, in the deconvoluted spectrum a peak outside the W *d*-band range at $E_B=6.0$ eV is observed.

B. Adsorption of hydrogen

Hydrogen adsorbs atomically on Pd and W surfaces.[7,8] In agreement with Ref. 7, on the Pd(111) surface no

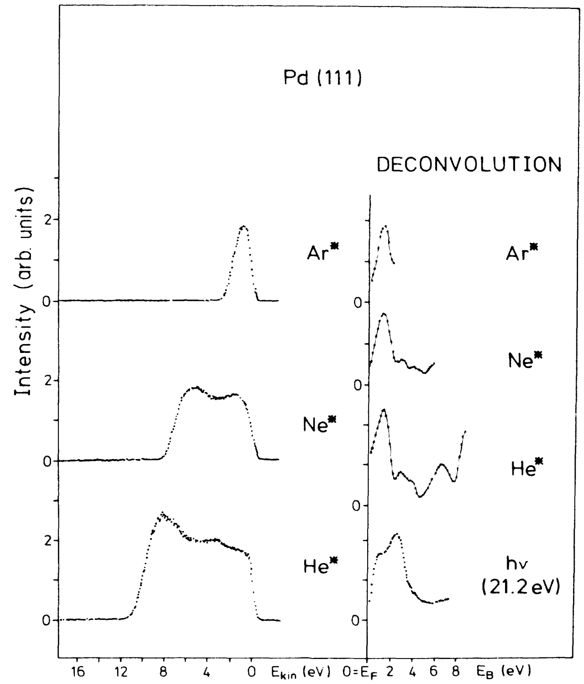

FIG. 1. Electron energy distributions from a clean Pd(111) surface due to Auger neutralization of He*, Ne*, and Ar* atoms (AN spectra), the deconvolution of these spectra, and a UV (21.2 eV) photoelectron spectrum (UP spectrum).

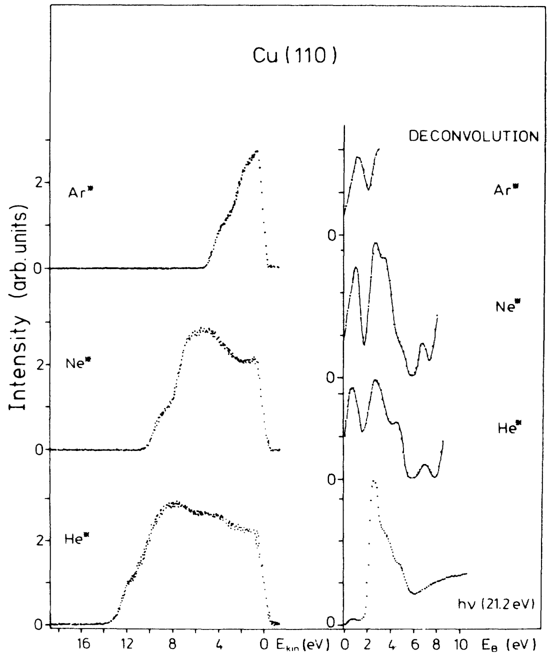

FIG. 2. AN spectra with He*, Ne*, and Ar* atoms from a clean Cu(110) surface, the deconvolution of these spectra, and a 21.2 eV UP spectrum.

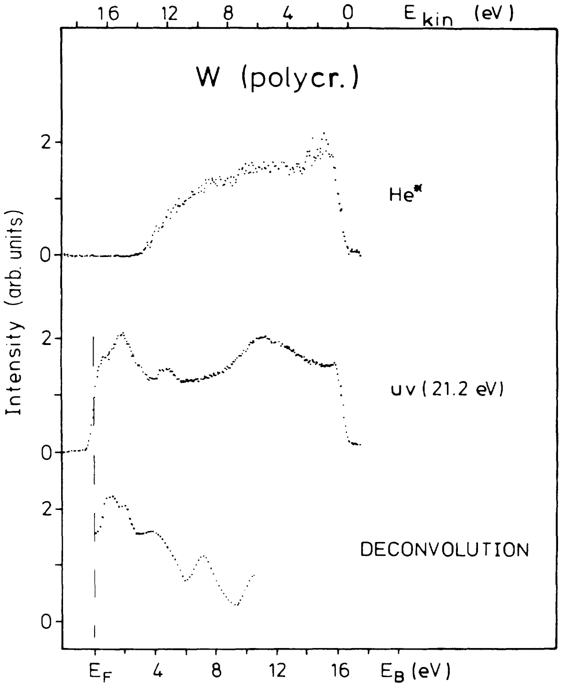

FIG. 3. He* spectrum from a clean W surface, a 21.2 eV UP spectrum, and the deconvolution of the He* spectrum.

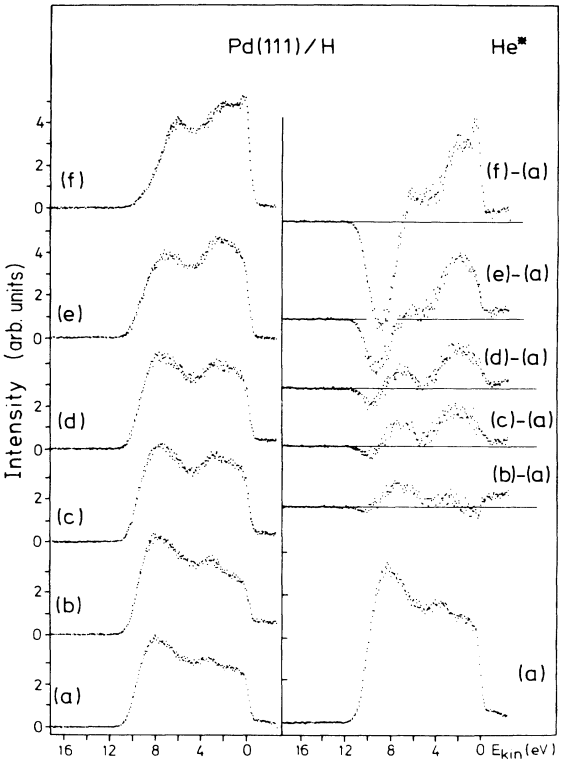

FIG. 4. He* spectra and difference spectra from (a) a clean Pd(111) surface and exposed at 300 K to (b) 1 L, (c) 10 L, (d) 100 L, (e) a constant pressure of 1×10^{-7} Torr, and (f) at 140 K to a constant pressure of 1×10^{-7} Torr hydrogen.

LEED superstructure is detected at 300 K, and at full coverage the work function increases by 0.2 eV. For the polycrystalline W surface, a work function increase by 0.6 eV is observed. Adsorption of hydrogen on Pd(111) has been studied by He* atoms at 300 K for exposures of 1 L, 10 L, 100 L, [1 L (langmuir)$=10^{-6}$ Torr sec] and constant pressure of 1×10^{-7} Torr H_2 which has also been applied at 140 K (Fig. 4). The He* spectra show with increasing exposure an intensity decrease directly at the onset of the spectra and an intensity increase at about 4 eV kinetic energy. In contrast to the spectra with adsorbed oxygen where the intensity decreases over the whole Pd *d* band region (Fig. 9), upon adsorption of hydrogen just the intensity onset becomes weaker and is followed even by an intensity increase at about 7 eV kinetic energy. Also, the intensity increase at low kinetic energies is less pronounced than with oxygen. The deconvoluted spectra in Fig. 5 show an intensity decrease at E_F up to about $E_B=1.5$ eV and a strong peak emerging at $E_B=6.5$ eV. The difference spectra exhibit additional maxima at $E_B=2.8$ eV and 4.2 eV which are related to the intensity increase in the He* spectra at $E_{\text{kin}}=7$ eV. At 140 K the adsorbate induced structures in the spectra are much more pronounced than at 300 K which indicates additional hydrogen adsorption at low temperature. In the UP spectrum (Fig. 6) only a sharp peak at 1.5 eV can be observed at 1×10^{-7} Torr H_2. In the difference spectrum in addition to the peak at 1.5 eV a maximum at 3.5 eV and a very weak structure around 6.5 eV can be detected. Intensity minima occur at E_F and at $E_B=2.5$ eV.

Hydrogen adsorption on the W surface causes similar changes in the He* spectrum (Fig. 7) as with Pd. The deconvolution shows a significant intensity attenuation close to E_F and a strong maximum at about $E_B=6.2$ eV. In Fig. 8 the deconvoluted He* spectrum of the hydrogen covered W surface, of the clean surface, the difference spectrum, and a UP difference spectrum are shown. The latter two are similar in shape but with the He* spectrum the intensity attenuation at E_F and the broad intensity maximum around 6.2 eV is much more pronounced.

C. Adsorption of oxygen

At room temperature oxygen adsorbs on Pd, Cu, and W surfaces dissociatively.[9] Chemisorption of oxygen on a Pd(111) surface causes a 2×2 LEED pattern and a work function increase of 0.5 eV. The 2×2 LEED pattern is associated with a coverage $\theta=0.25$.[10] Increased exposure to O_2 leads to a strong decrease in the emission intensity in the *d*-band region of the AN spectra between $E_{\text{kin}}=8$ eV and 12 eV and a continuous increase at about $E_{\text{kin}}=2$ eV (Fig. 9). Figure 10 compares He* spectra at 1 L and 100 L O_2 exposure with the spectrum of the clean surface. These data clearly demonstrate the suppression of electron emission at high kinetic energies due to oxygen adsorption and the formation of a new maximum at low kinetic energies. At 1 L the main effect is the decrease of emission from the Pd *d*-band region close to the Fermi energy whereas the intensity increase at low kinetic energies is small. At higher exposures (100 L), however, the dom-

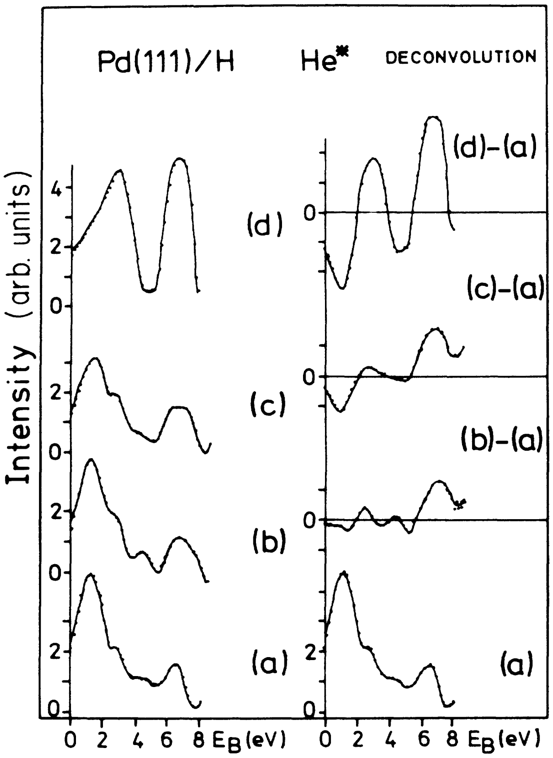

FIG. 5. Deconvolution of the He* spectra from a Pd(111) surface exposed at 300 K to (a) 1 L, (b) 10 L, (c) a constant pressure of 1×10^{-7} Torr, and (d) at 140 K to a constant pressure of 1×10^{-7} Torr hydrogen. Also shown are difference spectra of the deconvolution.

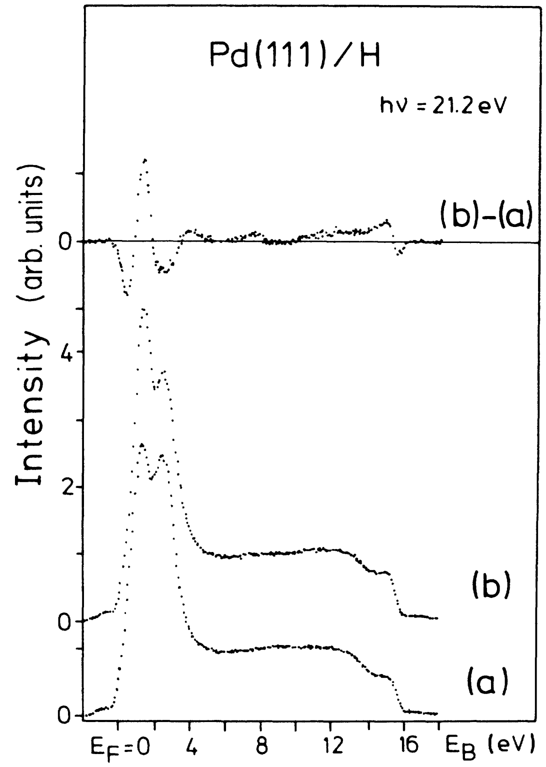

FIG. 6. UP spectra from (a) a clean Pd(111) surface, (b) exposed at 300 K to a constant pressure of 1×10^{-7} Torr hydrogen, and the difference spectrum (b)−(a).

inant effect is the emission increase at about 2 eV kinetic energy. Deconvolution of the spectra shows very clearly the decrease of the intensity maximum close to E_F with increasing O_2 exposure (Fig. 11). The peak at $E_B=5.5$ eV corresponds to the emission maximum in the original spectra at $E_{\text{kin}}=2$ eV. In accordance with the experimental spectra of Figs. 9 and 10, this peak increases continuously up to 100 L exposure. At very high exposures a pronounced peak exists and the intensity at E_F is strongly reduced. In the difference spectra it becomes evident that the peak at 5.5 eV shifts towards 5.0 eV at high O_2 exposures and two additional emission maxima are found at 1.7 eV and 3.8 eV. Intensity minima occur at E_F and at 2.7 eV. At 10^5 L the peak at 3.6 eV obviously merges into the strong maximum at 5.0 eV. The UP difference spectrum at 10^5 L (Fig. 12) shows intensity minima at E_F and 2.1 eV. Emission maxima occur at 1.7 eV and 3.2 eV. However, almost no additional emission can be detected at about 5.5 eV below E_F.

For the Cu(110) surface O_2 exposure from 1 L to 100 L causes a 2×1 LEED pattern and a work function increase of 0.2 eV is observed in accordance with earlier studies.[11] The 2×1 LEED pattern corresponds to a surface coverage of $\theta=0.5$.[11] At very high exposures (10^5 L) the LEED spots are found to become broadened and diffuse. He* spectra of the Cu(110) surface show drastic variations upon exposure to O_2 (Fig. 13). The shoulder at high ki-

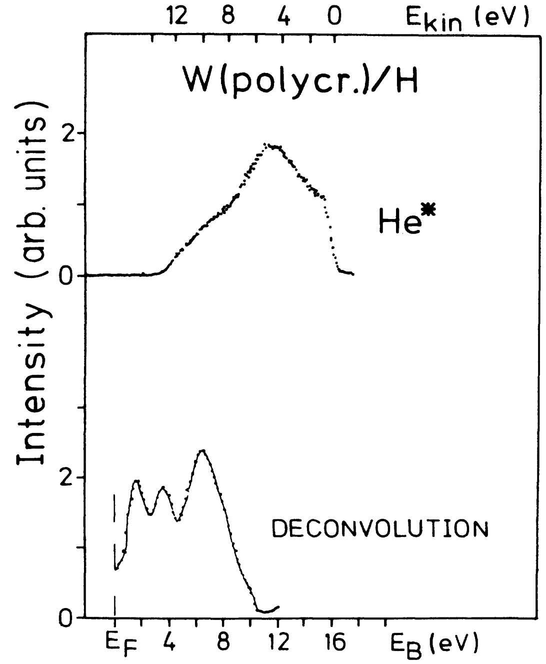

FIG. 7. He* spectrum and the deconvolution from a polycrystalline W surface at saturation coverage with hydrogen at 300 K.

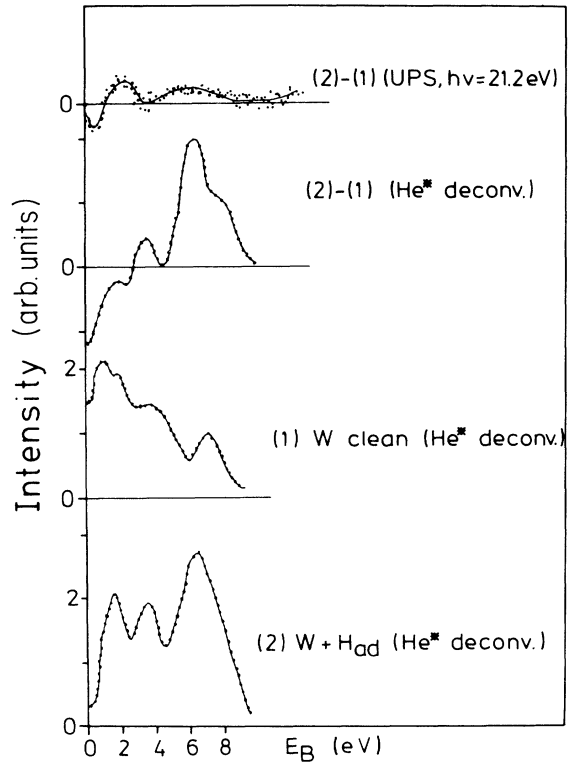

FIG. 8. Deconvolutions of the He* spectra from a hydrogen covered (2) and a clean W surface (1). Also shown are the difference spectrum (2)–(1) and the UP difference spectrum from the hydrogen covered and the clean W surface.

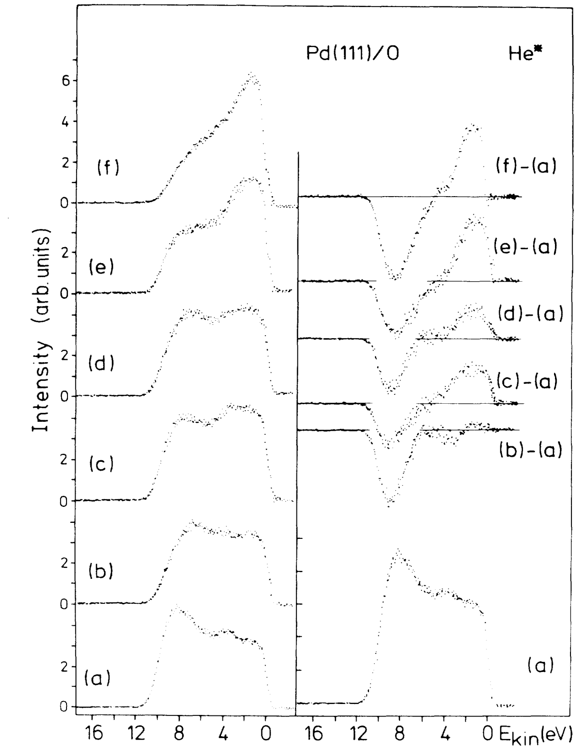

FIG. 9. He* spectra from (a) a clean Pd(111) surface and exposed at 300 K to (b) 1 L, (c) 10 L, (d) 30 L, (e) 100 L, and (f) 10^5 L of oxygen. Also shown are the difference spectra.

netic energies decreases very rapidly in intensity and vanishes at about 10 L O_2 exposure. Also the broad maximum at about 9 eV decreases in intensity whereas a strong emission maximum emerges at about 4 eV kinetic energy. These changes can be detected very clearly in the difference spectra of Fig. 13. Deconvolution of the He* spectra of the clean Cu(110) surface and after 10 L O_2 exposure (Fig. 14) show that the peak at $E_B = 0.8$ eV disappears; at the top of the Cu *d* band the intensity increases ($E_B = 1.8$ eV) and a very intense peak at $E_B = 6.5$ eV occurs. This becomes even more evident in the difference spectrum where at 1.8, 3.2, and 6.5 eV peaks are found and at 0.8, 2.6, and 3.9 eV intensity minima occur. Similar results have been obtained from AN spectra with Ne* atoms.[2] The UP spectra in Fig. 15 exhibit relatively small changes with increasing O_2 exposure. In the difference spectra a decrease of the Cu *d*-band maximum at 2.7 eV and peaks at 1.8, 3.5, and 6.2 eV can be detected. As already pointed out, the decrease in emission at high kinetic energies is one of the prominent features of AN spectra upon chemisorption. This intensity decrease corresponds to a decrease of the SDOS near E_F. Because of the low ionization energy of Ar, only the SDOS close to E_F is probed by using Ar* atoms. Therefore, the Ar* spectra in Fig. 16 very nicely demonstrate the gradual decrease of the SDOS near E_F of the Pd(111) and Cu(110) surfaces when oxygen chemisorbs at these surfaces.

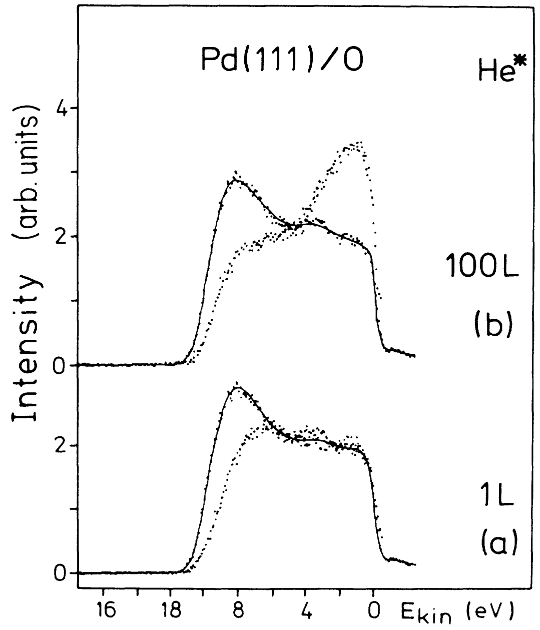

FIG. 10. He* spectra from a clean Pd(111) surface (solid curve) and exposed at 300 K to (a) 1 L, and (b) 100 L of oxygen (dotted curves).

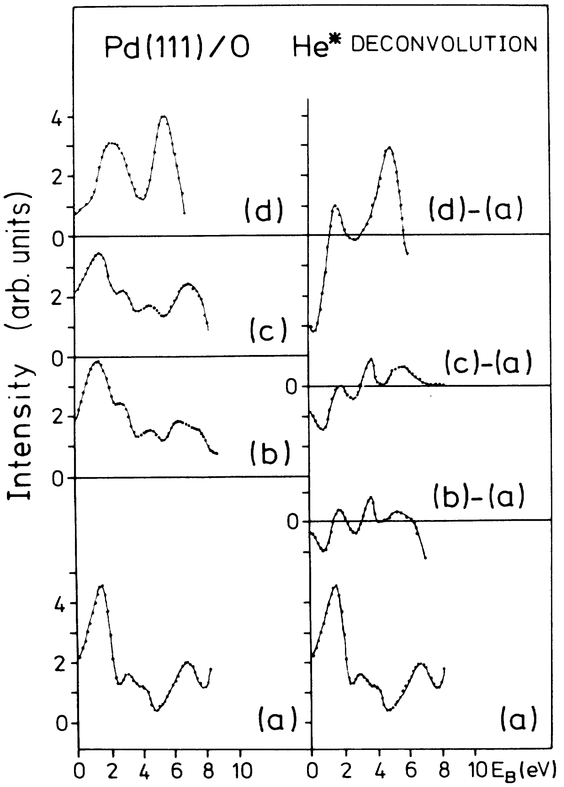

FIG. 11. Deconvolution of the He* spectra from (a) a clean Pd(111) surface and exposed at 300 K to (b) 10 L, (c) 100 L, and (d) 10^5 L of oxygen. Also shown are the difference spectra of the deconvolution.

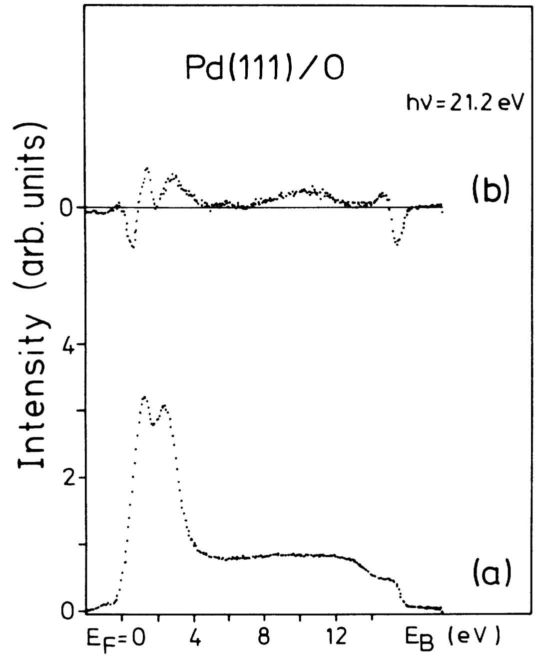

FIG. 12. (a) UP spectrum from a clean Pd(111) surface and (b) UP difference spectrum between the Pd(111) surface exposed at 300 K to 10^5 L of oxygen and the clean surface.

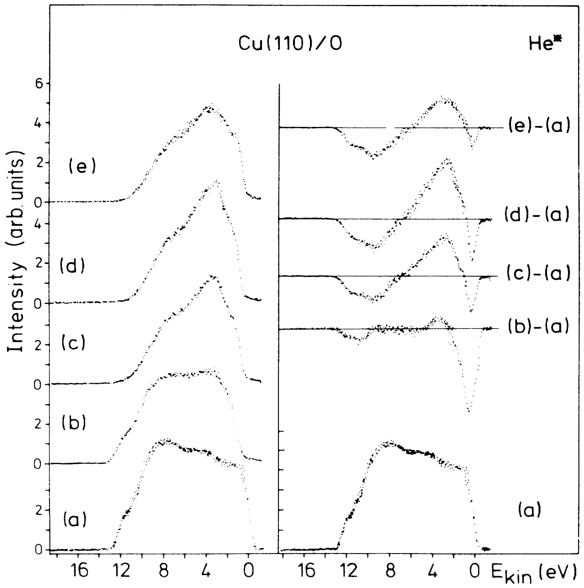

FIG. 13. He* spectra and difference spectra from a Cu(110) surface (a) clean and exposed at 300 K to (b) 1 L, (c) 10 L, (d) 100 L, and (e) 10^5 L of oxygen.

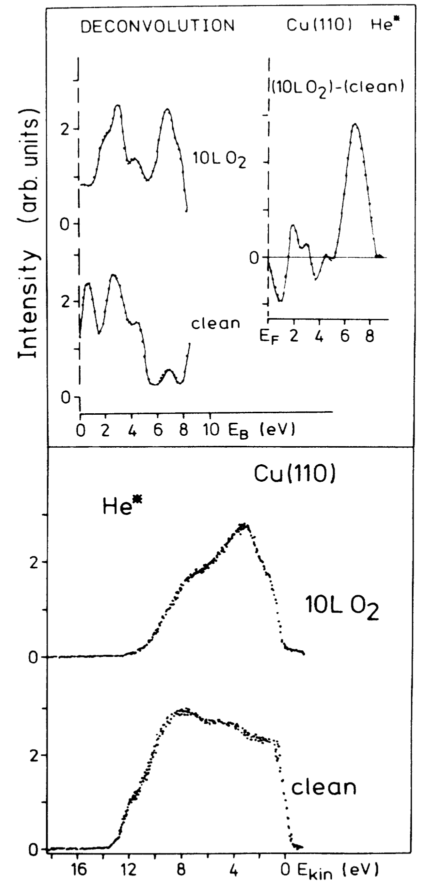

FIG. 14. He* spectra and the deconvolution from a clean Cu (110) surface and the surface exposed at 300 K to 10 L oxygen. Also shown is the difference spectrum of the deconvolution.

On polycrystalline W adsorption of 10 L O_2 causes an increase of the work function by 0.5 eV. Figure 17 shows the He* spectra of the clean and the oxygen covered surface as well as the deconvolutions. The chemisorption of 10 L oxygen considerably modifies the AN spectrum in the metal d-band region. This is also reflected in the deconvoluted spectra. Most remarkable is the decrease in intensity at E_F, a consequence of the low intensity in the He* spectrum of the oxygen covered surface at high kinetic energies. A strong oxygen induced peak occurs at $E_B = 6.5$ eV. As a reliability check for the deconvolution, these deconvoluted spectra are shown in Ref. 1 to be in very good agreement with the first derivative of the experimental He* spectra.

IV. DISCUSSION

A. Clean surfaces

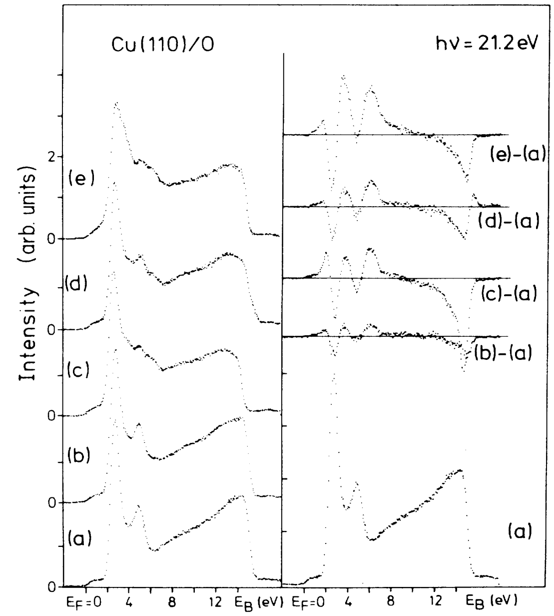

FIG. 15. UP spectra and difference spectra from (a) a clean Cu(110) surface and exposed at 300 K to (b) 1 L, (c) 10 L, (d) 100 L, and (e) 10^5 L of oxygen.

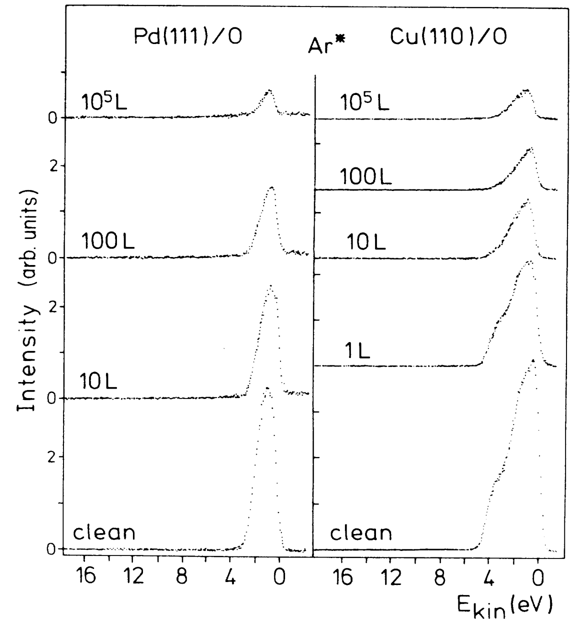

FIG. 16. Ar* spectra from a Pd(111) and Cu(110) surface at various exposures to oxygen.

For the Pd(111) surface the local electronic density of states of the first atomic layer (SDOS) and of the fourth atomic layer, which essentially represents the bulk density of states (BDOS), have been calculated by Louie[12] using a self-consistent pseudopotential theory. The results are shown in Fig. 18 together with the deconvolution of the He* spectrum. The structures of the deconvoluted spectrum (a) are in good agreement with the calculated SDOS (c). However, the intensity of the first peak near E_F is much more pronounced in the experimental spectrum. This is due to a matrix element effect of the Auger neutralization transition. The wave functions closer to the Fermi level protrude more into the vacuum than those at higher binding energies. Therefore, the wave function overlap with the 1s hole state of He^+ will be more effective and the Auger transition probability will be much higher from electronic states located close to E_F. Furthermore, at the Pd(111) surface the major part of surface states and surface resonances are located in the energy range from E_F to about 2 eV binding energy. Such electronic states exhibit a high local density in the outermost atomic layer. This becomes obvious from Louie's calculation where the SDOS exhibits higher intensity near E_F than the BDOS and below $E_B = 2$ eV the situation is just opposite [Fig. 18(d)–(c)]. Such surface states and surface resonances certainly interact very efficiently with the He^+ ion approaching the surface and, therefore, strongly contribute to the Auger neutralization process. This conclusion is confirmed by the calculated density of states at

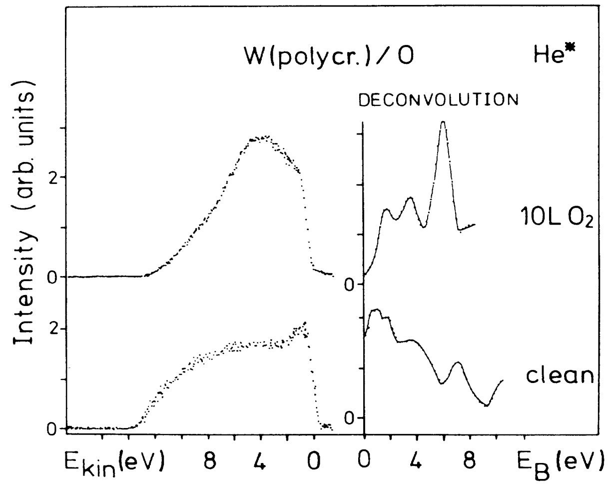

FIG. 17. He* spectra and deconvolution of a clean polycrystalline W surface and exposed to 10 L of oxygen.

a distance of one atomic layer in front of the surface [at 2.74 Å, Fig. 18(b)] where only electronic states in the energy range between E_F and 2 eV binding energy are present. Since the Auger neutralization transition occurs at about 3 Å in front of the surface,[1] obviously the electronic states from E_F up to $E_B = 2$ eV will dominate the experimental spectrum. AN spectra reflect the SDOS as probed by an atom approaching the metal surface. While the electronic properties of a transition-metal are mainly characterized by the *d* band electrons it is clear that for the electronic properties of the first atomic layer surface states and surface resonances play an important role. This is reflected directly by the AN spectra and will be discussed further in the context of chemisorption of oxygen and hydrogen. While AN spectroscopy probes the SDOS, the UP spectrum (Fig. 1) exhibits a higher intensity below $E_B = 2$ eV and is more related to the BDOS of Pd. From theoretical calculations[12,13] it is known that already for the second metal layer the electronic DOS is bulklike.

In contrast to Pd the *d* band of Cu is fully occupied and located 2 eV below E_F and only *s*- and *p*-states exist close to E_F.[14] This difference is clearly reflected in the AN spectra of the Cu(110) surface (Fig. 2) which exhibit at high kinetic energies an additional shoulder. This structure causes the intense peak just below E_F in the deconvoluted spectra. Between $E_B = 2$ eV and 5 eV the intensity is related to the Cu *d* band. In the UP spectrum of Fig. 2 the *s*-*p*-like emission below 2 eV is much weaker than the *d*-band emission whereas in the AN spectra and the deconvoluted spectra, respectively, the intensities are comparable. Also, studies of alkali-metal surfaces have shown the very high sensitivity of metastable atom deexcitation spectroscopy for *s*-like electronic states.[15] The intense peak of the deconvoluted spectra at E_F has to be identified most likely with the *s*-like surface state in the *s*-*p* band gap which has been observed by angle resolved UPS measurements at the Cu(110) surface,[16,17] although with much lower intensity than with AN spectroscopy. The energetic width in the deconvoluted spectra is, however, considerably larger than that derived with UPS because of three reasons: first, the experimental resolution of the electron energy analyzer used was only 0.3 eV; second, metastable deexcitation spectroscopy integrates over the whole wave vector **k** range[1] and, therefore, over the 0.4 eV energy dispersion of this surface state; third, the deconvolution additionally limits the energy resolution (see appendix of Ref. 1). Adsorption of oxygen immediately leads to a strong intensity attenuation of this peak which is characteristic for surface states (Figs. 4 and 5). Compared with UPS, metastable deexcitation spectroscopy shows this surface state with high intensity independent of the emission angle.[11]

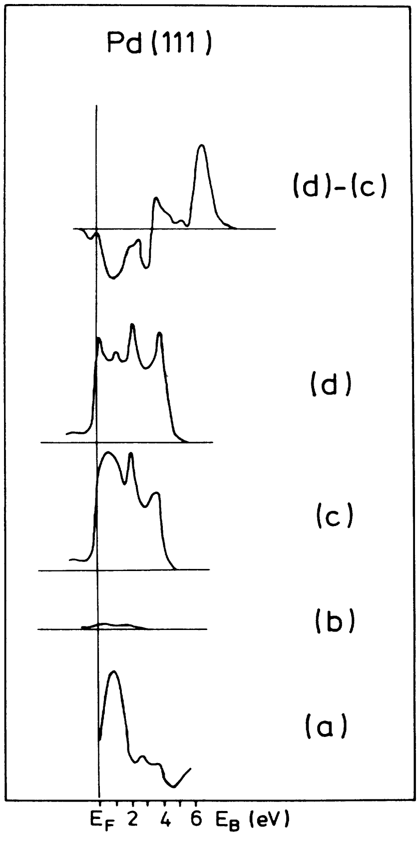

FIG. 18. (a) Deconvolution of the He* spectrum from a clean Pd(111) surface and the calculated [S. G. Louie, Phys. Rev. Lett. **40**, 1512 (1978)] local electronic density of states of the clean Pd(111) surfaces, (b) at a distance of 2.74 Å in front of the first metal layer, (c) at the first layer (SDOS), and (d) at the fourth layer (BDOS). Additionally shown is the difference (d)−(c) of the calculated BDOS and SDOS.

LCAO calculations[18] of the SDOS of a Cu(110) surface have shown extensive formation of surface states and resonances in the *d* band range. These surface states are concentrated especially at the *d*-band top edge. The calculated SDOS is in satisfactory agreement with the deconvoluted spectra in this energy range. Self-consistent calculations, so far, have been only performed for Cu(100) and (111) surfaces[19] but at least qualitatively support the conclusions drawn for the (110) surface. Similar to the findings with the Pd(111) surface, also the AN spectra of the Cu(110) surface and the deconvolutions, respectively, reflect the SDOS with emphasis on surface states and surface resonances due to their wave functions extending far from the surface and, therefore, having an effective overlap with the hole state of the noble gas ion.

Characteristic for the electronic structure of bcc transition-metals is a high density of surface states and surface resonances in the energy range between E_F and about 2 eV binding energy while the BDOS exhibits a relatively low density of states in this energy range.[20] A comparison of the deconvoluted He* spectrum of the W surface and the UP spectrum shows this general behavior. The deconvolution exhibits maximum intensity at E_F and is in qualitative agreement with calculated SDOS's of W surfaces.[20] The UP spectrum is low in intensity up to about 2 eV binding energy and rather reflects the BDOS of W.

All AN spectra discussed so far have been taken from surfaces which have to be considered as clean according to standard surface analysis techniques such as AES, LEED, and TDS. Nevertheless, in the deconvoluted spectra maxima are observed in the binding energy range from 6 eV to 7 eV which are clearly related to emission structures in the AN spectra but are not present in the UP spectra (Figs. 1 and 2). These peaks are energetically located below the metal valence states. Binding energies of 6 to 7 eV are typical for atomic adsorbates on metal surfaces.[21] Based on the detection sensitivities of the standard surface analysis techniques the concentration of impurities should be below 1%. This demonstrates the extreme sensitivity of AN spectroscopy for adsorbates. As will be further elucidated in the following sections, this is due to the fact that their wave functions extend considerably beyond the metal states into the vacuum[19] and, therefore, exhibit a very high AN transition probability. For the same reason in ion scattering experiments an adsorbate induced enhancement of the neutralization of noble-gas ions is observed.[22]

The residual gas in our UHV system contained mainly H_2, H_2O, and CO. None of these gases adsorbs at room temperature dissociatively at a Cu surface. As can be seen from Fig. 19 the peak in the AN spectrum at $E_{\mathrm{kin}}=4$ eV increases significantly in intensity if the freshly cleaned surface (a) is kept for 12 h under UHV conditions [spectrum (b)]. These emission peaks cause the shaded peaks in the deconvoluted spectra at $E_B=7$ eV. Most likely impurities dissolved in the bulk segregate to the surface and manifest themselves in the spectra. It is known that oxygen is easily dissolved in Cu,[11] whereas hydrogen dissolves in W.[23] In Pd, both species have a high solubility.[23,24] In any case, the surface contamination is so low that it can be detected only by AN spectroscopy. The existence of impurities and defects on "clean" surfaces undetectable by AES, LEED, and UPS has also been demonstrated indirectly by high-resolution angle-resolved photoemission studies due to a surface state broadening on Cu(110) and Cu(111) surfaces.[17,25]

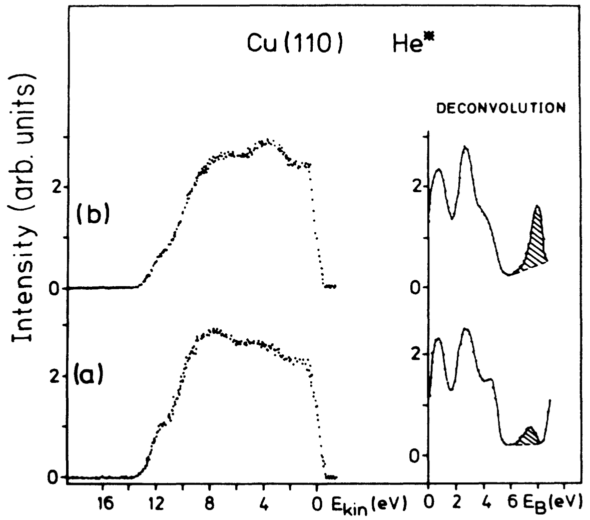

FIG. 19. He* spectra and deconvolution of (a) a freshly cleaned Cu(110) surface and (b) after 12 h under UHV conditions at 300 K.

B. Adsorption of hydrogen

For the Pd(111) surface covered with adsorbed hydrogen atoms, self-consistent pseudopotential calculations of the band structure and the SDOS have been performed by Louie.[26] These calculations show that H atoms are adsorbed in threefold hollow sites and that strong coupling between the H 1*s* orbital and the Pd *d* electrons occurs which results in dramatic changes in the Pd surface electronic structure. Surface states and resonances of clean Pd(111) are either shifted to higher binding energies or lose their surface-state (resonance) character because the major part of the electron density is no longer localized in the surface layer The dominant effects of H chemisorption on the SDOS are a drastic reduction of the density of states near E_F due to the removal of intrinsic surface states and resonances. Some of these states are shifted to higher binding energy and cause an enhancement of the SDOS around 2.5 eV and 4 eV compared with the SDOS of clean Pd(111). An additional intense peak outside the Pd *d*-band range at $E_B=6.5$ eV results from the bonding between the H 1*s* and Pd *d* orbitals. The deconvoluted He* spectra of a Pd(111) surface at various H_2 exposures (Fig. 5) clearly show the gradual reduction of the SDOS at E_F which can also directly be realized by inspection of the raw data in Fig. 4. Furthermore, in good agreement with the calculated SDOS, intensity maxima at 2.8, 4.2, and 6.5 eV occur in the difference spectra of the deconvolution (Fig. 5). At higher H_2 exposures the 2.8 and 6.5 eV peaks increase more in intensity than the 4.2 eV peak which probably mask the latter in the difference spectra. The spectra indicate that the surface states and resonances located close to E_F for clean Pd(111) are shifted mainly to binding energies around 2.5 eV as a consequence of the Pd—H bond. Thus, the changes of the SDOS upon hydrogen chemisorption as calculated by Louie[26] are well reproduced by the experimental results of AN spectroscopy. Apart from this good qualitative agreement, the deconvoluted He*-spectra exhibit an enhanced intensity near E_F due to the matrix element effects as already discussed for the clean surface.

The UP spectrum of the H-covered Pd(111) surface shows no distinct emission features around $E_B=6.5$ eV (Fig. 6) whereas at the same H_2 exposure the deconvoluted He* spectrum exhibits a strong peak (Fig. 5) which can also be clearly observed in the direct AN spectra of Fig. 4. With UPS only in the difference spectrum a weak emission around 6.5 eV can be detected at very high H_2 exposures (Fig. 6). Additionally, the UP difference spectrum shows, in agreement with the deconvoluted AN spectra, the intensity attenuation at E_F and a relative intensity maximum around 3.5 eV. In contrast to the AN results an intensity maximum at 1.5 eV occurs and a minimum is found at 2.5 eV where in the AN deconvolution difference spectra a maximum is observed. A theoretical UP difference spectrum has been calculated by Louie by averaging over the DOS of several layers.[26] This spectrum is in good agreement with the UP results from a Pd(111) surface exposed to 2 L H_2.[27] The analysis by Louie shows that the minimum at 2.5 eV can be correlated with a shift of surface states to about 1 eV higher binding energy causing the maximum around 3.5 eV. The peak at 1.5 eV seems to be characteristic for high H_2 exposures since it is not found in the experimental data of Ref. 27 but is observed in Ref. 28 at high H_2 exposures.

The comparison of AN spectroscopy and UPS results reveals differences due to the surface sensitivity of metastable atoms in relation to the finite sampling depth of UPS. In agreement with the calculations of Ref. 26 the deconvoluted He* spectra reflect the changes of the SDOS upon H chemisorption and the UP spectra show the changes of the DOS averaged over several layers.

Based on angle-resolved UPS data it has been suggested that on the (111) surfaces of Ni, Pd, and Pt hydrogen atoms adsorb at the surface above the first metal layer only at low temperatures (≤ 100 K), while at room temperature the H atoms are incorporated under the first metal layer.[29] This conclusion was based on the fact that with UPS at room temperature no additional emission outside the *d*-band range due to the H 1*s*-*d* bonding state and only very small changes in the metal *d*-band region were observed. The He*-spectra in Fig. 4, however, clearly show that at room temperature and after exposures of 1 L and 10 L in the *d*-band region as well as outside the metal *d*-band substantial changes occur which have to be attributed to a shift of surface states (resonances) to higher binding energies and to the formation of the H 1*s*-metal states bond resonance at 6.5 eV binding energy. The latter observation especially, proves that also at room temperature hydrogen atoms at such exposures as studied in Ref. 29 are adsorbed *on* the Pd surface. The extreme surface sensitivity of AN spectroscopy as well as the high cross section for *s*-like states due to the efficient overlap with the He *s*-orbitals allow us to readily identify the 1*s* bond state of hydrogen chemisorbed on metal surfaces.

Adsorption of hydrogen on the W surface leads to a He* spectrum and its deconvolution (Fig. 7) which can be interpreted similarly to Pd. The surface states and resonances which are on the clean W surface located from E_F up to 2 eV binding energy (see Sec. IV A) shift toward higher binding energies. This leads to the strong intensity minimum in the deconvolution difference spectrum between E_F and $E_B = 2$ eV and to the maximum at 3.3 eV (Fig. 8). The very intense peak at $E_B = 6.2$ eV in the deconvolution as well as in the difference spectrum is caused by the H 1*s* bond resonance. With UPS this peak can be detected in a difference spectrum only (Fig. 7). This UP difference spectrum is in the W *d*-band range similar to the deconvolution difference spectrum. However, the maximum at 3.3 eV is not present but a maximum at 2.6 eV which is seen in the deconvolution difference spectrum as a shoulder. This might again indicate differences between the SDOS of the H-covered W surface and the averaged DOS probed by UPS.

C. Adsorption of oxygen

Oxygen adsorption on the Pd(111) surface leads in the AN spectra to a strong intensity reduction in the *d*-band energy range and outside this range an intense emission at low kinetic energies emerges (Figs. 9 and 10). Consequently, in the deconvoluted spectra the intensity at E_F decreases with increasing O_2 exposure. Outside the *d*-band range the O 2*p*–derived metal-oxygen bond resonance is clearly observed at $E_B = 5.5$ eV and shifts at very high O_2 exposures to $E_B = 5.0$ eV. With UPS, this O 2*p* bond resonance is usually only discernible in the difference spectra (see Fig. 12 and Refs. 30–32). This is again a consequence of the surface sensitivity of AN spectroscopy as well as of the high Auger neutralization probability of He^+ ions at adsorbates.[22] Nevertheless, in the AN process an effective surface DOS is involved including metal states as well as adsorbate induced states. This becomes immediately obvious by inspection of Fig. 9 which shows the spectra of the clean and oxygen-covered Pd(111) surface. If the AN process would involve the O 2*p* state only, UPS-like spectra should be observed. Furthermore, the maximum kinetic energy of the emitted electrons should be of the order of 8 eV only. Also, the deconvoluted spectra (Fig. 11) clearly demonstrate that Auger neutralization involves not only the chemisorbed oxygen but also the metal states. This is obviously in contrast to conclusions made in Ref. 33.

In the Pd *d*-band energy range the deconvolution difference spectra exhibit, apart from the intensity reduction at E_F, peaks at 1.7 eV and 3.8 eV and a minimum at 2.7 eV (Fig. 11). As pointed out by Louie,[26] the shift of surface states and resonances to higher binding energies upon adsorption is not very sensitive to the nature of the adsorbate. In fact, as with hydrogen the intensity reduction at E_F and $E_B = 2.7$ eV as well as the intensity increase at $E_B = 3.8$ eV can be explained by the removal of surface states and resonances to higher binding energies. This is supported by the UP difference spectrum which exhibits, like in the case of hydrogen adsorption, intensity minima at E_F and $E_B = 2.1$ eV and an intensity maximum at $E_B = 3.2$ eV (Fig. 12). The peak at 1.7 eV present in the deconvolution and the UP difference spectra, however, cannot be readily identified as being due to shifted surface states and resonances. At high oxygen exposures in the deconvoluted spectrum the intensity increases like the O 2*p* bond resonance at 5 eV. Therefore, this peak might be identified as the occupied O 2*p* antibonding state.

The reduction of the SDOS near E_F due to the shift of surface states and resonances to higher binding energies by the formation of the adsorbate-surface bond is nicely demonstrated by the AN spectra with Ar* which only probe the SDOS near E_F (Fig. 16). In the case of the Cu(110) surface the rapid quenching of the *s*-like surface state above the Cu *d* band is clearly evident. After 10 L O_2 exposure the shoulder at high kinetic energies in the AN spectra and the peak in the deconvoluted spectra, respectively, is removed (Figs. 13, 14, and 16). On the other hand, a peak at about 4 eV kinetic energy in the He* spectra (Figs. 13 and 14) or $E_B = 6.5$ eV in the deconvoluted spectrum grows continuously in intensity. This feature is also observed with UPS (Fig. 15 and Refs. 11 and 31), albeit only in difference spectra, and is attributed to the bond state arising from the Cu—O 2*p* coupling. According to Sec. IV A, a high density of surface states and surface resonances is located at the top of the Cu *d*-band. Therefore, the intensity minima at 2.6 and 2.7 eV in the deconvolution and UP difference spectra, respectively, are due to the shift of these states to higher binding energies. Since no self-consistent calculation of the adsorbate covered Cu(110) surface exists, it is suggested that the relative maxima at 3.2 and 3.5 eV, respectively, are caused by the redistribution of the surface states and resonances in analogy to the behavior of the Pd(111) SDOS. Only in the deconvolution difference spectrum is an additional minimum at $E_B = 3.9$ eV observed. Both the UP and the deconvolution difference spectrum show a peak at $E_B = 1.8$ eV which increases with O_2 exposure and is ascribed to the antibonding Cu—O $2p$ level. Similar results as with He* atoms have been obtained with Ne* atoms.[2]

Adsorption of oxygen on Cu(110) gives rise to a (2×1) LEED pattern at exposures lower than 200 L and room temperature.[11] From ion scattering,[34] He diffraction,[35] and electron energy loss spectroscopy (EELS)[36] studies it had been concluded that the oxygen atom occupies a subsurface site below the topmost layer. Since already after 1 L O_2 exposure the AN spectra clearly exhibit the characteristic changes for adsorbed oxygen, especially the peak from the Cu—O bonding level, the oxygen atoms have, however, to be located slightly above the surface. Based on the surface sensitivity of metastable atoms which selectively investigate the electronic structure of the outmost atomic layer the subsurface site can be ruled out. Recently, also from surface extended x-ray-absorption fine structure (SEXAFS) studies an oxygen adsorption site above the first Cu layer has been concluded.[37]

For the W surface exposed to 10 L O_2 the He* spectrum and the deconvolution shown in Fig. 17 reveal a strong intensity reduction between E_F and $E_B = 2$ eV. In this energy range a high surface state and resonance density exists on clean bcc metal surfaces (see Sec. IV A). The additional peak at $E_B = 2.9$ eV might be identified with the antibonding W—O $2p$ state while the intense peak at $E_B = 6.5$ eV is ascribed to the bonding W—O $2p$ level.

V. SUMMARY

The valence electron structure of clean and with hydrogen or oxygen atoms covered Pd, Cu, and W surfaces was probed by AN spectroscopy. Proper analysis of the data yields information on the SDOS which cannot be obtained by methods like UPS with finite sampling depth. For clean surfaces good agreement with calculated SDOS's, if available, is observed. Due to matrix element effects for the Auger neutralization, transition surface states and surface resonances energetically located close to the Fermi energy are detected with enhanced sensitivity. AN spectra reflect the SDOS as probed by an atom approaching the metal surface. Chemisorption of hydrogen and oxygen strongly affects the metal *d*-states of the SDOS. Surface states and resonances are observed to shift to higher binding energies or to be strongly modified in their electronic surface state character by the adsorbate-metal bond. This causes intensity minima and maxima in the difference spectra. Additionally, occupied bonding as well as antibonding adsorbate-metal states are found. Upon chemisorption the deconvoluted AN spectra are found to reflect the changes of the SDOS. UP spectra are more related to changes of the electronic DOS averaged over several atomic layers. With AN spectroscopy the adsorbate-metal bond resonance outside the metal *d*-band range is detected with very high sensitivity for adsorbed hydrogen and oxygen atoms because the wave function overlap with the noble-gas atoms at the surface is very efficient and, therefore, leads to a high Auger neutralization probability. This allows to detect spurious amounts of impurities on the surfaces which are far below the detection limit of standard surface analysis methods. Furthermore, it can be proved that hydrogen atoms on Pd(111) and oxygen atoms on Cu(110) adsorb above the surface metal layer at 300 K in contrast to earlier studies which favored subsurfaces sites.

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