

Low Energy Photoelectron Diffraction at High Angular Resolution as a Surface Structure Probe

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The EDAC multiple scattering computer package has been used to simulate X-ray photoelectron diffraction experiments of Cu(100) surfaces at kinetic energies of 303.5 eV and below. At 1° angular resolution EDAC produces visually distinct patterns for bulk truncated Cu(100) and buckled Cu(100) surfaces with and without an Mn overlayer. Changes to Cu(100) surface relaxation parameters have discernable effects at kinetic energies of ~100eV.

1. Introduction

X-ray photoelectron diffraction (XPD) at energies above ~300 eV is already well established as a way of determining surface, near-surface and interfacial structural information [1,2]. Much structural information in diffraction patterns at energies above ~300 eV is identified from forward focusing and Kikuchi-like effects [3]. Furthermore, XPD analysis can be tuned to specific core levels and elements, allowing the discrimination of the positions of adsorbates and the atomic composition of alloys [4,5]. Using synchrotron sources, lower photon energies can be obtained, and below ~300eV forward focusing and Kikuchi-like bands are far less apparent [6].

This work is prompted by our interest in the interfaces of antiferromagnetic or ferromagnetic material with spin glasses beginning with Cu₃Mn. As part of our study it was decided to compare low energy XPD simulations of bulk truncated Cu(100) with other Cu(100) surfaces. The XPD experiments were simulated with the Electron Diffraction of Atomic Clusters (EDAC) [7] software, a multiple scattering simulation package. Multiple scattering algorithms are required to accurately simulate experimental interference patterns [8].

We have shown how EDAC can specifically be used to predict low energy XPD which is of particular interest. The corresponding sensitivity of low energy XPD is due in part to lower intensity XPD patterns that exhibit less forward focusing and a greater proportion of pattern intensity coming from backscattering. Comparison can be made between intensities in XPD patterns and those of I-V curves from Low Energy Electron Diffraction (LEED). However XPD patterns, being over a full hemisphere carry a plethora of information in comparison to LEED, where scans are restricted to directed beams. Low energy XPD could be used to discriminate small differences in structural parameters as are found in the modeling of surface relaxation and buckling.

2. Our work

In previous work [9] experimental patterns for a Cu(111) surface obtained with a toroidal analyser [10] at a resolution of 0.5° and kinetic energy of ~523 eV were reproduced with remarkable similarity by XPD patterns obtained by EDAC. The present work shows predictions of XPD patterns for Cu(100) surfaces at photoelectron kinetic energies of 73.5 and 103.5 eV and



an angular resolution of 1°. (Similar scans at 203.5 and 303.5 eV were also simulated but are not shown.) The surfaces compared were a) bulk truncated Cu(100), b) two different Cu(100) relaxed surfaces [11,12], c) a buckled Cu(100) surface with an Mn overlayer [13] and d) the same structure as in (c) with the Mn replaced by Cu.

To examine simulation data quantitatively, a modified R-factor formulation is used to compare the bulk truncated Cu(100) with the relaxed, buckled and Mn incorporated surfaces. This is found by first calculating a χ value that is the (normalized) difference between the intensity at a point $I(\vartheta, \phi)$ and the averaged azimuthal intensity over the corresponding polar angle $I(\vartheta)$, that is the $\chi(\vartheta, \phi) = [I(\vartheta, \phi) - I_0(\vartheta)]/I_0(\vartheta)$ [14]. This is then summed over the discrete angular positions:

$$R = \frac{\sum_i (\chi_{ci} - \chi_{ei})^2}{\sum_i (\chi_{ci}^2 + \chi_{ei}^2)} \quad (1)$$

where χ_{ci} are the simulated and χ_{ei} the experimental χ values [15]. For comparison purposes in the present work the bulk truncated Cu(100) simulation were taken as the “experimental” χ values.

3. Simulation results

Fig. 1 shows stereographic projection of diffraction patterns for different Cu(100) surfaces. In Fig. 1 (a) labels A, B and C mark respectively the [111], [011] and [001] principal axes. In Fig. 1 (c) D marks Kikuchi-like bands that make the central white cross E appear smaller. The parameters for the buckle in Figure 1 (c) and (d) comes from Wuttig et al [13].

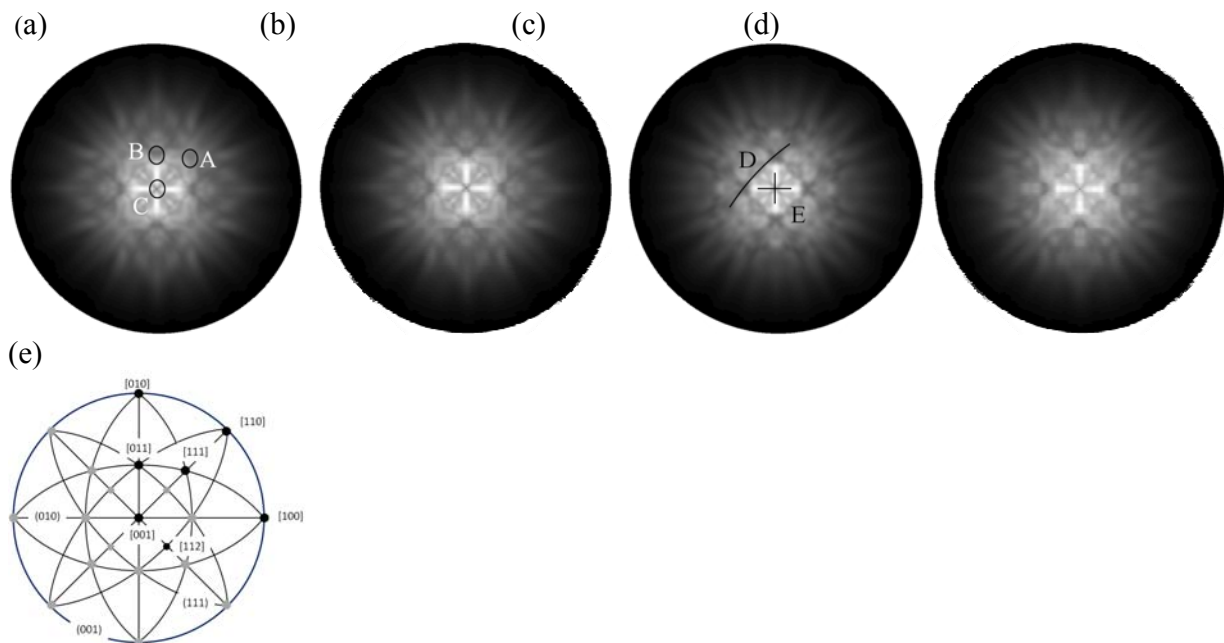


Fig. 1. Stereographic projection of diffraction patterns from (a) bulk truncated Cu(100) (b) Cu(100) with surface relaxation parameters from Davis and Noonan [11] -1.10% for first, +1.70% second, +1.0% third interlayer spacing (c) Cu(100) with an 0.5 ML Mn overlayer that is buckled and (d) Cu(100) with the same buckle as in (c) for electron kinetic energy of 73.5 eV and at a temperature of 300 K.



At 73.5 eV the simulated XPD pattern of bulk truncated Cu(100) in Fig. 1(a) is visually similar to the surface relaxed case in Fig 1(b). Intensity levels were also similar as shown by an R-factor between Fig. 1 (a) and (b) of 0.0041. The minima at an electron kinetic energy of 73.5 eV in the [001] direction (“C” in figure) can be compared with the [00] beam from LEED, where I-V curve exhibits an intensity minima at ~73 eV [16] for Cu(100).

The Cu/Mn surface with buckle (see Fig 1(c)) has an R-factor of 0.26 and shows extra features such as a pronounced band (D) and a smaller light cross in the centre (E). The Cu(100) surface with the Mn replaced by Cu shows only some discriminating features with a R-factor of 0.16, indicating intensity differences to bulk truncated Cu(100).

Similar observations can be made for these Cu(100) surfaces at an electron kinetic energy of 103.5eV (see Fig 2). The R-factors comparing Fig 2(a) bulk truncated Cu(100) with: 2(b) surface relaxed, 2(c) Mn buckled and Cu buckled are respectively 0.0015, 0.21 and 0.22 .

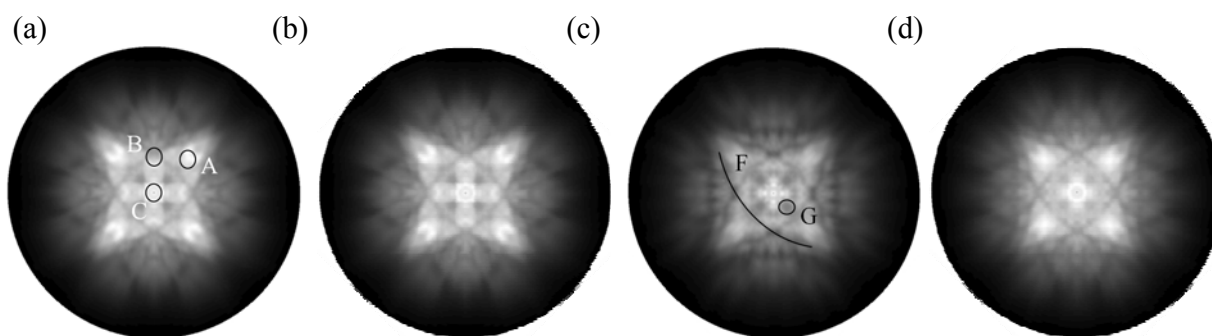


Figure 2. Simulated diffraction patterns with electron kinetic energy of 103.5 eV. Variations in structural parameters as in Fig. 1. Extra features in (c) include stronger Kikuchi patterns (F) and four intensity minima associated with [112] axes (G).

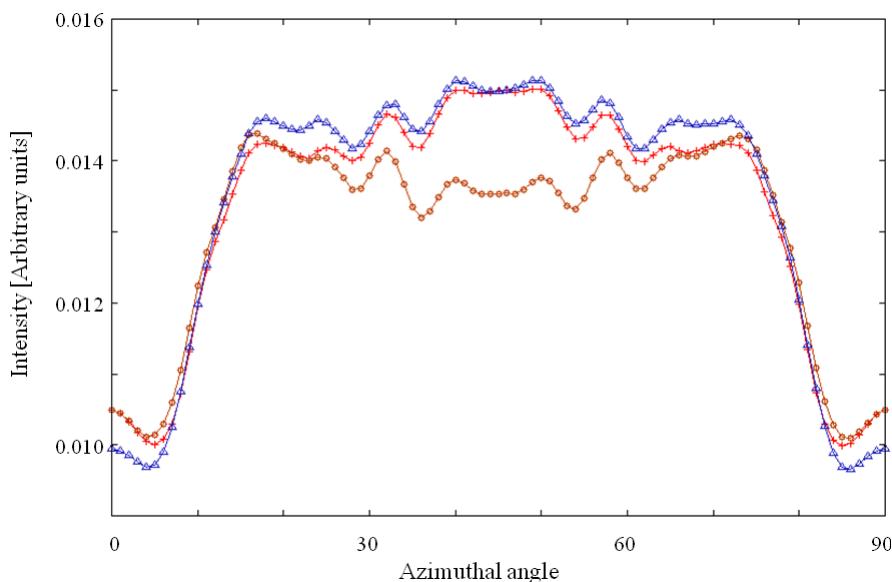


Figure 3. Comparison of Cu 3p-intensities for azimuthal scans at polar angle of 30° for Cu(100) at 300 K and electron kinetic energy of 103.5 eV. Surface parameters from (+) Davis and Noonan, (o) Fowler and Barth, (Δ) without surface relaxation.



Although not apparent from the simulated XPD patterns, Fig. 3 shows that up to 20% differences in intensity between bulk truncated and surface relaxed Cu(100) surfaces can be observed for specific azimuthal scans. In Fig. 3 results are shown for surfaces with relaxation parameters from (+) Davis and Noonan, Δd_{12} -1.10%, Δd_{23} +1.70%, Δd_{34} +1.0% [11], (o) Fowler and Barth, Δd_{12} -2.0%, Δd_{23} +1.0%, [12], (Δ) without surface relaxation. The intensity scale is linear. Note that at 0° and 90° the 3p-intensities for relaxed surfaces coalesce, whereas at 45° the intensity of the surface from Fowler and Barth exhibits marked difference.

4. Conclusion

Simulations of low energy and high resolution XPD patterns, using multiple scattering software (EDAC), indicate that at energies of 73.5 and 103.5 eV, XPD patterns can be used to visually discriminate the presence of Mn, with less visual effect seen at higher energies. Furthermore, they indicate that at a kinetic energy of 103.5 eV, XPD can identify small differences between relaxed surfaces. As it contains diffraction data over the full hemisphere, XPD at low energies and high resolution, used in conjunction with a simulation package such as EDAC and further R-factor analysis, can be used to probe small differences of structural parameters in crystalline materials.

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