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1992 J. Phys.: Condens. Matter 4 6587

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A UPS and XRD characterization of polycrystalline copper

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Received 6 April 1992, in final form 2 June 1992

Abstract. Previous ultraviolet photoelectron spectra (UPS) of polycrystalline Cu display a surprising variation in their d-band profiles. Here, samples from different sources were characterized using UPS and x-ray diffraction (XRD). The d-band profiles of the UP spectra (He I) of the two samples were found to differ substantially, with one also showing emission-angle dependence. XRD was used to confirm that this sample had a high degree of preferred crystallite orientation. This shows that the non-random distribution of the crystallographic orientations of the crystallites in polycrystalline samples easily accounts for the observed differences in their d-band structures. As a result of this work, a 'norm' for the d-band profile of random polycrystalline Cu is established

1. Introduction

While early photoemission studies of metals involved polycrystalline samples, work over the past decade has concentrated on well defined single-crystal surfaces (e.g. see [1] for a review of photoemission from single-crystal Cu). In this laboratory the particular emphasis has been on understanding the bonding between molecular adsorbates and the metal substrate. For this purpose copper has proved particularly useful, because of its narrow and individually resolved d-band components. Now that some coherent bonding picture is beginning to emerge, it seems apposite to return attention to 'real world' polycrystalline samples, in the anticipation that this time something more meaningful can be said about adsorbate-induced intensity changes of the substrate (in particular, within the Cu d-band region), and their relationship to chemisorption bonding. To this end it is important first to establish in detail the d-band profile of the clean surface, and for this purpose a sample of ultrapure metal (see below) was chosen. As will be seen, its d-band structure is, however, substantially different from that of the previously published UP spectrum [2] which is being used for reference. Subsequent examination of other published spectra [3–6] also revealed significant differences between their d bands (in both the intensity of the relative components and the band-width; see figure 1). Consequently, it is important not only to establish the true d-band shape, but also to account for these observed variations.

These differences in the polycrystalline Cu d-band region have indeed been previously noted, and tentatively attributed either to surface contamination [2] and/or different *in situ* cleaning procedures [7]. For example, the broad peak in figure 1(b) [4] around -6 eV BE was ascribed by McLachlan *et al* to be due either to chemisorbed

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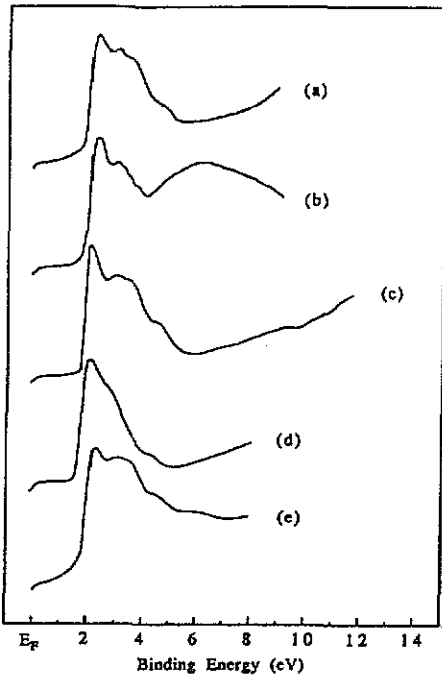


Figure 1. Summary of the previously published polycrystalline UPS Cu d-band spectra (He I, unless otherwise specified): (a) [6]; (b) [4]; (c) [2]; (d) evaporated polycrystalline Cu film [5]; (e) evaporated polycrystalline Cu film, and 21 eV photon used [3].

water or to the variation in scattering length between 20 eV and 40 eV electrons, since this peak is not present in He II spectra. We shall demonstrate, however, that apart from variations in surface contamination between various reported spectra, it is the non-random distribution of the crystallographic orientation of each grain in the sample ('partial crystallinity') that is the major determining factor in d-band spectral intensity of these variations. Through UPS and XRD analysis, a 'norm' for the d-band profile of random polycrystalline Cu is established.

2. Experimental details

Two polycrystalline Cu samples were examined and characterized. The first, hereafter referred to as S1, was cut from a small ingot of ultra-high-purity (99.9995%) copper obtained from OUTOKUMPO, Finland. The second (S2) was cut from a new conflat-flange gasket, and so can be assumed to represent typical oxygen-free high-conductivity copper. The two samples were prepared following the same procedure: polishing to a mirror finish using 6 μm diamond paste, followed by acid etching in a heated mixture of equal portions of nitric, orthophosphoric and glacial acetic acids. Grain size analysis using an optical microscope indicated the average grain dimension in these polycrystalline samples to be (S1) ≈ 0.08 mm and (S2) ≈ 0.05 mm, being significantly smaller than the size of the light beam (≈ 1 mm diameter).

The UV photoelectron spectrometer used is a custom-built UHV instrument with a fixed angle of 90° between the incident photon and electron emission beams, and is detailed elsewhere [1,8].

For the present study the sample was mounted on a rotary manipulator whose axis was collinear with the photon beam, such that the incident angle was fixed at 75° and the electron emission was variable. The *in situ* cleaning of the samples was carried out by repeated cycles of mild argon-ion bombardment (600 eV) and annealing (450°C). This was continued until reproducible UP spectra were obtained.

XPS and AES examination of the samples was performed under the same experimental conditions, in a VSW multi-technique UHV electron spectrometer [1]. XRD and SEM analysis were carried out using Philips x-ray generator with Polaroid camera, and a Siemens Autoscan electron microscope.

3. UPS results

The resulting UP spectra for each of S1 and S2 are shown in figures 2(a) and (b). To clarify the early suspicion that surface contamination may be responsible for the differences in the d-band profile, both S1 and S2 were analysed under similar experimental conditions by XPS and AES. No trace of contamination was detected. Also, different *in situ* surface cleaning procedures cannot account for the present results because exactly the same procedure was applied to both samples. Instead, the key to accounting for these differences is provided by the present observation that the d-band structure of S1 is angle dependent (figure 2(a), solid curve). This suggests that S1 possesses certain properties that are not characteristic of a random polycrystalline sample.

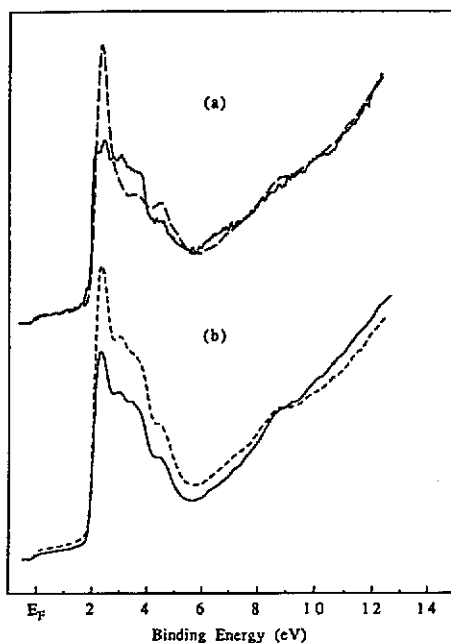


Figure 2. UP spectra of (a) S1 at emission angles of 15° (dashed curve) and 35° (solid curve); (b) S2 at emission angles of 15° (dashed curve) and 33° (solid curve). Emission angle measured relative to surface normal.

4. Discussion and XRD results

A polycrystalline metal may be described as an aggregate, consisting of minute single-crystal grains and clusters, with each grain normally having a crystallographic orientation different from those of its neighbours. Such a random distribution of crystallographic axes has an averaging effect on all orientation-dependent physical properties. Thus, the UPS valence-electron energy distribution curve of such a sample should not be dependent on orientation (or emission angle). This is the behaviour normally expected of an arbitrary polycrystalline sample.

Although prolonged high-temperature annealing may cause partial crystallization of a polycrystalline sample, SEM (as well as XRD, see below) examination of both S1 and S2 ruled out such a possibility by revealing that there were no obvious differences between their surface conditions.

It is possible, however, for small single-crystal grains in a polycrystalline aggregate to cluster (to a greater or lesser degree) about a particular orientation. Such aggregates are said to have a preferred orientation, which simply implies that the distribution of crystallite orientations is non-random. Under this circumstance, the photoemission valence-band structure of such a sample may well exhibit some angle dependence, depending on the extent of clustering. Furthermore, the preparation of polycrystalline samples with completely random crystallite orientations is a non-trivial matter, with some preferred orientation being the general rule, rather than the exception [9], and with the degree of randomness varying with the method of preparation (e.g. casting or evaporated film). This implies that some variation in UP spectra should in fact be normal expectation.

Now the Debye rings obtained from XRD are capable of qualitatively revealing the nature of the distribution of the crystallite orientations. A completely random distribution results in continuous and uniformly intense rings, whereas if this distribution is non-random their intensity is non-uniform. If there is a high degree of preferred orientation, the rings are discontinuous [9b]. (It should be noted that the presence or absence of a preferred orientation is not related to grain shape, and hence cannot be revealed by microscopic examination [9a].) XRD is also capable of providing information on grain size: a large grain size usually produces 'dotty' Debye rings, whereas for fine grain size the rings are smooth.

Figure 3 shows the XRD patterns of S1 and S2 (left and right respectively), taken by back diffraction. For S2, the Debye rings are continuous, although the intensity is slightly non-uniform around their circumference. For S1, the rings are discontinuous and substantial portions are missing. This clearly indicates that the distribution of crystallite orientations in S1 are highly non-random, with the orientation that would reflect these portions of the ring simply not present in the sample [9].

As mentioned above, the UPS valence-electron distribution curve of a totally random sample (i.e. S2) does not exhibit angle dependence, apart from a $\cos \theta$ intensity distribution (figure 2(b)). For samples that have some preferred crystallographic orientations, however, such averaging is expected not to be perfect. The observed angle dependence of photoemission from S1 reflects this point.

5. Conclusion

The remarkable spectral difference in the d bands of the two polycrystalline Cu samples, and in the emission-angle dependence of one of them (S1), is confirmed

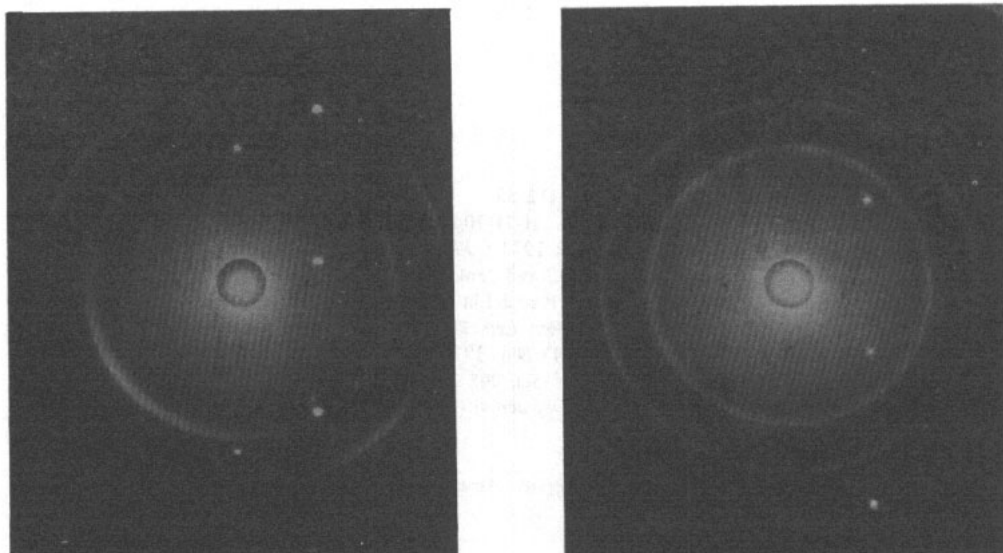


Figure 1. Electron diffraction patterns for (a) S1, (b) S2, (c) S3, (d) S4, (e) S5, (f) S6, (g) S7, (h) S8, (i) S9, (j) S10, (k) S11, (l) S12, (m) S13, (n) S14, (o) S15, (p) S16, (q) S17, (r) S18, (s) S19, (t) S20. Debye rings with slight non-uniformity around circumferences (discrete white dots are due to artifacts of the polaroid camera; discrete black dots are for orientation calibration provided by the camera).

by XRD to be due to the possession of a high degree of preferred orientation by the latter. It is therefore proposed that the similar spectral differences observed previously are likewise the direct result of different (non-random) distributions of their crystallite orientations. The XRD results also unambiguously indicate that S2 quite closely represents a genuine random polycrystalline sample. The UP spectrum, figure 2(b), obtained from S2 can thus be taken as characteristic of polycrystalline copper.

Of the previously reported spectra (figure 1), that of Evans (c) is the closest and in fact is almost identical to that for S2. Some common features shared by these two spectra are listed below.

(i) The d band is 3.3 eV in width, starting ≈ 2 eV below the Fermi level. There are three main components, of which the first (nearest E_F) is by far the most intense. Such a d-band intensity distribution is in good agreement with the earlier theoretical calculation of Burdick [10], which predicted the width of the d band as about 3 eV, with the density of states being much higher at the leading edge.

(ii) There is a small structure at about 9 eV below E_F (which is also found in the UP spectra of S1 and of a Cu(110) sample studied in this laboratory [1]). This could be expected to correspond to the bottom of the Cu 4s band [10]. This small structure is not so pronounced, but is nevertheless unambiguously observable in the spectrum published by Evans [2] (who, however, did not comment on it at all). These features thus established a 'norm' for the He I UPS of random polycrystalline Cu [11].

Acknowledgment

One of us (WS) would like to thank La Trobe University for a Postgraduate Research Scholarship (1987–1991).

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