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The use of 'forward focused' photoelectrons in analysis of an alloy surface: CuPd[85:15]{110}

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Abstract. The thermally induced transition from the (1×1) surface, produced after low-temperature sputtering of the CuPd[85:15]{110} surface, to a (2×1) ordered phase, has been studied using the variation of the intensity of the Pd $3d_{5/2}$ photoelectron line as a function of polar angle in the {112} azimuth. The applicability of the use of the forward scattering of core level photoelectrons to alloy surfaces is discussed. The results indicate that the transition from the high background (1×1) LEED pattern to the ordered (2×1) is not accompanied by a significant redistribution of Pd in the selvedge save for a removal of Pd from the uppermost layer. Comparisons are made with the behaviour of the analogous Cu₃Au{110} surface.

Forward scattering (FS) of core level XPS/Auger electrons in the 300–1500 eV energy window has, in recent years, been demonstrated to be a powerful tool in the elucidation of surface structure, adsorbate orientation at surfaces and modes of epitaxy. It may also be of use in the study of phase transitions at surfaces (for a pertinent review see [1]). The CuPd[85:15]{110} bulk alloy has been shown to give rise to a slightly Pd-rich, (1×1) surface in LEED following low-temperature argon ion (0.54 keV) sputtering (at 330 K and normal incidence to the sample for 30 min). The high electron background associated with this pattern is indicative of disorder in the surface though the fact that a (1×1) LEED pattern is obtained at all indicates that there remains a degree of periodicity. The (1×1) transforms to an ordered (2×1) surface in LEED upon annealing to above 500 K [2, 3] (in these experiments the sample was annealed at 670 K for 15 min to achieve the transition to a good (2×1) surface). The latter surface is proposed to consist of an all-Cu outermost layer, and an ordered second layer, enriched in Pd to a large degree (see figure 1(a)), on the basis of CO adsorption measurements [2], ARXPS, LEIS, TPD of HCOO_{ads} [3], and thermodynamic calculations based on the regular solution model [4]. This termination is one of the two possible terminations expected from a crystal of this composition and orientation, on the basis of bulk ordering toward the ideal $\text{Cu}_3\text{Pd}(\alpha')$ structure, predicted by the Cu/Pd phase diagram, the other possibility being Pd-rich in the outermost layer.

The proposed termination, if correct, should give rise to a significant FS enhancement in the Pd $3d_{5/2}$ photoelectron yield at approximately 60° from the surface normal, when a polar angle resolved intensity plot (PIP) of the core level peak is made in the azimuth corresponding to the {112} direction (see figure 1). This enhancement should be greater than that expected for a situation where there is no great enrichment of Pd in the second layer. Similar enhancements are also expected at 0° , 30°

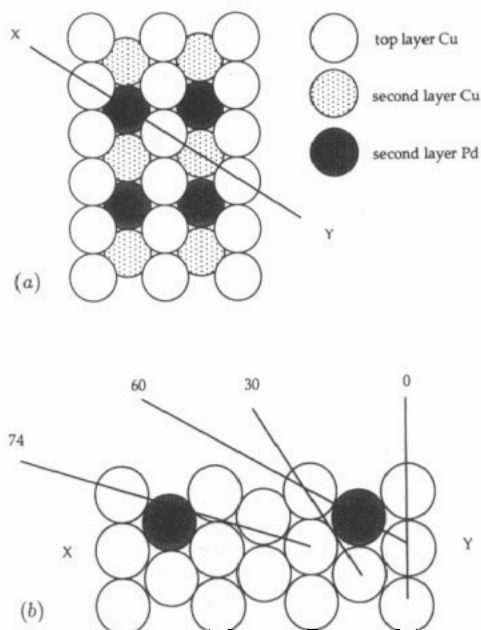


Figure 1. (a) Proposed structure of the CuPd[85:15]{110} (2×1) surface (after Holmes *et al* [2]). XY is the {112} azimuth in which polar angle scans across the surface were made. (b) Transverse section of the (2×1) surface in XY. The directions indicated correspond to the main focusing directions expected from this crystal azimuth, the polar angles relative to the surface normal to which these directions correspond are indicated.

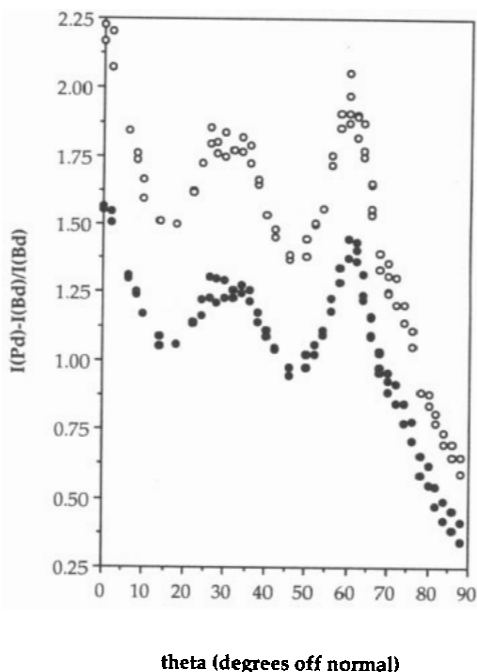


Figure 2. PIPs obtained for Pd $3d_{5/2}$ emission from the (1×1) (open circles, bombarded 'cold' at 330 K, 30 min); and (2×1) (filled circles, annealed at 670 K, 15 min) surfaces, corrected for the angular response function of the system. $I(\text{Bd})$ refers to the experimental background electron flux taken at 1080 eV.

and approximately 74° . These are only sensitive to layers below the second atomic plane (figure 1(b)). The enhancement at 60° should be a function of the amount of Pd in the second layer. This is due to the fact that the net observed intensity enhancement in the direction of an atom chain axis is a function of the chain length that the electron wave has to traverse before detection. Subsequent atoms in the chain may 'defocus' the forward scattered wave formed by the electrons interaction with the first scatterer in the chain. In a Cu matrix the chain length that is required to defocus an outgoing electron s -wave (KE = 917 eV) that has been initially focused by the first atom in the chain subsequent to the emitter has been calculated to be relatively short (~ 4 – 5 atoms) [5, 6]. The relative intensities of emitted electrons from layers within this region are approximately 1:0.75:0.4:0.12 (this result was derived for a chain of Cu atoms within a {100} surface with an axis 45° from normal emission (see [6] figure 3). The result for a three atom chain has been extrapolated from the data given for 1, 2 and 4 atom chains given in [6]. It should, however, serve to demonstrate a general effect in Cu that we can qualitatively extrapolate to the behaviour of a Pd $3d_{5/2}$ (KE ~ 1145 eV for the Al $K\alpha$ excitation used) photoelectron in a Cu matrix, where the flux detected for an emitter and a single scatterer is 1, and an emitter and a chain of

four scatterers is 0.12. Thus the total flux of the FS enhancement of component x in the alloy can be expressed as the following summation,

$$I_x^{\text{FS}} \propto \gamma_1[x_1] + \gamma_2[x_2] + \gamma_3[x_3] \dots \gamma_n[x_n] \quad (1)$$

where γ_y describes the attenuation of the FS signal due to defocusing for emission from layer y from the surface. $[x_y]$ is the concentration of component x in layer y , and $y = n$ for complete defocusing of an initially focused emission before it is detected. This type of dependence of FS intensity with layerwise composition will apply to all FS peaks though γ_n will vary according to the dimensions of the chain. As the photoelectron yields from different atomic chains within the surface sample the selvedge in different ways, and their components can be specified in terms of the layers from which they originate, they collectively represent a set of simultaneous equations the solution of which is the selvedge depth profile of component x . Thus, in principle, any changes in the relative intensities of these peaks within spectra will relate directly to changes in the layer-by-layer distribution of an element in the selvedge. Deconvolution of this information to construct a depth profile would require detailed information about the scattering properties of the system that is not readily available. Thus the present study tries to test this idea in a qualitative way by attempting to answer the following question. Does the $(1 \times 1)/(2 \times 1)$ transition at this crystal surface involve a gross redistribution of Pd in the surface region or simply an ordering of Pd with no change in the Pd distribution?

Figure 2 shows the PIPs that have been corrected for the angular response function of the apparatus. As has been demonstrated before [3] the transition involves the loss of Pd intensity (the corresponding Cu spectrum shows an increase in intensity indicating the segregation of Cu). More significantly perhaps this change in absolute intensities for both spectra appears, to all intents, isotropic with emission angle, as such there are no significant differences between the FS peak intensities relative to each other or relative to angles where FS is absent. Thus though there has been a change in the absolute intensity of signal obtained from the two surfaces, they appear practically identical in terms of FS. On the basis of the arguments presented earlier it would appear that this transition does not involve any change in the depth profile of Pd in the selvedge, below the uppermost layer, that is resolvable within the experimental error. This would therefore suggest that the composition below the surface layer is invariant within the temperature range of the transition and that the short-range order of the surface (which FS probes) appears not to have changed even though the long-range characteristics of this surface, as evidenced by LEED, have. However, we must account for the change in the absolute intensities in elemental signals at all angles that occurs during the transition. If the surface area of the sputtered (1×1) is significantly greater than the annealed surface then the reduction in the surface area of the crystal could account for a reduction in Pd flux. It is difficult, however, to explain how this effect could at the same time increase the Cu signal. The other option is that the transition does involve a significant movement of Pd into the bulk from the topmost layer but the selvedge responds to this by moving an equivalent amount further into the bulk such that no net change in the layer composition, below the topmost layer, is seen within the sampling depth of the experiment. The surface Pd that is lost must be moved far enough into the bulk such that any focused emission from it is subsequently defocused.

This result may explain why a segregation model that predicts the layerwise equilibrium compositions of Pd but takes no account of the ordering of the Pd in the

system succeeds in reproducing the compositional features of the top two layers of the (2×1) surface to a degree that is unexpected for such a simple model [4]. This fit to experiment is improved if the region below the topmost layer is compositionally invariant at temperatures less than the 500 K at which long-range ordering starts to occur and the (2×1) LEED structure is seen to evolve.

Thus from these experiments we would conclude that the $(1 \times 1)/(2 \times 1)$ transition at the surface of this alloy involves only a net two-dimensional ordering of Pd already in the second layer. This process, however, must involve some movement of Pd from the surface layer that is compensated for by moving an equivalent amount of Pd into the bulk. This represents a further difference between the behaviour of this alloy and the analogous $\text{Cu}_3\text{Au}\{110\}$ surface which produces a (4×1) LEED pattern after low-temperature sputtering, attributed to a mixed atomic termination of the bulk composition. This transforms to a (2×1) on annealing comprising an ordered CuAu top layer with a second layer becoming enriched in Cu in Au [7]. This transformation requires a measurable net change in the Au distribution in the selvedge as determined by LEIS [7]. As these two alloys are thermodynamically similar the only apparent cause of these differences is the degree of solute/solvent size mismatch. This mismatch is appreciable in both cases but is greater in the Cu/Au case ($r_{\text{Pd}}/r_{\text{Cu}} = 1.076$, $r_{\text{Au}}/r_{\text{Cu}} = 1.128$). That such similar systems produce such differing behaviour would seem to be an indication of the delicate balance between the factors controlling segregation at alloy surfaces.

Acknowledgments

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