Emission of correlated electron pairs from Au(111) and Cu(111) surfaces under low-energy electron impact: Contribution of surface states, d-states and spin effects

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ABSTRACT

The emission of correlated electron pairs excited from surfaces of Au(111) and Cu(111) by low-energy electrons is measured and analyzed. Energy and momentum conservation allows identification of electron pairs involving excitation of electrons from Shockley surface states and from valence d-states. The relative contributions of surface and d-states to the measured spectra of correlated electron pairs is shown to depend on the primary electron energy and is larger from surface states at relatively small primary energies. The use of a spin-polarized incident electron beam highlights the spin effects in producing an electron pair. Measurements show that spin effects are larger for the pair excitation from the valence d-states than for pairs excited from the surface states.

1. Introduction

Surface states on (111) surfaces of noble metals present an example of two-dimensional free electron-like electron systems. On a heavy-Z metal surface a spin-degeneracy of these states is lifted and a parabolic dispersion of surface states become spin-resolved, i.e. two dispersion curves separated in energy – momentum space appear. The dispersion of these states and their spin character for a Au(111) surface were studied using angle- and spin-resolved photoelectron spectroscopy [1–3]. Any new information on surface states, such as momentum distribution, for example, is desirable for deeper insight into their properties and for the possibility of influencing these properties. Surface states determine, to a large extent, the physical and chemical properties of surfaces and interfaces, such as adsorption, catalysis, conductivity, reflectivity and chemical reactions at surfaces. The spectra of electronic excitations, as well as the parameters of electron–electron and electron–phonon interactions, are important characteristics of such systems, but they are still largely unknown.

For experimental reasons, the confinement to the surface and the resulting two-dimensionality, make surface states ideally suitable for investigation by means of low-energy two-electron spectroscopy in reflection geometry [4–8], the essence of which is the detection of two time-correlated electrons generated from the surface by the impact of a single incident electron. Indeed, this technique possesses extremely high surface sensitivity because it involves three low-energy electrons: one incident and two outgoing. Hence, if the mean free path of each of the electrons is estimated by λ, then the probing depth of the technique is given by $\lambda/3$. In addition, conservation of the momentum parallel to the surface in the (e,2e) reaction, allows probing the momentum distribution of the surface states in a wide momentum range.

Low-energy two-electron spectroscopy (e,2e) in reflection geometry was applied previously to study the mechanism of correlated electron pairs excitation from the Shockley surface state of Cu(111) [6]. That study demonstrated the existence of an exchange-correlation hole in such a system, as well as diffraction of correlated electron pairs excited from a surface state.

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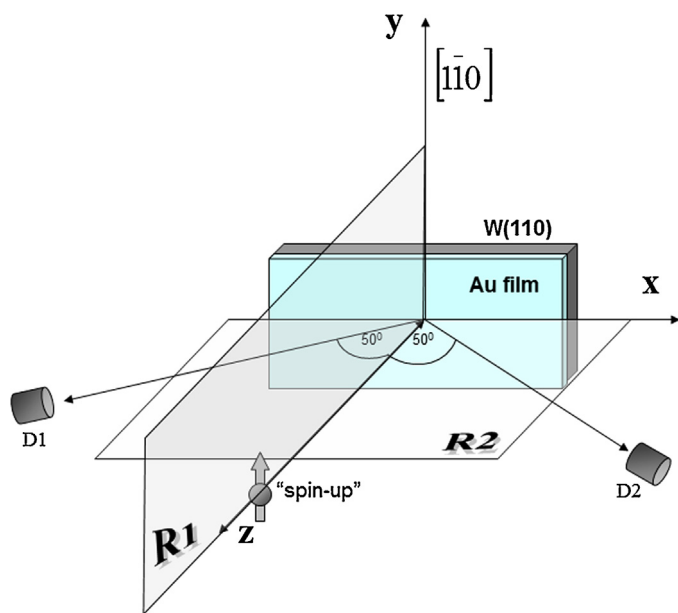E-mail address: samar@physics.uwa.edu.au (S. Samarin).

Fig. 1. Geometric arrangement of the experiment.

Fig. 2. Binding energy spectra of Au(111) film on W(110) for various primary energies. Zero point on x-scale corresponds to a position of the Fermi level.

In the present paper we compare the correlated pairs emission from the Shockley surface states and valence d-states of Cu(111) and Au(111) under low-energy spin-polarized electron impact.

2. Experimental details

All scattering experiments were performed in a vacuum with base pressure in the 10^{-11} Torr range. A few atomic layers of gold on a W(110) substrate form a good epitaxial layer with the (111) face parallel to the sample surface. The substrate was cleaned in vacuum prior to the gold deposition using a standard procedure [9,10] including oxygen treatment at 10^{-7} Torr oxygen pressure and 1400 K sample temperature followed by a few high-temperature flashes up to 2300 K. The cleanliness of the surface was monitored by Auger electron spectroscopy and Low energy electron diffraction as well as by two-electron coincidence spectroscopy, which is very sensitive to the presence of oxygen [11,12]. The gold film was deposited onto the W(110) substrate at room temperature by evaporation from a small piece of gold wire melted on a V-shaped tungsten filament heated resistively. The quality of the film was demonstrated by observing quantum well states in such a layer of gold using photoelectron spectroscopy [13] and layer-by-layer growth was confirmed by MEED oscillations [14]. We estimated the thickness of the gold layer via Auger peak intensity as a function of deposition time as well as by comparison of LEED patterns with a previous LEED study of the epitaxial layer of gold on (110) tungsten [15]. We found the gold coverage to be of 3–4 monolayers (ML).

The Cu(111) surface of a single crystal of Cu was cleaned in the vacuum prior to measurements using repetitive sputtering by 1 keV Ar ions and annealing at 500–700 K. The cleanliness and crystallinity of the surface were monitored using LEED and Auger electron spectroscopy.

We used two experimental set-ups, described elsewhere [16,17], for measuring the momentum distribution of correlated electron pairs. Our setup uses a spin-polarized incident beam and second has an extremely large acceptance angle that allows observation of the pair diffraction at a low primary electron energy [6]. In both experiments the time-of-flight (TOF) electron energy measurement was used [18]. A schematic of the experiment is shown in Fig. 1 to indicate a polarized/unpolarized incident electron beam impinges onto a sample surface at normal incidence and two
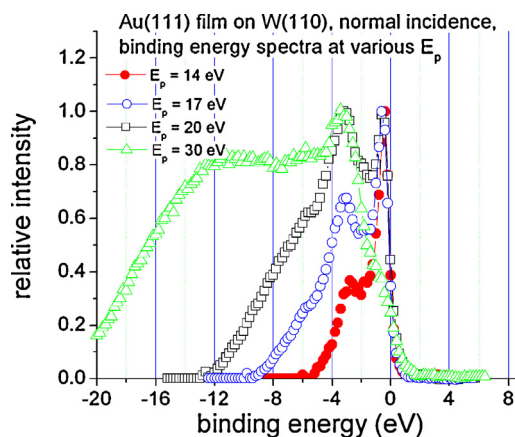
outgoing electrons are detected in a backwards directions at ±50° with respect to the surface normal within the 29° acceptance angle of each of the detectors. The energy resolution of the TOF electron energy analysis depends on the measured energy [19], and in the energy range of (5–15 eV) is characteristically 0.5 eV.

3. Results and discussion

It was demonstrated [19] that a substantial number of time-correlated electron pairs is generated in a single-step electron–electron collision. This implies that, in a single-particle band approximation, energy and momentum conservation allow a valence electron involved in the collision to be located in the energy and momentum space of the valence band:

$$E_b = E_1 + E_2 - E_p \qquad (1)$$

$$K_{b||} = K_{1||} + K_{2||} - K_{p||}, \qquad (2)$$

where E and K denote electron energy and electron wave vector and b, 1, 2, p correspond to bound electron, first and second emitted electrons and primary electron, respectively. The subscript $||$ denotes a parallel-to-the-surface component of the wave vectors. Hence we can construct a distribution of the number of correlated electron pairs involving a valence electron with a particular binding energy as a function of the binding energy. As shown below the probability of the (e,2e) reaction depends on the primary electron energy. On the other hand, excitation of electrons is possible only from the states with nonzero density. Therefore, the (e,2e) spectrum can be used for probing whether states are occupied or empty; in other words what is the extension of valence states in the energy-momentum space of a sample.

3.1. Excitation of electron pairs from Au surface

Using the above approach the binding energy spectra of Au(111) and Cu(111) were constructed for various primary energies. The zero on the energy scale denotes the position of the Fermi level. The set of curves for Au(111) is shown in Fig. 2. A sharp maximum just below the Fermi level, which is very prominent for low primary energy, corresponds to the surface state. The arguments in favor of this suggestion are the following. First, in the bulk density of states of gold there is a flat and low density of states in the energy range just below the Fermi level down to about 1.5 eV below the Fermi level. Hence, the maximum just below the Fermi level cannot be formed by the electron excitation from the bulk states. Second, its energy position (about 0.5 eV below the Fermi level) corresponds to the calculated and measured (by photo-electron spectroscopy)
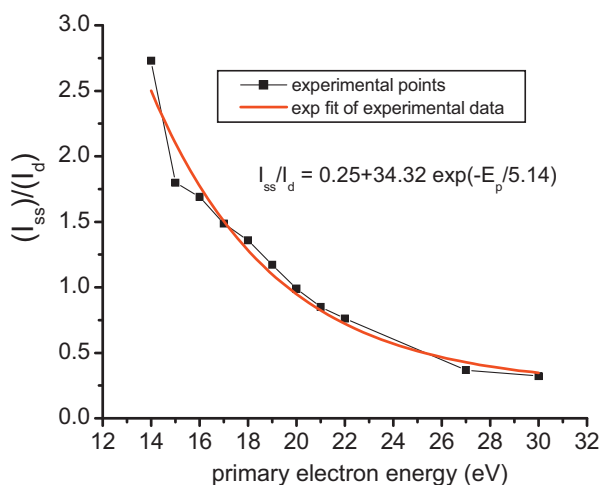
Fig. 3. Energy dependence of the relative contribution of surface and bulk states to the binding energy spectrum of Au(111) film on W(110).

Fig. 4. Binding energy spectra of Cu(111) (solid circles) and Cu(001) (open circles) surfaces.

position of Shockley surface states. The second maximum in the binding energy spectrum at about (2–3) eV below the Fermi level corresponds to the emission of pairs from the valence d-derived states.

Fig. 2 shows explicitly that the shape of the binding energy spectrum is changing with the primary electron energy. In particular, the relative intensity of the peak just below the Fermi energy decreases while the primary energy increases. It shows that the relative probability of excitation of surface and bulk states depends on the primary electron energy. The (e,2e) spectra of Au(111) were measured with increments of 1 eV in the incident electron energy. The relative contribution of surface states into the (e,2e) binding energy spectrum was analyzed by plotting the ratio of the surface – to d-derived bulk valence states intensity as a function of primary energy as shown in Fig. 3.

An exponential fit to this data gives the following relationship:

$$\frac{I_{SS}}{I_d} = 0.25 + 34.32 \cdot \exp\frac{-E_p}{5.14}. \tag{3}$$

It is seen that the relative contribution of surface states in the binding energy spectrum decreases with the increase of the primary electron energy and the ratio span an order of magnitude change in the primary energy range from 14 to 30 eV. The increase of the contribution of correlated pairs from surface states relative to the bulk contribution at low primary energies might be due to a few reasons. First, suppression of the contributions of d-states to the measured (e,2e) spectrum is expected when the primary electron energy drops below 15 eV because those d-states are located about 3.5 eV below the Fermi level and an electron from these states must gain energy of at least 8.5 eV (binding energy + the work function) to be excited above the vacuum level. If two electrons are excited by 15 eV primary energy and escape the surface, they will share an excess energy of 15−8.5 = 6.5 eV. If they share energy equally they can be detected, in principle, if both of them are within the acceptance angles of the detectors. If either of them is refracted out of the acceptance angle of a detector, the pair cannot be detected. If the pair of electrons shares energy unequally and one of them has energy below 2.5 eV it will not be detected because our time-of-flight analyzer is set to detect electrons only with energy greater than 2.5 eV. In summary, d-states with binding energy about −3.5 eV give small contributions to the (e,2e) spectrum at low primary electron energies. The second reason arises from the diffraction of correlated electron pares. Indeed, in our geometry and energy range we observe the 00 diffraction pattern of electron pairs [6]. Electrons of pairs excited from the surface
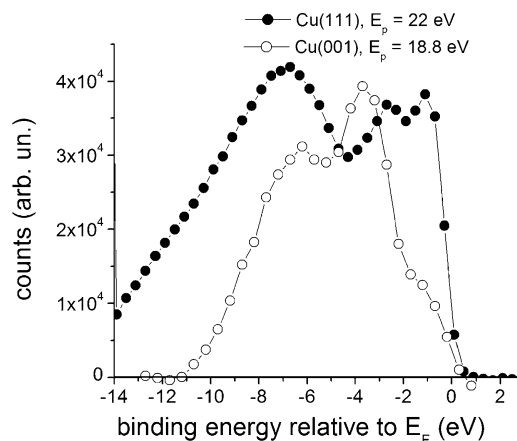
state have almost equal energies and their total momentum points along the normal to the surface. The intensity of this 00 pattern is energy dependent. One can assume that, in the studied energy range, the contribution (intensity) of the 00 patterns corresponding to the excitation of pairs from surface states and d-states changes in different ways with the change of primary energy. It will result in a substantial change of the relative intensity of the peaks in the binding energy spectrum.

The increase of the contribution of electron pairs in the binding energy spectrum at energies below −8 eV with increase of primary energy is most likely due to the contribution of multi-step electron scattering that generates "true secondary" electrons. It means that the incident electron undergoes an inelastic scattering with a valence electron of the target and before these two electrons escape from the surface they can participate in other one or few electron–electron collisions generating low-energy "true secondary" electrons.

3.2. Excitation of electron pairs from a Cu surface

Surface states on a Cu(111) surface were studied by the (e,2e) technique using different experimental set-ups [16,17]. We observed a pronounced maximum in the binding energy spectrum about 0.5 eV below the Fermi level (see Fig. 4) that was identified as a contribution from the surface state. In the binding energy spectrum of Cu(111) three maxima are visible: at −0.5 eV, at −2.7 eV, and at about −7 eV. Similar three maxima were observed in [6,7].

The relative intensity of the maximum that corresponds to the excitation of electron pairs from the surface states ($E_b = -0.5$ eV) depends on the primary electron energy and this dependence is similar to the case of Au(111) where its relative intensity decreases with increase of the primary electron energy.

Comparison of the binding energy spectra measured on Cu(111) and Cu(100) links the origin of maximum at the binding energy −0.5 eV to a surface state. Indeed, there is surface state on Cu(111), whereas there is no surface state on Cu(100). Fig. 4 shows a comparison of the binding energy spectra for two faces Cu(111) and Cu(001) of Cu. It is obvious from this comparison that on the (001) surface there is no surface state and in the energy range from the Fermi level down to −2 eV the contribution from low density sp-states is much lower than from the d-states located below −2 eV. In contrast, the Cu(111) surface demonstrates a substantial contribution of a surface state just below the Fermi level in the binding energy spectrum.

3.3. Energy sharing and momentum distribution of correlated electron pairs from Au and Cu

Correlated electron pairs emitted from surface states and from valence d-states have different energy sharing distributions. In other words, electrons share energy differently depending on the state where the bound electron is excited from and so reflect the dynamics of the scattering and momentum distribution of the bound electron. Fig. 5 shows the distributions of correlated electron pairs as a function of the K_x component of the bound electron wave vector at a fixed binding energy. Although these distributions do not represent the momentum distribution of the bound electrons, they do characterize the momentum *location* of the bound electrons, i.e. electrons can be excited only from occupied states.

These curves show a distinct difference between distributions of a pair from surface states and from valence d-states. The distributions corresponding to the generation of pairs from surface states

are about two times narrower than the distributions of pairs generated from flat d-bands. This indicates that the surface states are confined in a narrower momentum space than d-states. The same conclusion was made for Cu(111) in [6].

3.4. Spin effects in the electron pair emission: surface states and valence d-states

Using spin-polarized incident electrons we were able to study the spin effects in the generation of electron pairs [20–22]. The spin effects were demonstrated by constructing the asymmetry of (e,2e) spectra defined as:

$$A = \frac{I^+ - I^-}{I^+ + I^-},$$

where I^+ and I^- denote spectra recorded with spin polarization vector of the incident beam pointing "up" or "down", respectively.
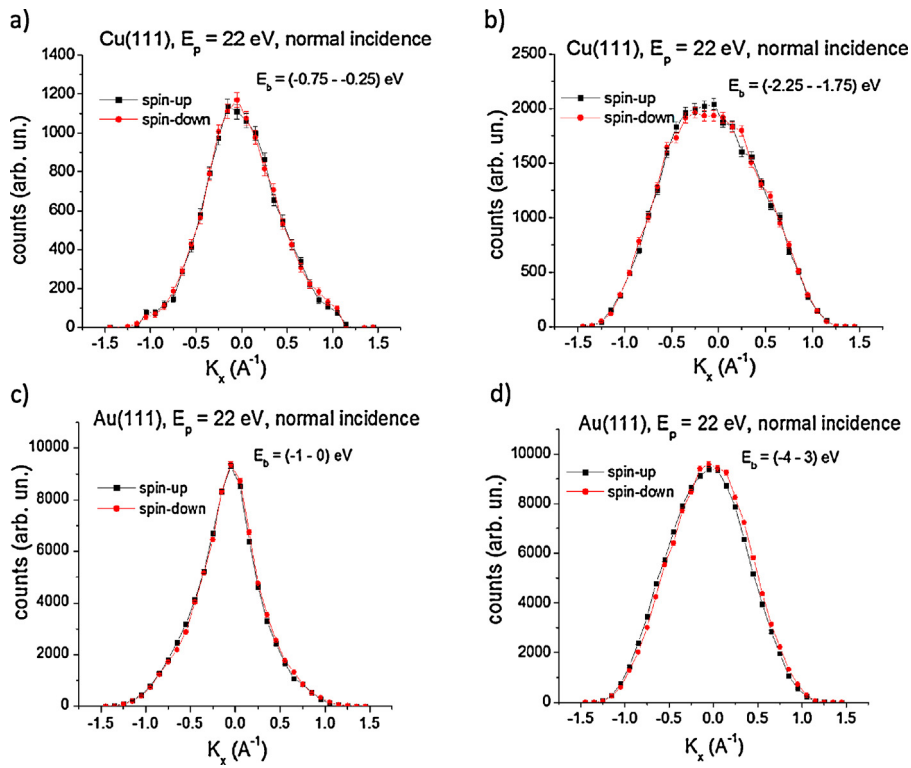

Fig. 5. K_x-distributions of correlated electron pairs excited from Cu(111) (a) and (b) and Au(111) (c) and (d). Distributions (a) and (c) correspond to the excitation from surface states whereas distributions (b) and (d) correspond to the excitation from valence d-states. K_x is the x-component of the valence electron wave vector (see Fig. 1).
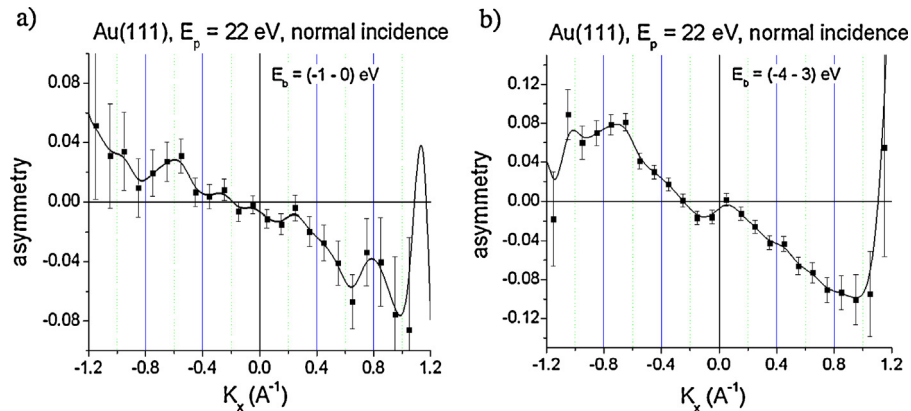

Fig. 6. Asymmetry of K_x-distributions of pairs excited from surface states (a) and from d-states (b).

The K_x – distributions presented in Fig. 5 were recorded for spin-up and spin-down polarization of the incident beam. Hence one can construct asymmetry spectra of K_x – distributions, which are presented in Fig. 6.

In Fig. 6 only asymmetries of the (e,2e) spectra from Au(111) are presented. Similar analyses of spectra measured from Cu(111) shows much smaller asymmetries which falls within the measured statistical uncertainties.

It is evident from Fig. 6 that for both the surface states and for the valence d-states, the origin of the asymmetry is a spin-orbit interaction. Indeed, the asymmetry spectra show "left–right" symmetry, i.e. if we exchange left and right detectors, the sign of the asymmetry changes. This is consistent with the symmetry property of the experiment, i.e. the geometrical arrangement including the crystal structure of the sample, which is mirror symmetric with respect to the plane normal to the sample surface and to the scattering plane. It means the mirror reflection in the symmetry plane does not change anything but the spin of the incident electron, which is an axial vector, which therefore changes sign during mirror reflection. By consequence, if there is some asymmetry (for a mirror symmetric non-magnetic sample) it will possess such "left–right" symmetry.

Regarding the magnitude, the asymmetry corresponding to d-states is about twice the asymmetry corresponding to the surface states. It is most likely due to the orbital properties of these states: the surface Shockley states are of the sp character, whereas d-states originate from an atomic d-state with larger orbital momentum. In each of the asymmetry spectra the maximum value of the asymmetry is reached far from the center of the Brillouin zone.

4. Conclusions

We have compared the excitation of correlated electron pairs from surface states and from valence d-states of Au(111) and Cu(111). It is possible to identify surface states and d-states in the (e,2e) spectrum due to the energy and momentum conservation in the (e,2e) reaction and to the fact that a substantial number of correlated electron pairs is excited in a single-step scattering event. The distribution of pairs excited from surface states is much narrower on the K_x scale than the distribution of pairs excited from d-states, i.e. a narrower momentum distribution. Spectra measured from Au(111) demonstrate spin asymmetry in both contributions, from the surface states and from d-states, whereas in the spectra of Cu(111) a spin effect is negligible. It is obviously related to the large Z of gold. The size of the spin effect on surface states is smaller than on d-states and is related to the orbital symmetry of the states.

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