Strong subthreshold photoemission from Ag(111) islands

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Dedicated to the 65th birthday of Henning Neddermeyer

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Abstract. – Epitaxial silver islands of (111) orientation of 50–100 nm diameter and multilayer thickness grow without strain on WSe\textsubscript{2}. Besides the common photoelectron emission (PE) out of the occupied Shockley surface state S\textsubscript{1} on Ag(111) strong subthreshold PE is observed at photon energies down to 0.7 eV below the work function of Ag(111) and with final energies down to 0.7 eV below the vacuum level of Ag(111). The subthreshold PE is assigned to direct transitions into the image potential states (IS) \( n = 1 \) and \( n = 2, 3, 4 \) and an elastic escape from these states into vacuum. The escape path is tentatively assigned to the area of the slopes of the islands where the local work function is reduced.

Introduction. – Textbooks on the photoelectric effect usually start with Einstein’s quantum theory of photoemission, according to which the photon energy has to exceed the work function and the photoelectron energies are above the vacuum level \( E_{\nu} \). Here we report on a very strong sub-vacuum-level photoemission at subthreshold photon energies, not observed before. The samples are silver islands with a smooth (111) surface parallel to the substrate with a homogeneous work function at the island surface, on a substrate of higher work function. The subthreshold photons excite electrons from states below the Fermi energy to image potential states (IS) below the vacuum level of the Ag(111) surface [1]. The ISs form a series of energy \( E_n \) \( (n = 1, 2, \ldots) \) whose series limit is \( E_{\nu} \), similar to the electronic states of a hydrogen atom, with energies \( E_n = E_{\nu} - \frac{R/16}{(n+a)^2} \), where \( R \) is one Rydberg and \( a \) is a quantum defect [2,3]. We propose an explanation of this surprising effect, of course without contradicting Einstein, as to how the electrons leave this bound state without any further uptake of energy.

Experimental. – Ag films were deposited from an effusion cell onto ultra high vacuum (UHV) cleaved WSe\textsubscript{2} (0001) surfaces. The Ag film thickness is given as nominal thickness as determined by a quartz micro-balance. Angular-dependent PE spectra were taken with a VG ADES spectrometer in normal emission. For photon energies from 10 to 120 eV, the TGM7 beamline at BESSY was used. Photon energies in the near ultraviolet (UV) between

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Fig. 1 – Normal electron emission intensity at 21.2 eV photon energy vs. binding energy, referenced to the Fermi energy of the metallic back contact of the WSe$_2$ sample, for the clean UHV cleaved WSe$_2$ sample, subsequently covered by Ag with the average mass thickness of 3, 6, 12 and 30 Å. The inset shows the Ag(111) surface state S1 shifted by the surface photovoltage under the 21.2 eV radiation (SR) and under the additional white light irradiation (SR + bias).

3.5 and 5.5 eV were realized by a Xe arc lamp and a 250 nm UV grating monochromator. The unpolarized light was focussed by a MgF$_2$ lens through a sapphire window under 45° onto the sample. Photon energies were calibrated by a Hg lamp and intensity was measured by a calibrated Si diode. Spectral positions in the PE are given in $E - E_F$ and were determined with reference to the Fermi level of a thick Ag film on a metallic sample holder using HeI. In fig. 1 electron energies are conventionally given in binding energies. A sample bias of $-6$ V (corrected in the spectra) is applied between the sample and the spectrometer to separate the photoelectrons and the intrinsic secondaries from the sample and the extrinsic secondaries from the electron spectrometer in the low-kinetic-energy region. Scanning tunneling microscopy (STM) data were obtained on a UHV cleaved WSe$_2$ sample by using the same Ag source in an equivalent geometry.

Results. – UV-PE valence band spectra at normal emission and 21.2 photon energy of the UHV cleaved (0001) $p$-doped WSe$_2$ surface show a valence band onset at a binding energy of $-0.15$ eV and a work function of 5.0 eV [4], see fig. 1. The PE spectra after silver deposition resemble the sum of PE spectra of $p$-WSe$_2$ and of the clean Ag(111) surface including the Shockley surface state S1 on Ag(111) in normal emission [5], shifted by the surface photovoltage (SPV) induced by the synchrotron radiation (SR) and additional white bias light of a quartz-tungsten lamp with intensity 20 mW/cm$^2$ (see inset in fig. 1). Ag grows epitaxially with its own lattice constant, as demonstrated by the LEED pattern in fig. 2a), in azimuthally
ordered islands with the (111) face to the interface [6]. The 3-fold symmetry of the Ag islands and the 6-fold one of the WSe$_2$ substrate are evident. STM images of 50–100 nm diameter Ag islands in fig. 2b) were obtained for a nominal 12Å Ag film. The islands are flat with triangular or six-cornered shape and are of uniform thickness of about 3 nm. The latter value is estimated from the fraction of the WSe$_2$ covered by Ag and the nominal thickness [7]. In fig. 3 the PE intensity at normal emission is scanned for different near UV photon energies without 21.2 eV excitation for nominal silver thickness of 3 and 6 Å. Figure 3 shows surprisingly strong PE for photon energies below the work function threshold and final photoelectron energies below the vacuum level of the Ag(111) islands.

With increasing photon energy ($\hbar\omega$), emission structures grow in whose energies are rather independent of $\hbar\omega$. For $\hbar\omega > 4.4$ eV, a third emission is observed (see fig. 3) which shifts for $\hbar\omega > 4.7$ eV linearly with $\hbar\omega$ (fig. 4). This emission is assigned to normal photoemission out of the Shockley state S1 which is situated only 62.5 meV below the Fermi level of silver [5]. The straight line in fig. 4 given by $E = E_F + E_{\text{phot}}$ denotes, for $E - E_F > \Phi$ ($\Phi$ is the work function of Ag(111)), the position of the photoelectrons from the Fermi level of silver if no SPV is generated. The PE from the S1 state of the silver islands has its intensity maximum right at the threshold of appearance when the photon energy reaches the value of the work function of clean silver (111) at 4.5 eV, see fig. 5. For $\hbar\omega$ below 4.7 eV and films of 3, 6 and 12 Å nominal thickness, the surface state S1 is found about 100 meV above the position $E_F + E_{\text{phot}}$ ($E_F$ is the Fermi level at the back contact of the WSe$_2$ substrate) due to the SPV $U_{\text{phot}}$. As the intensity of the exciting light decreases from 3.8 to 5.3 eV by a factor of 10 due to the transmission characteristics of the optical elements and the absorption in air, the deviation is explained by the generation of a SPV of the p-doped substrate setting in below about 4.6 eV and increasing with decreasing photon energies. To account for the SPV, the experimental PE energies of the subthreshold structures in figs. 3 and 4 have to be shifted downwards in energy by about 0.14 eV at $\hbar\omega = 4.5$ eV (see fig. 4) to obtain their position with respect to $E_F$ of the back contact of the sample.

Discussion. – The PE features for photon energies $\hbar\omega$ below the threshold are attributed to transitions to the first and second image states IS of the Ag(111) surface as final states and an energy-conserving escape mechanism towards the vacuum due to the island shape.
Fig. 3 – Near-UV spectra excited with the indicated photon energies for nominal Ag film thickness of 3 and 6 Å.

The observed PE is only weakly accessible to the usually used photon energies of 10–30 eV as shown for the secondaries in fig. 1. The electron transition from the Shockley-type Ag surface state S1 to the first IS \( n = 1 \) of the Ag(111) surface has been found by 2PPE at \( h\omega = 3.8 \) eV [8]. At this photon energy, see figs. 3 and 5, the lowest structure in energy \( E - E_F \) appears for the Ag islands with nominal thickness 3 Å and 6 Å. The energy of the emitted electrons in the low-energy structure is, given the uncertainties of the SPV (see fig. 4), in relatively good agreement with data of Fauster and Steinmann [1]. They reported the first IS on Ag(111) at 0.77 eV below the vacuum level, as measured by 2PPE, which will give \( E = 3.73 \) eV above \( E_F \) of Ag. The second structure is excited with photon energies at and above \( h\omega \sim 4.3 \) eV and has an energy \( E \) of about 4.1 eV above \( E_F \) of Ag (taking into account the SPV of 0.14 V), see fig. 4 for Ag film thickness of 6 Å. We attribute this structure to an emission out of IS \( n = 2, 3, 4, \ldots \), see fig. 4, in good agreement with the expected onset at \( h\omega = 4.35 \) eV and in approximate agreement with \( E - E_F = 4.27 \) eV from 2PPE for IS \( n = 2 \). Attributing this emission to electrons originating from ISs of monolayer (ML) islands as in the case of Ag on Pd [9] will be in conflict with our STM data. We observed only islands of uniform thickness showing no parts of 1 ML height. In addition, an emission from the first ML Ag should vanish for thicker Ag film, which we do not observe.
Fig. 4 – Experimental energy above $E_F$ (at the back contact of the p-WSe$_2$ sample) vs. photon excitation energy for the structures in fig. 3 of the 6Å film. Peak positions are obtained by fitting the spectra by Gauss/Lorentz peaks, see inset for the photon energy of 4.35 eV. The straight line above $E = E_F + \Phi$ will give the position of the photoelectrons from $E_F$ as observed in ordinary UV photoemission without photovoltage. Photovoltages of 140 meV (300 meV) at $E_{\text{phot}} = 4.6$ eV (3.8 eV) are indicated. Different symbols refer to the film thickness: crosses: 6 Å, open circles: 3 Å, full circles: 30 Å.

Fig. 5 – Intensities of the electron emission from S1 and the image states IS1 and IS2 obtained from the Gauss/Lorentz fits of the spectra in fig. 4 for the nominal Ag film thickness of 6 Å.

At nominal film thickness above 12 Å, the low-energy structures merge, probably caused by contacts between the Ag islands. When a thick continuous film (< 10 nm) is formed, the subthreshold PE is lost, as measured with light from a mercury lamp and an edge filter WG 305 transmitting monochromatic photons of 4.28 eV energy [10]. For Cu on WSe$_2$, the subthreshold emission is lost for excitation with 6 eV synchrotron radiation. The intensities in fig. 5 show that the excitation into the image states IS1 and IS2 below the onset of the normal photoemission at a photon energy of 4.5 eV and an escape into vacuum is as strong as the direct emission out of S1 into the continuum of vacuum states. Theoretical calculations are not known to us, hence we consider the qualitative correspondence to the hydrogen atom, where the total oscillator strength in the Rydberg series ($1s$ to $np$) is 1.3 times larger than the integrated oscillator strength of all the continuous transitions from $1s$ to states above the ionization limit (from table 14 in [11]). This will qualitatively hold also in our case and explains why the subthreshold photoemission is so strong, provided there are escape routes from the image states to the vacuum.

**Hypothesis.** – The mechanism responsible for the elastic-energy-conserving escape of the near UV excited electrons with energies down to about 700 meV below the threshold of the (111) surface of the Ag islands must be related to the peculiar morphology of the Ag
islands. The (111) surface of these islands is well defined and clean as deduced from the existence of S1 and the appearance and resonance of S1 at the photon threshold of 4.5 eV corresponding to the work function of Ag(111) of $\Phi_{\text{Ag}(111)} = 4.5 \text{eV}$ [12], see fig. 5. But at the circumference of an island we conjecture slopes as schematically given at the top of fig. 6, with steps, kinks and other atomic defects, especially near the corners of the triangular and six-cornered island with locally lowered work functions. As determined by STM [13], the mean full width at half-maximum and depth of the local work function valleys for single steps on Au(111) (Cu(111)) are about 6.5 Å (10 Å) wide by a lowering of $\Phi$ by 0.9 eV (1.9 eV). The extension of the slopes is at least as large as the island thickness (which is about the average thickness divided by the island coverage (see fig. 2)). The slopes contains about 12 monatomic steps for the islands of 12 Å nominal thickness. We conjecture that at some parts of the slopes the vacuum level averaged over the slope falls below the energy level of the IS at Ag(111) $n = 2$ (right side of the island in fig. 6) and even, maybe at the corners of the islands, below $n = 1$ (left side of the island in fig. 6). The extension of these areas of lowered work function (see fig. 6, bottom) opens a window of escape for electrons excited into the image states. Ley et al. developed an inhomogeneous emission model for graphite patches on diamond, where electrons from graphite patches escaped into vacuum via a negative electron affinity exhibiting diamond surface. Field-assisted emission due to a $-6 \text{V}$ sample bias is ruled out as the subthreshold emissions were observed for bias as low as $-2 \text{V}$. For WSe$_2$, no surface states are known [4,14] which can deliver efficiently electrons to the troughs (see fig. 6) around the Ag islands. The experimental observation of ISs by direct photoemission is neither restricted
to the specific system Ag/WSe$_2$ as stated above, nor limited to Ag islands. So far we observed subthreshold emission for Cu, Ag and Au island films. For Cu island films on oxidized Si(111), strong subthreshold photoemission effects have been observed by Soloviev and Otto.

The influence of the Schottky barrier between the islands and the substrate and of the photovoltage is of secondary importance, because the 3 features seen in the PE spectra of fig. 3 are also observed for silver deposited on $n$-WSe$_2$, $n$-MoTe$_2$ and metallic 1T-TaS$_2$.

Apparently, only the direct excitation of electrons by near-UV light will strongly populate ISs of the Ag islands which emit electrons into vacuum. In common UV PE experiments a population of IS by secondaries is less probable as indicated by the weak structures below the secondary cut-off, see fig. 1. These features were generally attributed to “dirty patches” of the samples in the past. The observed emission process via the image states might be responsible for the imaging contrast in PE electron microscopy (PEEM) carried out with near-UV light. To clarify the emission path for the electrons emitted at subthreshold energies PEEM experiments with high spatial resolution are planned. Nevertheless, the observation reported here might open up a new field using UV photoemission to study the electronic structure of rough surfaces and the related defects.

REFERENCES


[7] Due to the work function difference of 0.5 eV between substrate and film (see discussion below) the overall thickness of the islands and the width of the edges of the islands is not easily deducible from the STM data.


