Emission of correlated electron pairs from clean and oxygen covered W(110) upon spin-polarized electron impact

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Abstract. Low-energy spin-polarized two-electron spectroscopy in reflection geometry has been applied for studying spin-dependent electron scattering dynamics and electronic structure of clean and oxygen covered W(110) surface. Strong spin-orbit asymmetry was observed in the energy sharing spectra of clean tungsten for binding energy close to the Fermi level. This asymmetry was suppressed by oxygen adsorption although the bonding $2p$ - state is located 6 eV below the Fermi level. It indicates an extended influence of the oxygen adsorption on the electronic structure of the substrate and the surface barrier.

1. Introduction
The tungsten surface and oxygen adsorption on W(110) are the most studied model systems of surface science. They have been studied using most of the surface science techniques. The geometrical and electronic structures have been characterized by low-energy electron diffraction (LEED) [1,2,3], Electron Energy Loss Spectroscopy [4,5], core-level photoelectron spectroscopy[6 - 9], photoelectron diffraction and holography [10] etc. Order – disorder transition as well as adatom - adatom interactions in an oxygen layer on W(110) have been theoretically analyzed [11,12]. In essence it was found that the W(110) surface can be prepared clean and unreconstructed whereas the ordered oxygen layer exhibits several structural phases depending on the exposure and temperature treatment [13].

Much less is known regarding details of the modification of the electronic structure of W(110) upon oxygen adsorption. Core-level shift induced by oxygen adsorption and indicating of a strong oxygen-tungsten interaction was observed using photoelectron spectroscopy [7,8,9]. Even less
information is available on the modification of the valence states of W(110) upon oxygen adsorption [8,9,14]. The main modification due to the oxygen adsorption in the photoelectron spectrum from the valence band of the W(110) is the appearance of a broad maximum approximately 6 eV below the Fermi level. It was attributed to the emission from O(2p) levels. Some variation of intensity in the energy range from O(2p) band up to the Fermi level was also reported [8,9].

The objectives of this contribution are to look at the influence of ordered oxygen adsorption on the spin-dependent emission of correlated electron pairs from W(110) and get some information on the modification of the spin-dependent surface electronic structure of tungsten upon oxygen adsorption.

2. Experimental details
The experiments were performed in UHV conditions with the base pressure in the 10^{-11} Torr range. The residual magnetic field within the vacuum chamber was reduced to less than 5 mG using a combination of static and dynamic Helmholtz coils. The W(110) crystal was cleaned using standard procedure including oxygen treatment at 1400 °C followed by high temperature flashes. The cleanliness of the sample was monitored by Auger Electron Spectroscopy and Low Energy Electron Diffraction. An oxygen ordered layer was formed at 1300 °C sample temperature and exposure to the oxygen at pressure 2x10^{-8} Torr for 4 minutes. Figure 1 presents LEED patterns for clean and oxygen covered W(110) surfaces. One can see that oxygen atoms form p(2x2) structure (with probable presence of the p(2x1) domains [13]).

![Figure 1](image.png)

Figure 1. LEED picture for clean and oxygen covered W(110), E_p = 100.8 eV

We applied spin-polarized two-electron spectroscopy in reflection geometry (referred to here as (e,2e) spectroscopy) [15] for studying electron scattering dynamics and electronic properties of the surface. The geometrical arrangement of the experiment is shown in figure 2. The incident electron beam was spin-polarized with (60-70) % degree of polarization (measured in separate experiment). The spin-polarized electron source is based on photoemission from a strained GaAs photocathode [16]. The polarization of photoelectrons emitted from the photocathode is parallel or anti-parallel to the momentum of the electrons depending on the helicity of the incident light, which was computer controlled. After emission from the GaAs crystal electrons were deflected by a hemi-spherical deflector by 90° making a transversally polarized beam from a longitudinally polarized beam. During measurements, the polarization of the beam was altered every 5 seconds to avoid the influence of the incident electron current drift or the sample surface modification (contamination) on the spin-asymmetry.
We combined a coincidence technique [17] with a time-of-flight electron energy measurement [18] to measure energy- and angular distribution of correlated electron pairs from the sample. The incident electron beam was pulsed to create a reference point on the time scale. The pulse width was about 1 ns and the repetition rate 4.5 MHz. Each pulse contained less that one electron on average and this increased the true/accidental coincidences ratio. The position-sensitive detectors based on micro-channel plates allowed a correction of the flight time of electrons from the sample to the different parts of the detectors. Position sensitivity also provided the angular electron distribution within the acceptance angles of the detectors (± 16°).

A correlated electron pair recorded by the acquisition system is represented by six numbers: \( X_1, Y_1, T_1, X_2, Y_2 \) and \( T_2 \), where \( X_i, Y_i \) are electrons detection coordinates on the first and second detector, \( T_i \) are corresponding electron flight times. Such a six-dimensional distribution of correlated pairs was recorded for spin-up and spin-down polarization of the incident beam. We define spin-up polarization as depicted in Fig. 2. The six-dimensional data array can be projected on various two-and single-dimensional distributions. For example, a two-dimensional energy distribution \( I(E_1, E_2) \) can be constructed if we integrate events over the acceptance angles of the detectors and convert time-of-flight to the electron energy. Each point on this distribution corresponds to a correlated electron pair with energies \( E_1 \) and \( E_2 \). The spin effect can be extracted by comparing distributions recorded for spin-up and spin-down incident electron polarization and presented as difference between these spectra \( (I_{\text{up}} - I_{\text{down}}) \) or normalized asymmetry \( A = (I_{\text{up}} - I_{\text{down}})/(I_{\text{up}} + I_{\text{down}}) \).

3. Results and discussion

The energy conservation law in the \((e,2e)\) reaction allows us to extract the binding energy of the valence electron, \( E_b \), from measured energies of two correlated electrons: \( E_b = (E_1 + E_2) - E_o \), where \( E_o \) is the incident electron energy, \( E_1 \) and \( E_2 \) are the two detected electrons energy. It has previously been shown [19] that single step scattering is the primary process in the total energy region 3 - 4 eV below the Fermi edge \( (E_o = 0) \). Below this energy slice a multi-step scattering dominates and the momentum-energy-conservation equations are no longer applicable. Within a total energy band \( \Delta E_{\text{tot}} \) where the single-step processes are dominant the energy sharing distribution would show how two correlated electrons share the total energy of the pair.

In the case of a single crystal target, the electron momentum parallel to the surface is conserved and we can trace the bound electron momentum: \( \mathbf{k}_{\text{obj}} = (\mathbf{k}_{1||} + \mathbf{k}_{2||}) - \mathbf{k}_{\text{obj}} \), where \( \mathbf{k}_o \) is the incident electron momentum, \( \mathbf{k}_1 \) and \( \mathbf{k}_2 \) are the two detected electron momenta. We note here that measurements of the distributions collected under these conditions do not directly represent the density of states as a function of the binding energy or the momentum density distribution. This is because in the low-
energy (e,2e) reaction the cross-section depends on the Coulomb matrix elements and on the reflectivities of the primary and ejected electrons at the surface [20]. Also the dynamics of scattering is energy- and angular-dependent. On the other hand to obtain a significant scattering cross section an appreciable density of states in momentum space is necessary [20]. In other words, if upon oxygen adsorption, a maximum appears in the binding energy spectrum it would indicate, most likely, an increase of the density of states at a corresponding binding energy.

![Figure 3](image.png)

**Figure 3.** Binding energy spectra (a and c) and energy sharing distributions (b and d) for clean (a and b) and oxygen covered (c and d) W(110), $E_p = 27$ eV, normal incidence.

Figures 3 a and c present binding energy spectra $I_b(E_b)$ of clean and oxygen covered W(110) surfaces recorded at normal incidence with 27 eV primary energy. In both cases spin-up and spin-down spectra are identical; therefore they are represented by single lines. The main difference between two spectra is a broad maximum in the spectrum of the oxygen covered tungsten (figure 3c) at the binding energy of 6 eV. It indicates most likely an increase of the density of states at this energy because each value of the binding energy spectrum results from integration of the cross section over a range of both electrons energies along the total energy band. Therefore dynamical features are largely smeared out. This maximum is due to the 2p- orbital of oxygen that establishes the bonding between oxygen atom and the W(110) surface and consequently increases the density of state at the surface in this energy range. A similar feature in the binding energy spectrum of oxidized tungsten surface was observed in the earlier study of oxygen adsorption on W (001) by (e,2e) spectroscopy [21]. Photoelectron spectroscopy also reveals this maximum in the W(110)/O system [22].

Beside the O(2p)–derived orbital centered at 6 eV binding energy the photoelectron spectroscopy showed as well a drastic changes in the W(5d) region induced by the oxygen adsorption [22]. The new features in the photoemission spectrum in this energy range (close to the Fermi level) clearly show a two-dimensional character. No reconstruction in the top most layer of tungsten was detected. Therefore this extra structure in the spectrum was interpreted as an emission from W(5d)-O(2p) hybridized orbitals energetically split off the bulk bands due to the action of a modified surface potential.
In the binding energy spectrum in figure 3c these new features due to the oxygen adsorption in the energy range 3 eV below the Fermi level are not visible. Only the slope of the onset in the clean W spectrum is larger than in the oxidized W spectrum. The energy resolution of the time-of-flight technique in our experiment depends on the measured energy and is estimated to be about 0.5 eV at an energy of 20 eV. Therefore the fine structure in the binding energy spectrum of the oxidized W(110) below the Fermi level is not resolved. We analyze instead the energy sharing of two correlated electrons within energy slice of 2 eV below the Fermi level. Figures 3b and 3d show the energy sharing distributions for clean and oxygen covered W(110) surfaces for two spin polarizations of the incident beam. One can see a dramatic change in the shape of the sharing distribution when the W(110) surface is covered by the oxygen layer. The difference between spin-up and spin-down spectra is substantially reduced for the oxidized surface. This effect is clearly seen in figure 4 where normalized asymmetries for clean and oxygen covered surfaces are presented. In the case of the clean tungsten surface the asymmetry reaches 15 % and – 15 % at (E₁ – E₂) = – 7.5 eV and (E₁ – E₂) = + 7.5 eV, respectively. It shows typical “left-right” spin-orbit symmetry. When oxygen is adsorbed the asymmetry drops down by a factor of three. We note that these sharing distributions are taken in the binding energy range of 2 eV below the Fermi level that is far from the O(2p) band located at 6 eV binding energy. This means the correlated electron pairs are excited predominantly from the W(5d) band. The decrease of asymmetry in the sharing distribution therefore is due to the modification of these states upon oxygen adsorption. Another reason for that might be the change of the surface barrier at the oxidized surface. A qualitative discussion of this effect follows.

The intensity asymmetry in the (e,2e) spectra excited by spin-polarized electrons from nonmagnetic surfaces was analyzed theoretically in application to the electron scattering from W(001). It was pointed out [20] that the origin of this asymmetry is the spin-orbit coupling in at least one of the four relevant electron states: incident electron state, two outgoing electron states and a valence electron state. The contribution of each of them to the observed spin-asymmetry can be revealed by a comparison of the measured spectra at different geometries with the appropriate calculations. As evidenced from additional calculations when the spin-orbit interaction was “switched off” in each of these states the major contribution to the measured asymmetry is related to the valence states [20]. In addition, the shape of the surface barrier also plays an important role in the escape process of the two outgoing electrons. They undergo refraction and spin-orbit scattering while traversing the barrier. At this stage a spin-filter effect may occur as was observed in case of the photoemission from nonmagnetic material [23] and in case of the secondary emission excited by spin-polarized electrons from W(110) [24]. Indeed, the scattered and ejected electrons might have opposite spin projections on the quantization axis (polarization of the incident beam) due to a dominant singlet scattering in this energy range and therefore experience different potentials while travelling through the surface barrier. It results in the spin-filter effect. The oxygen adsorption modifying the surface barrier influences (reduces) the spin-filter effect.
A strong influence of the oxygen adsorption on the emission of correlated electron pairs from W(110) can be seen in Ks – distributions (figure 5). In this experiment the sample was rotated around the normal to the surface such that [110] direction was in the scattering plane containing the sample normal and two detectors. It was shown that for this azimuthal orientation of the sample the spin-orbit asymmetry in the sharing distributions (see Fig.3) is weaker than for the first one [25], but when the sample was tilted towards detector 1 or detector 2 the strong asymmetry shows up in the binding energy spectra as well as in the sharing distributions [15]. We took advantage of the position sensitive detection and extracted from the measured data the Ks – distributions, that are the number of correlated pairs as a function of the bound electron parallel-to-the surface momentum. Figures 5 represent such distributions for clean (a and c) and oxygen covered (b and d) W(110) surfaces. The geometries of the experiment are denoted in the inserts of panels a) and c). For the clean surface the Ks – distributions exhibit a strong maximum located at Ks = 0.5 Å⁻¹ and a shoulder at Ks = 1.7 Å⁻¹ for geometry a) and maximum at Ks = - 0.5 Å⁻¹ and a shoulder at Ks = - 1.7 Å⁻¹ for geometry c). At the same Ks - locations there are strong differences between spectra recorded with spin-up and spin-down incident electrons, but for geometry a) it is positive and for geometry c) it is negative. The Iup(Ks) and Idown(Ks) spectra and difference spectrum D = (Iup - Idown) show an interesting symmetry property. Let us denote by Π and Γ spectra recorded at geometry (a) and geometry (c), respectively. Reflection at the (y,z)-plane reverses the spin of the primary electron and transforms the geometry (a) into geometry (c) with interchange of the outgoing electrons. It implies that Πup(Ks) = Γdown(-Ks) and, by consequence, D(Ks) = - D(-Ks). Comparing the spectra in panels (a) and (c) one can see that difference spectra exhibit such symmetry.

Adsorption of the oxygen on the surface of the sample changes dramatically the shape of Ks – distributions for both geometries. Now a strong maximum is located at Ks = 1.5 Å⁻¹ and a shoulder at Ks = 0.5 Å⁻¹ for geometry a) and a maximum at Ks = - 1.5 Å⁻¹ and a shoulder at Ks = - 0.5 Å⁻¹ for geometry c).

**Figure 5.** Influence of the oxygen adsorption on the Ks-distributions of clean and oxygen covered surface of W(110). Ep = 25 eV, sample was tilted to detector 1 (a,b) and to detector 2 (c,d) by 12°. The distributions are taken within 2 eV slice of binding energy just below the Fermi level.
This modification of the shapes of $K_x$ – distributions upon oxygen adsorption cannot be directly related to the change of the momentum density distribution as was pointed out above. On the other hand, $K_x$ – distributions measured on oxygen-covered W(100) surface at very different geometry [21] also show maxima at $K_x = 0.5 \, \text{Å}^{-1}$ and $K_x = 1.5 \, \text{Å}^{-1}$ for binding energy around 6 eV. The corresponding calculated distribution reproduced reasonably well experimental curve [21]. It is interesting to note that momentum density distributions of the 2p state of free atomic oxygen show a broad maximum centred at $K_b = 1.5 \, \text{Å}^{-1}$ [21]. Although our $K_x$ – distributions are constructed for binding energy above O(2p) band they show oxygen-like behaviour in case of oxygen-covered W(110) surface. This might indicate the hybridization of O(2p) and W(5d) states and reconstruction of the momentum density distribution.

Concerning the spin-dependent asymmetry of the $K_x$ – distributions, the oxygen adsorption almost completely washes out the spin-dependence (figures 5 b and d). The reason for that is the modification of the valence states of the tungsten as well as the surface potential barrier.

4. Conclusions
Energy- and momentum-distributions of correlated electron pairs excited by low-energy spin-polarized electrons from clean and oxygen-covered W(110) surface were analyzed. A broad maximum in the binding energy spectrum of the oxidized surface at $E_b = 6 \, \text{eV}$ is attributed to the O(2p) band and is consistent with the results photoelectron spectroscopy. A strong spin-orbit asymmetry observed in the (e,2e) spectra of clean W(110) is substantially suppressed by oxygen adsorption. It suggests that the modification of the surface electronic structure of W(110) under oxygen adsorption occurs also beyond the O(2p) band up to the Fermi level.

5. Acknowledgments
This research was supported by the Australian Research Council and the University of Western Australia. We thank S. Key, G. Light (UWA) for their technical support. One of the authors (O.M.A.) is grateful to the RFBR (№ 06-02-17174-a) for financial support.

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