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Inverse photoemission and Auger electron spectroscopy of Rh thin films on Cu(100)

A B Hayden, T Valla† and D P Woodruff

Physics Department, University of Warwick, Coventry CV4 7AL, UK

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Abstract. The growth of Rh films on Cu(100) has been investigated using Auger electron spectroscopy and momentum- (k -) resolved inverse photoemission (KRIPES) with a view to probing the electronic structure of near-monolayer films and any possible magnetic ordering within these films. A pronounced change in the line-shape of the Rh $M_{4,5}VV$ Auger electron peak as a function of average layer thickness indicates significant d-band narrowing in the films of monolayer or submonolayer thickness relative to thicker films. KRIPES data indicate that in films grown at room temperature the spectra are dominated by density-of-states effects implying poor order, and showing the expected unoccupied d-band feature at the Fermi level. Annealing at 750–900 K leads to significant loss of Rh into the substrate, and KRIPES spectra dominated by surface-localized states showing significant dispersion in parallel momentum more characteristic of s–p-band features.

1. Introduction

In the last few years there has been growing interest in the possibility of novel magnetic properties of systems of reduced dimensionality (see e.g. [1, 2]). In particular, the possibility of spontaneous magnetization of 4d and 5d metals in the form of isolated monolayer films [3–9] or ultrafine particles [10, 11], or even surfaces of bulk materials [12], has been investigated, mainly through theoretical studies. One such material is Rh, and there have been quite a number of theoretical studies of small clusters [10, 11] and thin films [3–9] indicating that such magnetism should occur. So far, however, there have been rather few experimental studies, and many of these have failed to find any clear evidence to support the theoretical work. In the case of thin films, emphasis in both theoretical and experimental work has been on the growth of epitaxial Rh films on the surfaces of Au and Ag. In both cases there is a lattice mismatch of some 7%, with pseudomorphic growth leading to an expansion of the lattice parameter relative to bulk Rh. In view of the fact that calculations indicate that even three-dimensional fcc Rh should be ferromagnetic if the lattice can be expanded sufficiently [13], these growth systems may also be especially favourable for displaying spin ordering in two-dimensional films. Despite calculations which favour magnetic ordering in monolayer Rh films, however, there is no direct experimental evidence to support this prediction. Surface magneto-optic Kerr-effect (SMOKE) studies of Rh films on both Ag(100) [14] and Au(100) [15] have failed to find any evidence for ferromagnetism, although photoemission measurements of thin films on Ag(100) do indicate a splitting of the Rh 4s level in the very thinnest films which is attributed to the presence of local moments

† Permanent address: Institute of Physics of the University, POB 304, 41001 Zagreb, Croatia.

on the Rh atoms [16]. By contrast, experimental evidence has been found for ferromagnetic ordering in Rh monolayers on Fe(100), but in this case the effect is specifically attributed to direct overlayer–substrate hybridization rather than reduced dimensionality [17].

In this paper we present the results of an investigation of Rh films grown on Cu(100); in this case the lattice mismatch is smaller (5%) than for Au and Ag, but pseudomorphic growth would produce a contraction of the lattice relative to bulk Rh. The primary experimental probe we have used is momentum- (k -) resolved inverse photoemission spectroscopy (KRIPES), although in the course of using Auger electron spectroscopy to monitor the growth we have found evidence that this technique also provides valuable information concerning the electronic structure of the Rh films. Neither of these techniques is capable of providing direct measurement of any possible thin-film magnetism, but both provide information on the electronic structure which in some cases can provide a fingerprint of the necessary conditions for such magnetic phases.

2. Experimental details

The experiments were conducted in a purpose-built ultrahigh-vacuum KRIPES spectrometer system which has been described elsewhere [18]; briefly, the inverse photoemission [19] spectra are recorded as simultaneous isochromats at photon energies of 10.0 eV and 11.5 eV using a dispersive LiF lens to separate the different wavelengths of emission [20], and the direction of the incident electrons (fixed at 45° to the detector axis) can be varied relative to the sample by rotating the sample about an axis perpendicular to the plane of incidence (and photon emission). The spectrometer chamber is also fitted with a low-energy electron diffraction (LEED) optics, and a 50 mm mean radius hemispherical electrostatic deflection analyser (VSW HA50) for Auger electron spectroscopy.

The Cu(100) sample was prepared by the usual combination of x-ray Laue alignment, spark machining, polishing, and *in situ* argon ion bombardment and annealing cycles until a clean, well ordered sample was obtained as judged by Auger electron spectroscopy and LEED. Rh deposition was effected by evaporation from the tip of a 0.5 mm diameter Rh wire subjected to electron bombardment heating. The deposition was monitored using Auger electron spectroscopy, but also checked by LEED. These probes provide only limited characterization of the growth of the deposited Rh films, but provide a useful reference to the more extensive characterization of this system [21] (and the related Ag(100)/Rh and Au(100)/Rh systems [16, 22]) already available in the literature.

3. Results and discussion

3.1. Auger electron spectroscopy: growth modes and d -band width

The amplitudes of the Rh $M_{4,5}VV$ (302 eV) and Cu $M_{2,3}VV$ (60 eV) Auger electron peaks as a function of deposition time with the sample at room temperature are shown in figure 1, which also shows the effect of annealing the surface after a deposition of an estimated 2 LE (layer equivalents) to different temperatures, typically holding the sample at each temperature for 2 min. Note that at the highest temperatures (750–900 K) annealing for longer times led to no noticeable further reduction in the Rh Auger signal, indicating that some form of thermodynamic equilibrium had been achieved; the actual surface coverage appeared insensitive to the exact temperature, implying saturation of some surface phase. Further support for this idea is provided by the fact that essentially the same apparent coverage of Rh is obtained from different starting coverages of higher value. Note that in

this final state the combination of absolute Rh and Cu Auger electron peak amplitudes differs from those recorded at any point during the room temperature growth: simple modelling of different possible depth distributions of Rh indicate this effect is not simply due to a different film structure, but is also influenced by the change in surface order on annealing (see below) and the attendant change in incident electron beam diffraction effects on the Auger electron yields.

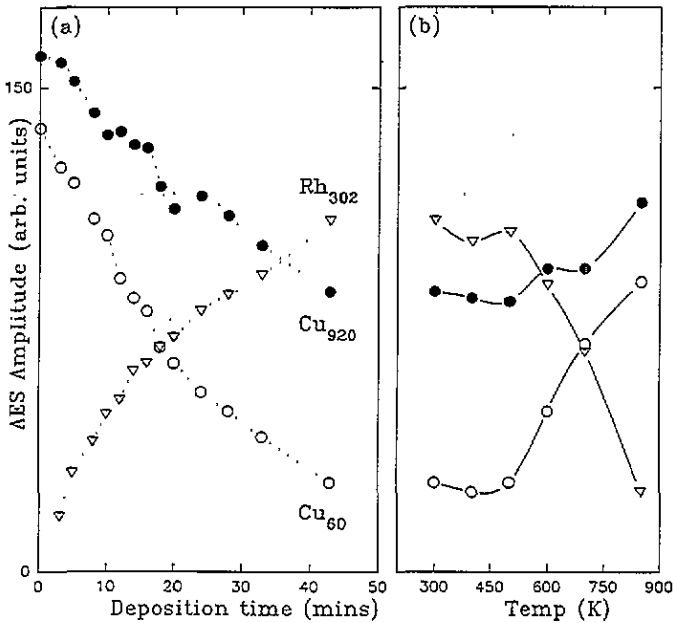


Figure 1. Amplitudes (peak to peak) of the Rh (302 eV), Cu (920 eV), and Cu (60 eV) Auger electron signals as a function of deposition time during growth at room temperature on Cu(100), and as a function of subsequent increasing-temperature annealing.

During deposition the (1×1) LEED pattern became increasingly diffuse beyond about 1 LE and by 2 LE no clear diffracted beams could be seen; on annealing on 850 K for 2 min, a reasonably well ordered (1×1) LEED pattern was restored. The rapid loss of a well ordered LEED pattern during deposition indicates that the growth, at least beyond about the first layer, is not pseudomorphic. Moreover, there are no very distinct breaks in the Auger peak amplitudes versus deposition time curve to provide convincing evidence for layer-by-layer growth. On the other hand, the generally exponential form of these curves does indicate that strong islanding is not occurring, and simple calculations based on the different attenuation of the low- and high-energy Cu Auger peaks (using published attenuation lengths [23]) is also consistent with complete substrate coverage of relatively even-thickness films. On the basis of low-energy ion scattering as well as Auger electron spectroscopy, Graham *et al* [21] have concluded that even during room-temperature growth of this system some Cu diffuses from the substrate onto the surface of the Rh, so the actual structure of the film may be some kind of Cu-Rh-Cu sandwich: our own modelling suggests that if this is so, the Cu surface coverage is less than 1 ML. As in our own data of figure 1, this earlier study also noted an attenuation of the Rh Auger electron peaks following annealing: by comparison with a similar study of Rh film deposition on Ag(100) [22], they speculated that a possible cause may be increased Cu overlayer thickness on heating, but our Auger electron peak

lineshape observations (see below) indicate that the main cause is probably Rh diffusion into the bulk of the substrate and an associated thinning of the (near-surface) Rh layer. In summary, therefore, we find that, during room-temperature growth, Rh films do not grow in a simple pseudomorphic layer-by-layer fashion; they have rather poor long-range order, but nevertheless the films probably do not show large inhomogeneities in their layer thickness. An implication of this conclusion is that despite the potential reduced dimensionality of these films, the Rh–Rh distances are presumably essentially those of bulk Rh. Annealing to 750–900 K appears to lead to diffusion of excess Rh into the substrate to produce a stable surface phase which is much better ordered, and which comprises approximately 0.5 ML of Rh. Graham *et al* [21] have reported the observation of a weak $c(2 \times 2)$ LEED pattern for a similarly-produced state. In this ordered state the nearest-neighbour Rh–Rh distances should be substantially larger than in bulk Rh.

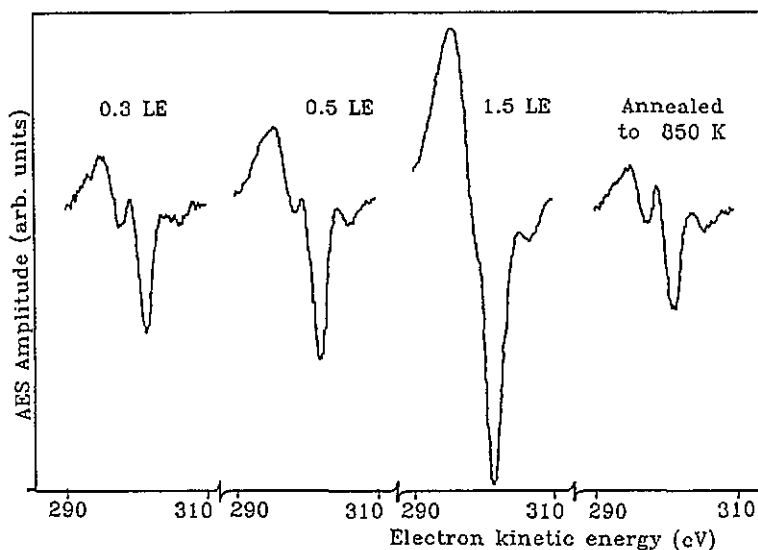


Figure 2. Rh $M_{4,5}VV$ (302 eV) Auger electron spectra (recorded in the usual derivative mode) for Rh deposition at room temperature on Cu(100) to various coverages, and after subsequent annealing.

During the course of this growth characterization, we noticed a very pronounced change in the lineshape of the Rh $M_{4,5}VV$ Auger electron peak as the average Rh layer thickness increased. The key changes are summarized in figure 2. It is clear that while at low coverages the Auger peak line-shape comprises two rather well-resolved (differentiated) peaks, at high coverage a substantial broadening of the line-shape occurs, and there is only the slightest hint of two components being present. The Auger electron spectrum recorded from the thick Rh film annealed to 850 K restores the sharp structure seen during low-coverage deposition, but with consistently even more clearly resolved features than at all but the very lowest-coverage as-deposited films. The most obvious origin of the double peak is that it is associated with separate M_4VV and M_5VV peaks, as the nominal binding energy difference of the initial $3d_{3/2}$ and $3d_{5/2}$ is 5 eV. Of greater interest, however, is the origin of the marked difference in apparent width of each of these features which occurs as the film thickens or is annealed. As both of these Auger electron peaks involve core–valence–valence transitions, the initial expectation is that the (undifferentiated) peak should reflect the self-convolution of the density of states of the valence band, and in particular

the total width of each peak should be twice the valence bandwidth. A narrowing of the peak thus indicates a narrowing of the bandwidth. We should also recall, however, that in core–valence–valence transitions, localization of the two final-state holes can occur if the hole–hole interaction energy is larger than twice the bandwidth (the width of the two-hole density of states) [24–26]: this means that in d-band solids, for example (e.g. the 3d band of Cu), extremely sharp atomic-like core–valence–valence Auger spectra are seen (see e.g. [25]). If we translate this idea to the present case, we find the same qualitative conclusion: valence band narrowing will cause a narrowing of the Auger peak line-shape, although if the two final-state holes become localized, the Auger peak sharpening will be more pronounced and the change in width may be significantly greater than the actual change in bandwidth.

This change of bandwidth is potentially important in the context of possible magnetic properties: we recall that the key physics which can lead to 2D magnetism in the 4d metals is a narrowing of the d band with decreased coordination, and thus an increase in the density of states at the Fermi level sufficient to overcome the Stoner criterion (see e.g. [5]). Our Auger line-shape data strongly indicate that both the low-coverage as-deposited films and the surface phase produced by annealing thick films lead to Rh structures which do show the required marked d-band narrowing. The fact that the lineshape appears even narrower in the nominal 0.5 ML films produced by annealing than in films of similar coverage produced directly by room-temperature deposition may be reconciled by partial islanding (and thus some atoms of increased Rh coordination) in the as-deposited films, or may be due to the formation of a (weakly ordered) substitutional surface alloy phase after annealing, similar to that found for Cu(100)c(2 × 2)–Mn [27–29]. Of course, these Auger electron spectroscopy data do not demonstrate that this band narrowing is necessarily sufficient to produce magnetic ordering in these Rh films.

3.2. Inverse photoemission

A summary of the KRIPES data recorded at normal incidence to the surface for different film thicknesses before and after elevated-temperature annealing are shown in figure 3. We should first remark that for the clean Cu(100) surface, the spectrum is dominated by a direct transition between s–p bands [30, 31] which appears at approximately 0.3 eV and 0.7 eV above the Fermi level in the 11.5 eV and 10.0 eV isochromats respectively. This feature shows the expected dispersion with photon energy and also disperses strongly in electron momentum parallel to the surface, k_{\parallel} . In addition there is a (Shockley) surface resonance at 1.2 eV above the Fermi level [32]. Two general points are immediately clear from figure 3. Firstly, as Rh is deposited onto the Cu(100) surface at room temperature, the normal incidence spectra show an increasing background as the coverage increases, but a clear persistent peak just above the Fermi level which is present in both photon energy isochromats; the somewhat sharper appearance of the peak in the 11.5 eV isochromats may be largely attributable to the improved resolution of the instrument at this higher energy [18]. This peak can readily be attributed to the unoccupied component of the Rh 4d band, which essentially all theoretical calculations show to be expected for both thin films and bulk Rh. Of course, in the thin-film (monolayer) calculations which show magnetic ordering, this peak would be attributed entirely to minority spin electrons, but our present experiments are unable to determine the spin. The second striking feature of figure 3 is that the normal incidence KRIPES spectra recorded from the Rh films annealed to elevated temperatures are quite different from those from the as-deposited films, even at the same nominal submonolayer coverages. This difference in the KRIPES data is in marked contrast to the behaviour of the Rh $M_{4,5}VV$ Auger electron spectrum lineshape which is qualitatively

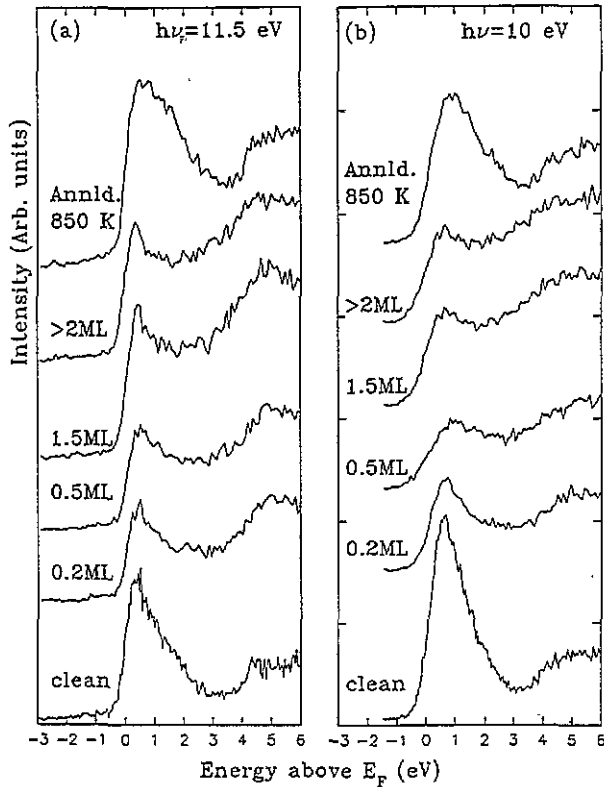


Figure 3. Normal incidence KRIPES from Cu(100), after deposition of various nominal (LE) coverages of Rh at room temperature, and after annealing a nominal 1.5 LE film to 850 K. (a) shows 11.5 eV iso-chromats, while (b) shows 10.0 eV iso-chromats.

similar for these two low-coverage conditions. Clearly the Auger line-shape and KRIPES are probing different aspects of the electronic structure.

Some further information as to the nature of the as-deposited and annealed films is also provided by KRIPES data recorded at different incidence angles in the [011] azimuth, as seen in figure 4. On the clean Cu(100) surface, both the bulk s-p-band transition and the surface resonance disperse up in energy as the incidence angle, and thus k_{\parallel} increases, in an almost free-electron-like fashion [30, 31]. Figure 4 shows that the behaviour of the as-deposited and annealed films behave quite differently when the incidence angle is changed. The spectra for the as-deposited films show very little dependence on incidence angle, whereas the spectra from the annealed state show dispersing features rather similar to those of the clean surface. Careful comparison of the spectra from the clean surface and the annealed films shows that at normal incidence the Rh films show additional intensity, relative to the clean surface, at an energy of approximately 1.0–1.5 eV above the Fermi level, and that at higher incidence angles this new feature appears to dominate and disperse up in energy more strongly than the substrate features. This strong dispersion clearly indicates that this feature is not related to the Rh d band, but is of more itinerant s-p character.

The overall picture of the KRIPES data is therefore rather different from that of the Rh Auger electron spectroscopy; the latter shows considerable similarity in the low-coverage phases, be they as deposited, or resulting from annealing, whereas the KRIPES distinguishes

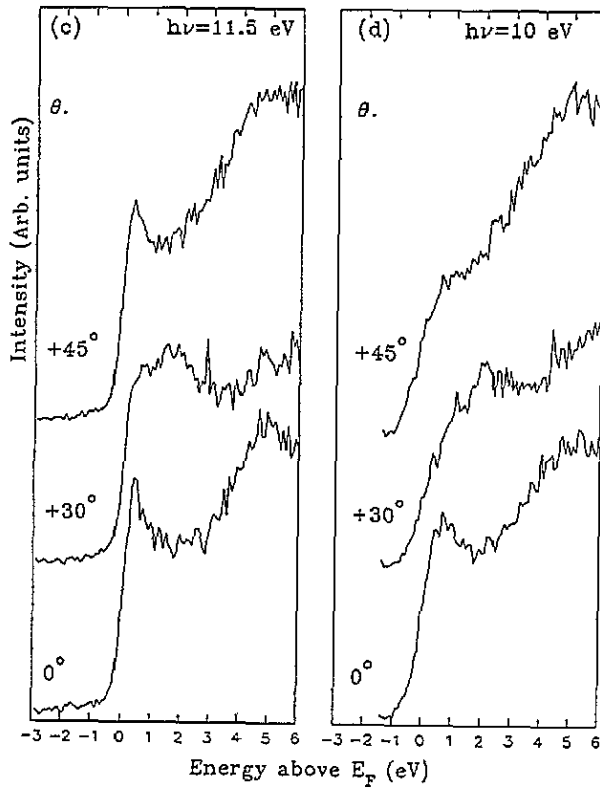
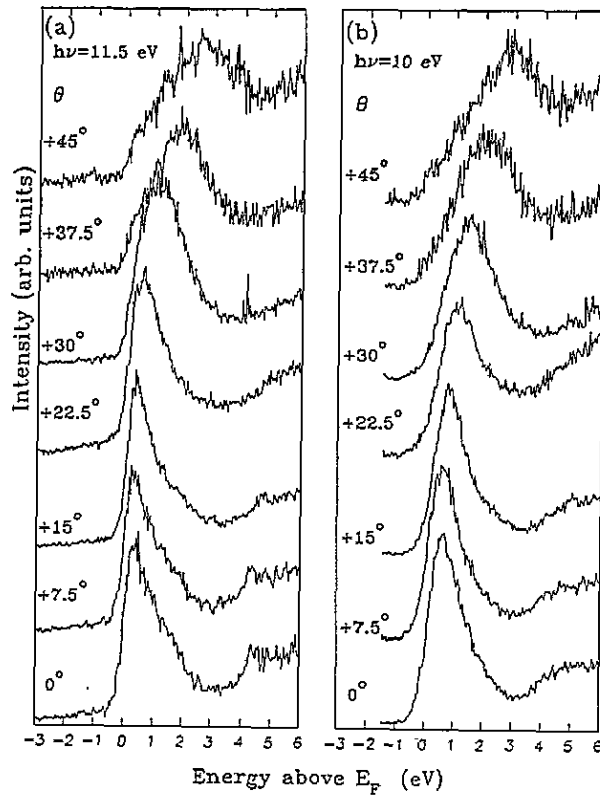
most clearly between the as-deposited films (at all coverages) and the annealed surface phase. Of the three states identified in this way, low-coverage as deposited, high-coverage as deposited, and annealed, the data from the thick as-deposited films appear to be the most straightforward to understand: both the Auger peak profile and the KRIPES data are compatible with bulk Rh metal showing a relatively broad d band and KRIPES spectra dominated by the anticipated sharp peak at the Fermi level in the unoccupied density of states. The poor order of these films implies that the KRIPES will average over all directions in k -space, but of course is still governed by direct (k -conserving) transitions. In view of the flat-band character of the unoccupied d states in Rh, one might expect this feature to dominate the KRIPES spectra. It is also notable that some rather flat bands are also seen about 11.5 eV higher in energy in bandstructure calculations (e.g. [33]), particularly favouring the appearance of this peak in the 11.5 eV isochromats, as is seen in our data.

In the case of the low-coverage, as-deposited films, the KRIPES data can be largely understood in terms of the Cu(100) substrate and a greatly increased disorder. No clear additional peaks can be identified, and while there may well be a small Rh 4d contribution just above the Fermi level, the fact that the substrate s-p bulk transition has considerable intensity in this region means that it is not really possible to demonstrate this in a convincing fashion. The Rh Auger electron lineshape, on the other hand, does show that the Rh-Rh coordination is low in these films, indicating either quite good spreading of a disordered but essentially single-monolayer film, or very small Rh particles. The former morphology seems to be favoured by the Auger peak intensity versus dosage curves, but small particles of no more than two atomic layers could also be reconciled with these data.

The electronic structure of the annealed films is of special interest. The Rh Auger electron spectra show rather clearly that a narrow atomic-like Rh d band must be associated with the Rh atoms, but at the relatively low coverage of these films it appears that here too the contribution to the KRIPES data of the empty d-band peak at the Fermi level is too small to resolve clearly. In this case of a relatively well ordered film, on the other hand, the absence of this peak could alternatively be due to a lack of suitable initial states of the same k_{\parallel} (although this could only be an issue if the Rh d states form true two-dimensional bands). For these annealed films, however, the KRIPES data are dominated by a peak which disperses strongly in k_{\parallel} , but which appears not to disperse in k_{\perp} , as the peak occurs at essentially identical energies in the 10 eV and 11.5 eV isochromat spectra at all incidence angles. This clearly indicates a surface-localized state. Whether this is described as an evolution of the original Shockley surface resonance of the Cu(100) surface, or as an ultrathin-film quantum well state may be a matter of semantics, at least in the simple multiple-scattering description of these states [19]. Whichever description is most appropriate, it is interesting to note that although the energy of this state at $k_{\parallel} = 0$ is essentially the same as that of the clean Cu(100) Shockley surface resonance, it shows a consistently higher intensity in the KRIPES data, and indeed becomes dominant, apparently with somewhat stronger dispersion, at high incidence angles (i.e. at higher k_{\parallel}). Neither the higher intensity, nor the higher dispersion, can be deduced without the aid of a more sophisticated calculation which specifically includes the role of the Rh atoms on the electronic structure.

4. General discussion and conclusions

Much of the motivation for studying the electron structure of Rh films on surfaces lies in the possibility of novel magnetic phases. The techniques we have used provide only indirect information on this issue. Perhaps of most direct relevance to this issue is the observation, via the Rh core-valence-valence Auger electron peak line-shape, that the Rh



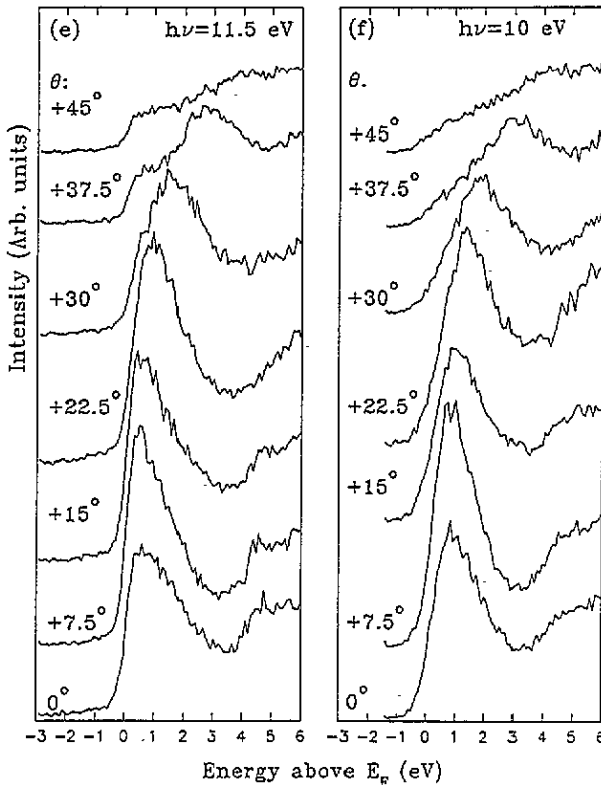


Figure 4. KRIPES data showing the incidence angle dependence of both the 11.5 eV (a, c, e) and 10.0 eV (b, d, f) isochromats recorded from a clean Cu(100) surface (a, b), from a nominal 1.5 LE film of Rh as deposited at room temperature (c, d), and from a Cu(100) surface annealed to 850 K after deposition of a nominal 1.5 LE Rh film (e, f).

4d bandwidth is very much narrower in both as-deposited submonolayer films and annealed submonolayer films on Cu(100) than in multilayer films. The atomic-like character of these states provides the possibility of the Rh atoms retaining their local magnetic moments and thus of possible magnetic spin ordering. KRIPES data (and LEED) shows the as-deposited films to have poor long-range order, indicating that their electronic structure could also be reconciled with very small particles. By contrast, the annealed films are found to be very much better ordered, although whether this is in the form of an overlayer or substitutional surface alloy layer is not known; in this case however, the KRIPES data are dominated not by Rh 4d states, but by a surface-localized *s*-*p* state typical of a metallic quantum well or a modified Shockley surface state.

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