Vacuum/volume 41/numbers 4–6/pages 1118 to 1120/1990
Printed in Great Britain

0042–207X/90$3.00+.00

Spin-resolved core and valence electron photoemission from non-epitaxially grown Pb layers on Pt(111)

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The core and valence levels of Pb adsorbates on Pt(111) have been studied by means of spin, angle and energy-resolved photoemission with circularly polarized synchrotron radiation of BESSY. For an eight layer Stranski–Krastanov grown Pb adsorbate (which is thus non-epitaxial) the d core level peaks show a spin–orbit splitting of 2.7 eV and no shift with photon energy. Spin-resolved photoemision for normal light incidence and normal electron emission from the $5d_{5/2}$ level reveals a m_j splitting in addition to the spin–orbit splitting and in addition to the core level shifts known. The valence levels were studied with photon energies of about 12 eV. Two peaks corresponding to the $6p_{3/2}$ and $6p_{1/2}$-derived levels could be detected for the highly symmetrical setup of normal light incidence and normal electron emission. Off normal electron emission from the $6p_{3/2}$-derived level yields the opposite sign for the spin polarization component parallel to the photon spin when compared to the normal electron emission results. This is in agreement with earlier photoionization studies on free Pb atoms.

Introduction

Angle-resolved photoemission experiments have been performed up to now on a Pb(111) crystal[1] and on Pb adsorbates on Al(111) and Ni(111)[2,3], spin-resolved photoionization experiments on free Pb atoms[4–6]. The studies of Pb(111) single-crystals[1] allowed a bandmapping of the valence range in the ΓL-direction with recognition of a p-like band. The experiments with a He discharge tube on Pb adsorbates[2,3] showed only weak emission from p-derived states, while the d core levels could be well investigated. Core level binding energy shifts were measured which fit quite well in a model proposed[7,8]. In the so called Born–Haber cycle[2,3,7,8] the change of the binding energy of a core level when going from a free atom to a solid is given by changes in the configuration, i.e. the re-distribution of electrons between s, p and d states, by the chemical shift (displacement of the core level while changing the chemical environment) and by the relaxation shift. This model only takes energetic shifts into account, but does not include splittings. Spin-resolved photoemission should show whether the 5d core levels are split.

Whether spin–polarization of the photoelectrons can be observed can depend on the ordering of atoms in solids as was shown for Ge[9]: spin polarization of photoelectrons from amorphous Ge has not been observed within the experimental uncertainty; for polycrystalline Ge, however, spin-polarized photoelectrons have been observed.

The possibility to vary the photon energy when using synchrotron radiation supports the examination of the 6p valence levels, because one can use photon energies where the photoemission cross-sections for transitions from these levels is highest.

Experimental

The experiments were performed at the 6.5 m normal incidence vuv monochromator[10] at BESSY. The apparatus used for the measurements is described elsewhere[11] in general.

All photoemission data were obtained for normal incidence of the circularly polarized light and—with the exception of the off-normal data of Figure 3—also for normal electron emission. The angle between surface normal and electron emission angle is denoted as Θ. The photoelectrons were analysed with respect to their kinetic energy and emission angle by a rotatable pseudohemispherical electron spectrometer[12]. The overall energetic resolution (electrons plus photons) was better than 200 meV at an angular resolution of $\pm 3°$.

The surface normal of the Pt(111) crystal mounted on top of a manipulator coincided within 0.5° with the [111] direction and within 0.3° with the light direction. The clean crystal surface was prepared by cycles of Ar^+ and Ne^+ bombardment, heating in oxygen, and flashing. It was controlled by Auger electron spectroscopy (AES) and LEED.

The evaporation was performed with the substrate at room temperature with a resistively heated Pb evaporator, surrounded by a cooled shield. It is placed ≈ 20 cm away from the target. The Pb beam was collimated by a small tube. After an initial outgasing the evaporator worked without strong influence on the uhv conditions. It was used for short periods, between them the surface was controlled by LEED and AES.

Results and discussion

The growth mechanism was studied by AES and LEED. In analogy to Pb on other substrates[2,3,13–15] we observed a Stranski–Krastanov growth of Pb/Pt(111), too. Ordered structures: first a (4 × 4), then a hexagonal closed packed layer, occured up to coverages of one layer.

Because of weak photoemission intensities and strong secondary emission for lower coverages we chose a coverage of eight layers for our photoemission studies. Photoemission intensities for photon energies between 24 and 28 eV are presented in the left part of Figure 1. The two peaks at binding energies at about 17.9 and 20.6 eV below E_F correspond to emission from the $5d_{5/2}$ and $5d_{3/2}$ level, respectively. This attribution was done in analogy to Ref 2, 3 because the energetic position is close to that of thick Pb adsorbates on other substrates[2,3], with the $5d_{3/2}$ level at higher binding energy. In the photon energy range between 24 and 28 eV no variation of the binding energies of the $5d_{3/2}$ and $5d_{5/2}$ core levels could be observed.

In the right part of Figure 1 a spin-resolved photoemission spectrum of the $5d_{5/2}$ level for hν = 24 eV and a coverage of eight layers is shown. The total intensity I (dots) is separated into the partial intensities I_+ (dashed lines) and I_- (solid lines), corresponding to the spin direction parallel or antiparallel to the photon spin, respectively, by means of the formula $I_\pm = I/2\ (1 \pm P)$, where P denotes the measured spin polarization component parallel to the photon spin.

For these Pb 'clusters on a surface' we observe spin polarization of the emitted photoelectrons ($I_+ \neq I_-$). The peak is also split by about 30 ± 15 meV (difference between the peak centres) with the I_+ peak at higher binding energy. In addition to

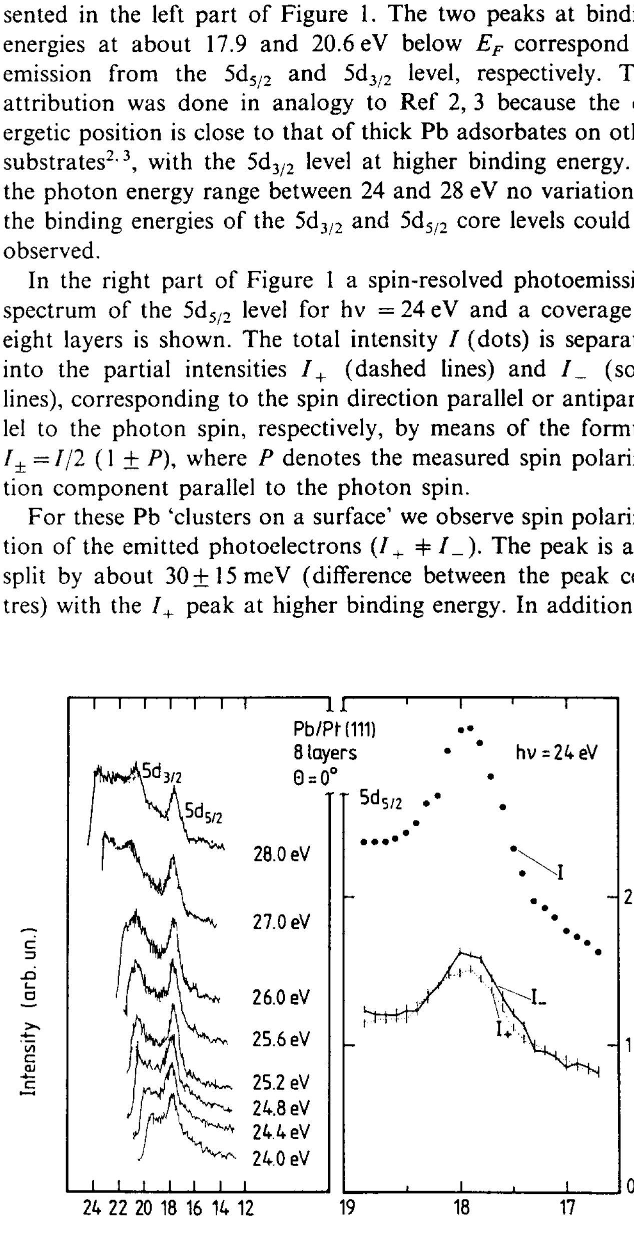

Figure 1. Left part: photoelectron spectra of Pb/Pt(111) for photon energies between 24 and 28 eV at a coverage of eight layers in normal emission. Right part: spin-resolved photoemission from Pb core levels: the data were obtained for hν = 24 eV and a coverage of eight layers in normal emission.

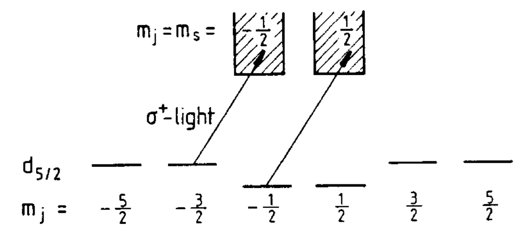

Figure 2. Level scheme for the normal photoemission process from the $5d_{5/2}$ regime of Pb with circularly polarized σ^+ light in normal incidence. Solid lines represent initial states, the hatched area final states and arrows allowed transitions.

the spin–orbit splitting $d_{5/2}/d_{3/2}$ the spectra show thus a further splitting of the 5d core levels which is up to now not considered it the model describing the d core levels of adsorbed metal atoms[2,3,7,8].

To get a better understanding of the spin polarization measured we describe the normal photoemission process with final states with $m_l = 0$ as caused by symmetry reasons for free atoms[16] and adsorbates with C_{6v} symmetry[17] or for a Pb(111) single-crystal where a free electron parabola is assumed as final state[1].

Figure 2 shows a schematic diagram of the initial and final states involved and the transitions allowed for normal incident σ^+ light and normal photoemission. Because of $m_l = 0$, $m_j = m_s = \pm 1/2$ states are possible as final electronic states. Starting from $5d_{5/2}$ the $m_j = -1/2$ and $m_j = 1/2$ final states can only be reached from the $m_j = -3/2$ and $m_j = -1/2$ ground-state sublevels, respectively, due to the dipole selection rule $\Delta m_j = +1$ for σ^+ light. The corresponding photoelectrons are totally polarized with opposite signs of spin polarization −1 and +1, respectively, because of $m_j = m_s$. For the excitation with σ^- light the behavior is vice versa. As the photoelectrons corresponding to the $|m_j| = 3/2$ sublevels can be attributed to a peak in I_- and the photoelectrons corresponding to the $|m_j| = 1/2$ sublevels can be attributed to a peak in I_+ the results of Figure 1 show that the $|m_j| = 1/2$ sublevels of the $5d_{5/2}$ level of Pb have a higher binding energy than the $|m_j| = 3/2$ sublevels.

The results presented up to now regarded the d core electrons. The following data were obtained for photoemission from the Pb valence levels. The left part of Figure 3 shows spin-resolved photoelectron spectra at a coverage of eight layers and a photon energy of hν = 12 eV. The total intensity I (dots) is again as in Figure 1 separated into the partial intensities I_+ (dashed lines) and I_- (solid lines). The two peaks at about 2.2 eV below E_F with positive spin polarization sign and at about 3.9 eV below E_F with negative spin polarization sign are attributed to transitions from states derived from the $6p_{1/2}$ and $6p_{3/2}$ level, respectively. This is done because the energetic difference is equivalent to the spin–orbit splitting of the free atom[18] and because the spin polarization sign is also equivalent to the case of the free atom in this energy range[6]. Thus we observe emission from the p-derived levels of a Pb adsorbate at 12 eV.

Additionally we also measured photoelectron spin polarization for emission from the $6p_{3/2}$ derived states at emission angles Θ different from normal emission. The result is presented in the right part of Figure 3. The spin polarization of the background corrected and energy integrated peak in the photoelectron spectra is given with the statistical error as full circles in the Pb adsorbate case for hν = 12 eV. A change in the sign

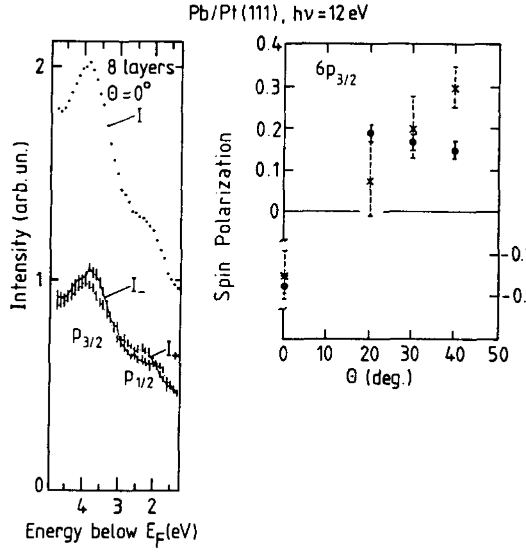

Figure 3. Left part: spin-resolved photoemission from the Pb valence levels of Pb/Pt(111). The data were obtained for $h\nu = 12$ eV and a coverage of eight layers in normal emission. Right part: off-normal photoemission from Pb valence levels; component of the spin polarization parallel to the light direction for photoelectrons corresponding to $6p_{3/2}$-derived states of Pb/Pt(111) for $h\nu = 12$ eV (full circles), and spin polarization of photoelectrons corresponding to the $6p_{3/2}$ orbital of free Pb atoms for $h\nu = 11.7$ eV[6] (crosses), as function of the emission angle.

of the polarization from negative to positive is observed. To get a better understanding of this change we compare our data in the right part of Figure 3 with the corresponding data (crosses) obtained from measurements on the free atom[6].* For the free atom the same change in the sign of the spin polarization has already been observed; even a quantitative agreement in the angular dependence of the spin polarization is observed between gas phase and adsorbate.

It is known[19] that for a $\sqrt{3} \times \sqrt{3}R30°$ Xe layer on Pd(111) the angular dependence of the photoelectron spin polarization can be quantitatively parametrized according to the behavior of gas phase photoionization; as in Xe also in Pb, a sign change of the spin polarization component parallel to the light direction is observed in both the adsorbate, as well as the free atom case, when increasing the emission angle. Even for an eight layer Stranski–Krastanov-grown Pb adsorbate the angular dependence of the off-normal photoemission spin polarization has been seen to be atomic-like. The idea that some atomic features are preserved in 'adsorbed clusters' in contrast to a single-crystal is also supported by the energetic positions for which emission from the 6p-derived states takes place. For a (111) single-crystal the p-derived band crosses the Fermi level. Thus no emission from the occupied band can be got for photon energies below 20 eV[1]. Except for some additional features, only one peak is observed above 20 eV corresponding to a p-derived band[1].

*Our data for $h\nu = 12$ eV are compared with free atom data for $h\nu = 11.7$ eV which is the closest energy for which data was available.

Summary

Summarizing we studied a Stranski–Krastanov-grown Pb adsorbate on Pt(111) with spin, energy and angle-resolved photoemission. We observed two spin–orbit split peaks corresponding to the $5d_{5/2}$ and $5d_{3/2}$ core levels which show no dispersion. The $5d_{5/2}$ level shows an additional splitting of 30 ± 15 meV with its $|m_j| = 1/2$ sublevel at higher binding energy than the $|m_j| = 3/2$ sublevel. For photon energies of $h\nu = 12$ eV also emission from 6p-derived states could be obtained. Two peaks corresponding to the $6p_{3/2}$ and the $6p_{1/2}$-derived states could be observed. The magnitude of spin–orbit splitting is equivalent to the one of free atoms, while no such splitting was found earlier for a Pb(111) crystal. In accordance with free atom photoionization we find a sign change in the spin polarization, when going from normal to off-normal photoelectron emission. This supports that photoemission from Stranski–Krastanov Pb clusters shows similarities rather to gas phase photoelectron spectroscopy than to bulk photoemission.

Acknowledgements

We greatly appreciate discussions with K Jacobi, B Kessler and N Müller and express our thanks to the BESSY staff for their assistance. The work was financially supported by the BMFT (05331 and 431 AX).

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