Pulsed growth and electronic structure of layered CuFe films on Cu(100)

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Abstract. We have attempted the preparation of CuFe superlattice structures by pulsed metal deposition in an atomic layer-by-layer fashion upon a Cu(100) substrate at 300 K. The electronic structure of a single crystal $6 \times (1 \text{ ML Fe} : 1 \text{ ML Cu})(100)$ CuFe film has been probed by angle-resolved ultraviolet photoemission spectroscopy. Experimental photoemission results have been critically compared with both fully self-consistent linear muffin-tin orbital (LMTO) predictions of the ground state electronic structure and with photocurrent calculations using time reversed LEED formalism. Theoretical predictions indicate the expected large rearrangements in the valence electron states which are shown to be large enough in certain $E(k)$ points to provide a definite 'fingerprint' of superlattice formation. Despite LEED/AES measurements which indicate a high quality $p(1 \times 1)$ single crystal film exhibiting strong compositional modulation we show by comparing experimental and theoretical angle-resolved photoemission spectra that the attempted Brillouin zone folding in the growth direction has not been imposed. Our result suggests that formation of metallic superlattice with short repeat periods (2 ML) is a non-trivial task despite the apparent ideality of the CuFe system for this purpose. Results presented here are supportive of non-ideality in the growth mechanism of Fe/Cu(100).

1. Introduction

Considerable interest has recently been focused on the growth mechanism, geometric structure and electronic and magnetic properties of thin (1–5 ML) Fe films supported on Cu single crystal substrates [1]. While the primary motivation of most studies has been the investigation of magnetic properties of the Fe thin film system, substantial parallel effort has been input to characterise the exact growth mechanism and structure. It is now well established that thin (<5 ML) films of Fe deposited on Cu(100) at 300 K adopt a face-centred-cubic (FCC) structure of high crystal quality [2]. The majority of studies addressing the Fe growth mechanism favour a near ideal layer-by-layer mechanism on the basis of Auger signal versus deposition time (AS-t) plots exhibiting up to three linear segments with differing gradient [3]. This mechanism has recently been supported by energy loss studies which exhibit low elastic diffuse scattering which the authors claim indicates complete wetting of the Cu surface at 1 ML Fe coverage [4]. The view of perfect layer growth has, however, also been challenged by groups who, utilising angle-resolved Auger and x-ray photoemission (XPS), claim that the growth mechanism is far from ideal, possibly due to Fe clustering and/or Cu surface segregation [5, 6]. The growth mechanism of Cu on thin FCC Fe films formed by deposition on Cu(100) has also been carefully

studied. A range of techniques including angle-resolved Auger measurements [5], angle-resolved XPS, UPS and AS-*t* studies [7] are in full agreement that Cu grows in a perfect and indefinite layer-by-layer fashion with complete wetting of the underlying Fe(100) substrate. Thus, motivated by large bodies of evidence favouring ideal growth of both Fe/Cu(100) and Cu/Fe(100) we considered this system an ideal candidate for an attempt to prepare a lattice matched (mismatch < 1%) bimetallic superlattice (SL) by controlled alternate pulsed deposition of Fe and Cu monolayers.

In this article we report the results of attempted growth of a 6 × (1 ML Fe : 1 ML Cu) film on a Cu(100) substrate combined with *in situ* measurements of the electronic structure utilising angle-resolved ultra-violet photoemission spectroscopy (ARUPS). We show that although low-energy electron diffraction (LEED) and Auger data may easily be interpreted in favour of formation of a bimetallic SL, ARUPS spectra which provide a fingerprint of the periodicity normal to the surface show no evidence to support Brillouin zone folding. This is clearly demonstrated by critical comparison with the ground state electronic structure computed using linear muffin-tin orbital (LMTO) fully self-consistent band structure calculations [8]. We also present photocurrent calculations using the time reversed LEED formalism [9] to aid further comparison and interpretation of experimental results. Formation of true bimetallic SL structures with minimum repeat periodicities (2 atomic layers) in the growth direction appears to be a non-trivial task even for the apparently favourable CuFe system. Our results favour the view that epitaxy of the Fe/Cu(100) is imperfect, supporting the conclusions of angle-resolved Auger and XPS studies.
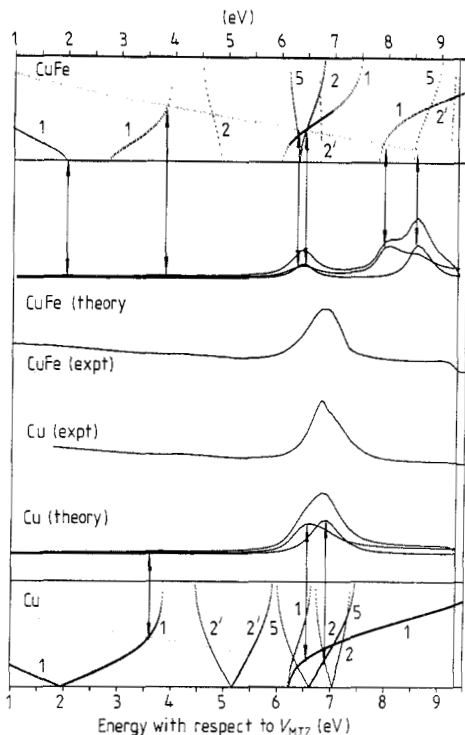
2. Experimental

Experiments were performed in a UHV chamber with facilities for LEED, Auger electron spectroscopy (utilising the LEED optics as a retarding field analyser) and angle-resolved ultra-violet photoemission spectroscopy. The base pressure of the chamber was 5×10^{-11} torr. The Fe and Cu films were evaporated from two evaporators consisting of resistively heated tantalum boats containing charges of high purity Fe and Cu. The evaporators were mounted at the upper LEED/AES analysis level 130 degrees apart, allowing sequential dosing by a simple sample rotation. After prolonged degassing both sources could be operated simultaneously with the system pressure remaining in the 10^{-10} torr range. Evaporation rates utilised were about 1 ML min^{-1}. Contamination during film growth was minimal as verified by AES. We do not expect low levels of carbon and/or oxygen contamination below the detection limits of our AES system (<5 at%) to effect the film growth mechanism although both magnetic and surface reconstruction phenomena are indeed likely to be sensitive to even such low level contamination [4]. The evaporators were calibrated by construction of AS-*t* plots for both Fe/Cu(100) and Cu upon FCC Fe(100) films at 300 K. The AS-*t* plot for Cu on FCC Fe(100) yielded a well defined series of linear segments of differing gradient typical of ideal layer-by-layer growth [7]. The AS-*t* plots for Fe/Cu(100) were in very good agreement with previous studies of this particular system. Auger transitions utilised were the highly surface sensitive Cu (59/61 eV) and Fe (47 eV) peaks. The sample temperature was held at or slightly above (<350 K) room temperature during film growth in an attempt to minimise interdiffusion which readily occurs at temperatures >450 K [4].

During film growth upon completion of each metal pulse the sample was rotated to the LEED/AES analysis position and the copper (61/59 eV) and iron (47 eV) Auger peak-to-peak heights measured. Figure 1(*a*) illustrates a plot of the iron to copper ratio as a
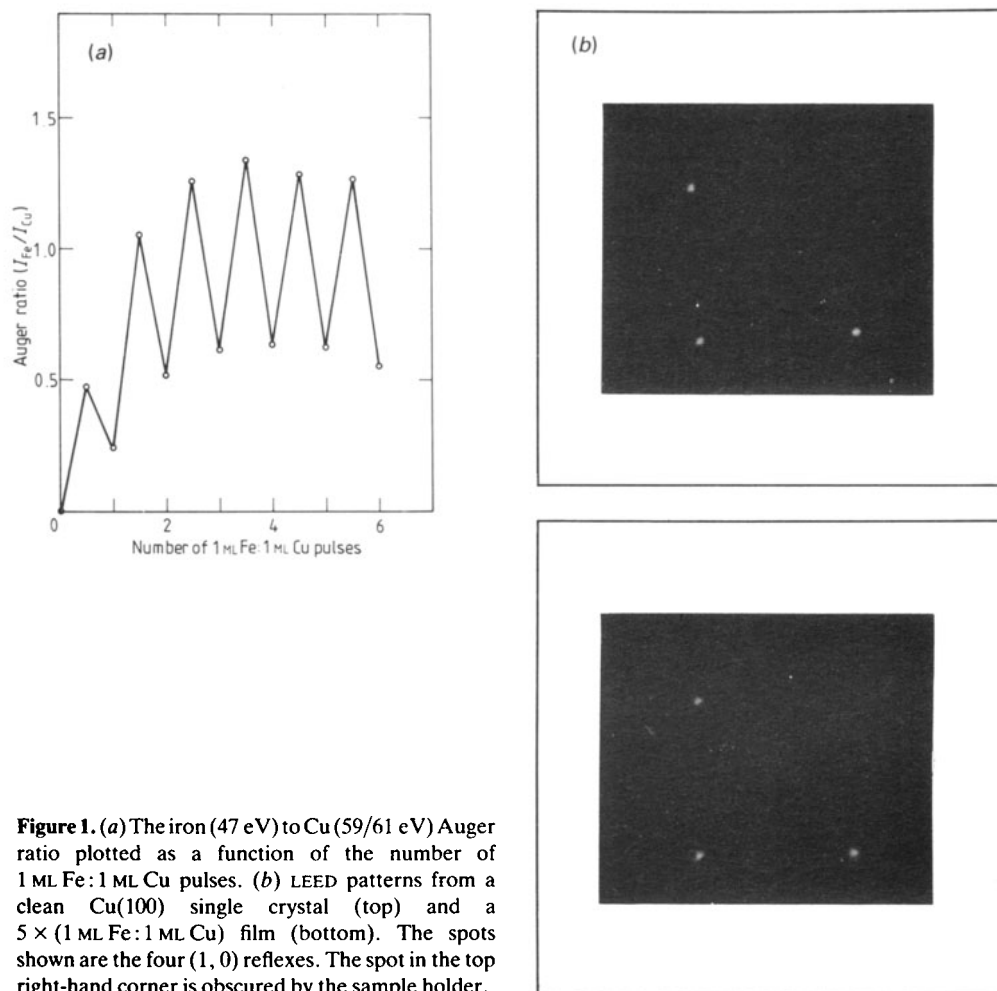
Figure 1. (*a*) The iron (47 eV) to Cu (59/61 eV) Auger ratio plotted as a function of the number of 1 ML Fe : 1 ML Cu pulses. (*b*) LEED patterns from a clean Cu(100) single crystal (top) and a 5 × (1 ML Fe : 1 ML Cu) film (bottom). The spots shown are the four (1, 0) reflexes. The spot in the top right-hand corner is obscured by the sample holder.

function of the number of metal layers deposited. A strong variation in the Fe/Cu ratio upon completion of each pulse can be discerned. After completion of two full (1 ML Fe : 1 ML Cu) cycles a regular variation of the Auger amplitude period equal to one full growth cycle can be seen, as would be expected for surface sensitive Auger electrons with effective sampling depths of only 3–4 atomic layers. We point out that the Auger amplitude modulation illustrated in figure 1(*a*) do not prove that SL growth is ideal, rather they merely attest to the fact that strong compositional modulation has been imposed. As indicated in figure 1(*a*) films of 6 × (1 ML Fe : 1 ML Cu) cycles were generally grown, i.e. 12 atomic layers in all. This thickness was sufficient to effectively damp unwanted emission from the underlying Cu substrate and to allow full convergence to the bulk CuFe bandstructure for ideal layer-by-layer growth [10]. SLs grown in this manner yielded sharp low background $p(1 \times 1)$ LEED patterns indicative of pseudo-morphic films of high crystalline quality. Figure 1(*b*) shows a typical LEED pattern from the clean Cu(100) substrate and a 5 × (1 ML Fe : 1 ML Cu) film. SL films were always terminated with a Cu pulse to protect the film from undue contamination during following photoemission measurements.

Figure 2. Figures illustrating experimetal and theoretical Ne I (16.85 eV) normal emission ARUPS spectra from a pure Cu(100) single crystal and a 6 × (1 ML Fe : 1 ML Cu) film. Also shown are the LMTO ground state band structure for a 1 : 1 SL (top) and for pure Cu(100) folded into the tetragonal Brillouin zone (bottom). Spectra shown (from top) are: 1 : 1 SL (theory), 1 : 1 SL (experiment), Cu(100) (experiment) and Cu(100) (theory).
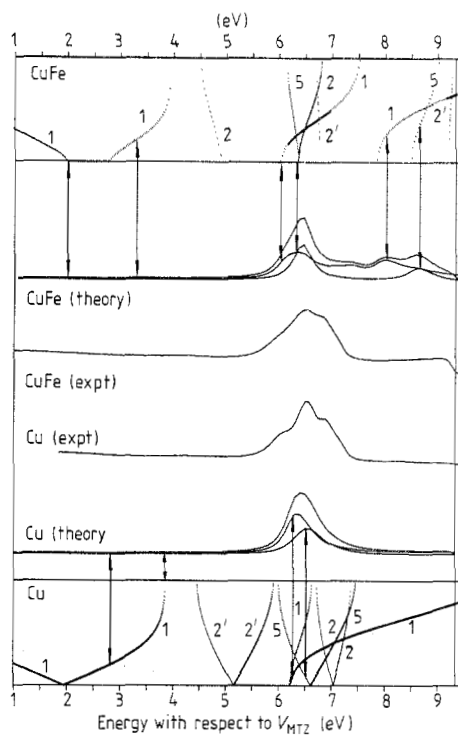
Figure 3. As figure 2; $h\nu = 21.22$ eV.

After LEED/AES analysis the electronic structure of freshly prepared films was measured with ARUPS. Spectra were recorded at normal emission probing the ΓZ direction in the bulk Brillouin zone of the tetragonal primitive super-cell. Unpolarised radiation was incident at an angle of 45 degrees with respect to the surface normal yielding a mixture of A_x, A_y and A_z components of the electric field vector. Four photon lines from a windowless differentially pumped noble gas discharge lamp were utilised namely He I (21.22 eV), He II (40.82 eV), Ne I (16.85 eV) and Ne II (26.9 eV). Spectra were recorded with a dispersive electrostatic analyser operated at a pass energy of 5 eV yielding a total instrumental resolution of about 100 meV. Figures 2 to 5 illustrate normal emission spectra from a 6 × (1 ML Fe : 1 ML Cu) film and from the pure Cu(100) substrate. The normal emission spectra from thick FCC Fe(100) films, measured by Amiri Hezaveh *et al* [11], show featureless broad peaks near the Fermi level. The high level of crystal quality of the CuFe films can immediately be noted from the low background and sharp photoemission features visible at all four photon energies. Initial comparison with spectra from pure Cu and FCC Fe (not shown in the figures) rather surprisingly indicates
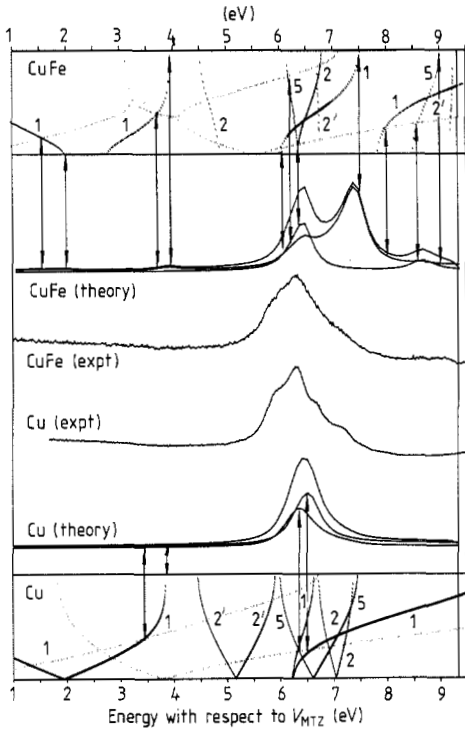
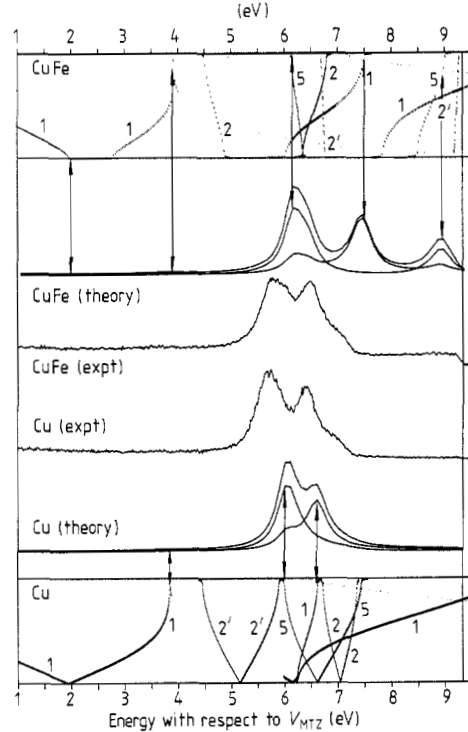**Figure 4.** As figure 2; $h\nu = 26.85$ eV.

Figure 5. As figure 2; $h\nu = 40.82$ eV.

that the photoemission spectra from the CuFe films could be rather well described by a simple combination of pure Cu(100) and FCC Fe(100) which yields considerably weaker emission than that of Cu(100). No radical changes in the form of new emissions or peak shifts to be expected due to the Brillouin zone folding or re-arrangement of the valence band structure upon SL formation can be identified.

3. Theoretical predictions

To assist interpretation of the experimental ARUPS data we also show a comparison between theoretical and experimental data in figures 2 to 5 for each measured photon energy. In the lowest part of each figure the theoretical band structure from an artificial CuCu SL is displayed. In the upper part of each figure the calculated band structure of the CuFe SL is shown. Dotted lines indicate the final state bands shifted to lower energy by subtraction of the relevant photon energy. Thus, the crossing points of bands of initial and final states predict locations of spectral features in ARUPS spectra. We must keep in mind that for normal emission conditions selection rules may lead to certain band crossings to yield zero intensity (bands other than 1 and 5 symmetry). Furthermore we note that in the case of the artificial CuCu SL direct transitions associated with initial—final state band crossings are shown only for transitions yielding non-zero intensity, i.e. allowed transitions in normal FCC 1 atom per unit cell calculations. Band structures and predicted photoemission spectra are calculated using Pendry's formulation of photoemission process and using the NEWPOOL computer code of Hopkinson *et al* [12]. Theoretical photoemission spectra for s-polarised light, p-polarised light and their sum are shown separately in figures 2–5.

Crystal potentials for all three materials (CuCu, FeFe and CuFe SLs) were calculated self-consistently using the density functional theory in the local approximation in connection with the standard linear muffin-tin orbital (LMTO) method. We used slightly modified versions of the scalar relativistic codes by Skriver [8]. In all calculations we assumed a paramagnetic ground state. The exchange and correlation part of the electron–electron interaction has been treated within the von Barth–Hedin description. We assumed the same tetragonal structure with two atoms per primitive cell for all three materials, because it yields the band structure of the pure materials readily folded into the tetragonal Brillouin zone (BZ), which makes comparison between various band structures easier. The experimental lattice constant of pure copper (3.61 Å) was used throughout as our substrate was a Cu(100) crystal. This would seem a good choice as it has been shown experimentally using LEED $I(E)$ analysis that the interlayer spacing of face-centred-cubic Fe films supported on Cu(100) is equal to within a few per cent of pure Cu [2]. To ensure sufficient accuracy in the density of states calculations the bands were computed in a uniform grid of 624 k-points within the irreducible (1/16th) part of the BZ. The iteration procedure towards self-consistency was continued until the energy eigenvalues were stabilised to within less than 1 mRyd. Muffin-tin forms of crystal potential (needed in photoemission calculations) were obtained by averaging LMTO potentials between muffin-tin and Wigner–Seitz radii and taking this average value for constant zero potential outside the muffin-tin radius.

The comparison between the LMTO band structure and the presented band structure obtained from muffin-tin potentials utilising NEWPOOL photoemission code reveals that the bands agree within 0.1–0.2 eV. The discrepancy is mostly due to the fact that in LMTO we include relativistic corrections other than spin–orbit interaction, whereas the non-relativistic Schrödinger equation is solved within the NEWPOOL suite of programs. In the photoemission program no energy or space dependence of the complex optical constant was taken into account. Thus, the obtained theoretical intensities must be considered only qualitatively correct whereas the position of intensity features (usually directly connected to the crossing bands) are quantitatively as correct as crystal potential used as input. The band structures of CuFe SL and all theoretical and experimental spectra in the middle of figures 2–5 are shifted so that the Fermi levels become coincident.

4. Discussion

The theoretical band structures for the artificial Cu–Cu and the Cu–Fe SL shown in figures 2–5 illustrate that at the Z-point in reciprocal space we have generated band gaps in the CuFe SL whereas in our artificial Cu–Cu SL we have merely folding due to the smaller repeat length in the ΓZ direction. The band gap clearly results in a general flattening of the CuFe SL bands producing a possibility to observe differences in photoemission from a CuFe SL and Cu bulk.

A direct comparison between calculated Fe–Fe photoemission spectra (not shown) and the experimental spectra of Amiri Hezaveh [11] display fair agreement. The experimental spectra seem to yield broader peaks than theoretically predicted, indicating that the imaginary part of the iron potential should be much larger than that of copper. Within the present programs it is not possible to input different imaginary parts of potentials for Cu and Fe in our CuFe SL calculations. We have utilised a value which agrees with experimental structures originating from Cu. In the experimental CuFe SL spectra the intensity from the Fe d-bands just below the Fermi level is rather broad and

weak, hence this energy range is not a promising region to detect SL effects in spectra from the pulsed CuFe film. We thus rely heavily on detection of possible SL features in the Cu dominated region of the spectra at higher binding energy.

Figure 2 illustrates a reasonable fit between measured photoemission spectra and theoretical prediction in the d-band regime for the Ne I photon energies. The weak lower binding energy sp-band features are generally less well reproduced. Clearly with the limited photon frequencies available and low intensities of sp-band emission the d-band region offers the greatest chance to unambiguously determine whether new superlattice states can be detected. This holds also for spectra recorded with other photon frequencies. In the case of Ne I theory predicts a net downward shifting of the SL d-band emission (of about 0.5 eV with respect to pure Cu). No evidence for this shift exists experimentally, the experimentally measured d-band maxima are almost coincident. Furthermore, the sp-band emissions observed experimentally at higher binding energies are also very similar.

Figure 3 exhibits similar characteristics for experimental data at $h\nu = 21.22$ eV. We note at this point the disagreement in the d-band regime for pure Cu. Theoretically we produce only two well defined peaks while three transitions are experimentally observed. This disagreement is not particular to this work and has been observed by other groups [19] who assign the third emission to a transition from a Δ_2 band which is disallowed at normal emission. We note that these dipole selection rules may be changed by relativistic effects, thus providing nonzero emission by lifting the degeneracy of the doubly degenerate Δ_2 band and allowing emission from the band labeled Δ_2 in nonrelativistic representation. Perhaps the best chance to observe SL photoemission features are with Ne II and He II photon energies: theory predicts an intense peak at a binding energy of about 1.8 eV from the CuFe SL (figure 4, $h\nu = 26.90$ eV), clearly not observed in experimental spectra of the pulsed film. The contamination of the Ne II spectra with strong satellites in the resonance radiation does not in any way alter the fact that the theoretically predicted SL emission is not observed experimentally.

Finally, figure 5 again indicates a theoretical prediction of an intense emission at a binding energy of 1.8 eV. The emission arises from the same SL Δ_1 band probed by Ne II, having 35% Cu-d character at the $E(k)$ point probed by He II. Again there is no evidence for emission in the experimental spectra from the pulsed film.

Thus, a comparison of experimental spectra from pure Cu and CuFe layer structure indicates almost identical structure and none of the indicated predicted SL emissions. We are forced to conclude that our attempt to impose the enforced periodicity in the growth direction has been unsuccessful.

Perhaps the most definitive possibility to resolve whether our experimental system is a real SL come from off-normal ARUPS spectra. Here we can once again expect large changes in energy positions of peaks from Cu and SL crystals. In figure 6 we show energy positions of both experimental and theoretical spectra from pure Cu(100) and the Cu/Fe film. Our experimental results excited by nearly s-polarised light (angle of incidence, $\Psi = 15°$ with respect to the surface normal) follow closely the bands of pure Cu whereas theoretically we predict large changes in energy positions of spectral structures for the CuFe SL. In particular we note the existence of a SL band dispersing upwards from a binding energy of 3.85 eV to 3.25 eV with increasing polar emission angle which is well separated (by almost 1 eV at most polar angles) from any corresponding pure Cu band. No emission is observed experimentally at any polar angle. This allows us to conclude that our attempt to prepare a lattice matched ($\Delta a/a < 1\%$) CuFe SL with the smallest possible periodicity in the growth direction (2 atomic layers, <4 Å) has been unsuccessful.
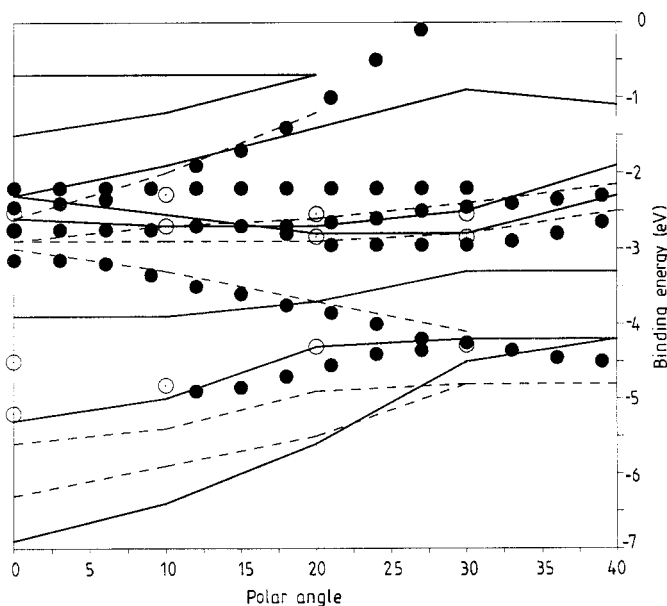
Figure 6. Off-normal band structures. Full lines indicate the theoretical bands of a pure Cu(100) single crystal and brokenlines a 1:1 Cu/Fe SL with detectable intensity by photo-emission. Also shown are ARUPS measurements from pure Cu (●) and the CuFe SL (○).

Past studies of the growth of metallic SL materials have concentrated on preparation of structures with a considerably greater repeat period (generally >10 Å). Several groups have prepared metallic SLs, with the most successful attempts to date for pairs of metallic systems with similar melting points, e.g. Nb (T_M = 2742 K)/Ta (3293 K), Ir (2720 K)/Ru (2607 K) and Y (1795 K)/Dy (1685 K) [13]. With layer thickness in the range of ~10 to 100 Å constructive and destructive interference will give rise to a series of superlattice lines in x-ray diffraction spectra proving conclusively that a coherent SL has been fabricated. The Nb–Ta system has been studied extensively, even for relatively small repeat periods, establishing that Nb and Ta interdiffuse over several lattice planes in Nb (28 Å)–Ta (22 Å) samples [14]. The authors also conclude that 'it does not appear possible to choose a growth temperature and evaporation rate such that the interfaces remain sharp while the growth perfection remains satisfactory'.

Zhu *et al* [10] have prepared CuNi 'quantum wells' by sequential metallic deposition and studied the structures utilising the technique of low energy electron transmission. The period in this case was somewhat smaller (7 Å–14 Å). The authors present convincing evidence that periodicity has been enforced and further suggest that three periods is sufficient to yield the SL regime in the material band structure. Thus, it appears that by careful evaporation techniques upon well defined single crystal surfaces in ultra-high-vacuum SLs with periods of as little as 7 Å can be achieved in certain cases, although interdiffusion and/or clustering may remain a problem in many systems. The ultimate control over metallic SL formation would be formation of sharp interfaces for structures of the smallest possible periodicity, i.e. two atomic monolayers and repeat thickness <4 Å. Reports of attempts to prepare well characterised metallic SL of this nature are scarce. The only report which we are aware of to date is that of Salokatve *et al* [15]. In this study growth was attempted of a strained 6 × (1 ML Cu : 1 ML Pd) SL upon a Pd(100) substrate ($\Delta a/a$ = 7.7%) at 300 K. A crystalline $p(1 \times 1)$ structure was reported. Ion milling revealed a weakly discernible periodic oscillation in the Cu MNN Auger signal as

a function of depth for 2–3 surface layers of a 2 ML Cu/2 ML Pd SL while ion scattering spectroscopy (ISS) gave supportive evidence of strong compositional modulation. Measurements of electronic structure *in situ* indicated a new emission at a binding energy of 5.9 eV which was utilised as evidence for successful formation of a metallic SL, with the fundamental repeat distance. However, the limited photon energies available did not allow a full band mapping of the new emission which via comparison with LMTO band structure calculations would have added considerable strength to the claim of SL formation. Hence, as good structural proof of SL formation is also lacking, we must conclude that although all evidence gathered supports SL formation the study is by no means definitive.

The ARUPS results of Salokatve *et al* contrast rather strongly with our own. Clearly in the 6 × (1 ML Cu : 1 ML Pd) system the valence state re-organisation is considerable with not only new emission at 5.9 eV but radical changes in shape and position of the Cu and Pd d-band regime. This contrasts sharply with the 6 × (1 ML Cu : 1 ML Fe) structure in which the Cu d-band emission remains sharp and peak shifts are small. Experimental error leading to a very small incorporation of Fe in the Cu/Fe SL may be clearly ruled out as the relative Fe (47 eV) and Cu (61/59 eV) peaks indicate that a significant quantity of Fe is indeed present at all stages during growth. The observed CuFe photoemission can be described fairly well by a combination of pure Cu(100) and FCC Fe(100) while this is clearly not the case for the CuPd system. At first sight this is a little surprising as CuFe is lattice matched ($\Delta a/a < 1\%$) while considerable lattice strain exists within the CuPd system which would appear to favour CuFe SL formation over the less favourable CuPd case. However, account must also be taken of the fact that the epitaxial Fe film is in a metal-stable phase i.e. FCC rather than BCC, the latter being the stable bulk phase at 300 K. This additional energy term complicates a direct comparison of strain energies due to lattice mismatch in this system. Fe and Pd have similar latent heats of evaporation and hence surface energies, thus there is no overriding reason to favour CuPd over CuFe for reasons of minimisation of surface energy. Furthermore growth kinetics clearly can not be invoked to explain the difference as both systems were grown under almost identical conditions. A rationalisation may, however, be proposed as to why the CuPd system may form a bimetallic SL and CuFe not. Clearly, formation of a 'strained' CuPd SL and not a 'lattice matched' CuFe system requires that a more favourable interfacial energy term stabilises SL growth in the former case. Indeed, copper and palladium form a series of solid solutions throughout the composition range and have an exothermic heat of mixing while copper and iron are relatively insoluble [16]. Thus, provided that intermixing is kinetically limited at 300 K then it is conceivable that the more favourable CuPd interfacial interaction stabilises two-dimensional growth of the Pd monolayer and allows SL formation in this case. We also note at this point that attempted growth of a CuPd SL upon a Cu(100) rather than Pd(100) yielded experimental photoemission spectra lacking emission at 5.9 eV, i.e. the main evidence for superlattice formation [17]. This would seem to indicate that the elastic strain energy of a 7–8% compressed palladium lattice is higher than that of a 7–8% expanded Cu lattice and it is this additional strain energy within the film which destabilised CuPd SL growth upon Cu(100). Clearly the free energy balance determining whether or not a meta-stable bimetallic SL may be prepared is very delicate. For example, it may be conceivable that CuFe SL formation may be stabilised by growth upon a Cu(100) supported thick FCC Fe(100) film. In this case the first Fe pulse leads to an Fe layer separated from a thick epitaxial FCC Fe(100) buffer layer by only one monolayer of Cu. As the FCC (100) surface is fairly open the interaction between the underlying thick epitaxial Fe film and the pulsed Fe monolayer

may be sufficient to stabilise two dimensional growth. Clearly, this Fe–Fe interaction is not present for the first pulsed Fe monolayer for a superlattice grown directly on a Cu(100) substrate leading to the speculation of possible Fe clustering to increase the effective Fe–Fe interaction. Clearly, clustering will prevent SL formation and would indeed give rise to the photoemission features observed, as in this case areas of pure Cu and pure Fe of at least two and possibly several layer thickness would exist within the film.

Upon completion of the first Fe pulse a fraction of the Cu(100) substrate could be covered with Fe islands at least of a two monolayer thickness with the remaining area being pure Cu. Cu transported during the first Cu pulse is likely to cover the surface of the Fe islands [7] with any excess presumably filling the gaps between the Cu covered Fe islands. The situation rapidly becomes more complex upon arrival of the second and subsequential pulses, the only organising feature being the preference of Cu to adsorb on-top of Fe islands to reduce the system surface energy. Thus, within this model the film would consist of islands of only a few atomic layers thickness of pure Cu and pure Fe, i.e. there would be partial phase separation of Fe and Cu but the thickness of these regions would be small due to the tendency of Cu to adsorb above Fe.

The situation would be neither a random substitutional binary alloy or a periodic metallic SL but rather somewhere between the two extremes. This model adequately explains the observation of a pseudomorphic (1 × 1) crystal structure and the occurrence of strong Auger oscillations. It also explains the relatively sharp Cu-based photoemission features observed in the pulsed film and the fact that the data may be adequately described by a combination of the clean surface spectra. We suggest this is the likely mechanism of growth. Such a mechanism may allow thicker 'SL' samples to be formed due to the smoothing actions of the Cu, i.e. longer Cu pulses of several monolayers will initially cover the Fe island surfaces and then fill in the gaps between islands providing a relatively smooth surface for the next Fe pulse. Thus, periodicity may still be enforced although the film may by no means be true Cu/Fe SLs in the strict sense. We hope to further investigate the Cu/Fe system by attempted formation of both SLs of larger periodicity and SLs grown upon a 5 ML Fe buffer layer supported on Cu(100).

Clearly future work in the field of bimetallic SLs of short repeat periods would benefit greatly from the use of a direct structural probe to allow the film structure and periodicity in the growth direction to be unambiguously defined as has been possible via X-Ray diffraction from thicker metallic SLs. A promising and simple technique for this purpose would seem to be collection of specular beam $I(E)$ curves in the normal LEED and very low energy electron diffraction regimes. For growth of metallic SLs of components with significant differences in electron scattering properties, e.g. Cu and Pd, comparison of measured spectra with theoretical predictions should allow definite discrimination between an intermixed film or a true metallic SL with atomically sharp interfaces and consequent Brillouin zone folding. We note that in the case of the CuFe system this technique is likely to be unsuccessful due to the similar scattering properties of Fe and Cu at LEED energies [18].

To summarise we have attempted the growth of a Cu/Fe SL with the shortest possible repeat distance on a Cu(100) single crystal surface by pulsed sequential evaporation in an ultra-high-vacuum environment in a controlled manner. LEED observation indicate a single crystal pseudomorphic film of reasonable crystal quality while AES measurements during growth attest to strong compositional modulation. Self-consistent ground state electronic structure and photocurrent calculations indicate that the valence electron state re-arrangement is large enough at certain $E(k)$ points to provide a definite fingerprint of

SL formation. Despite LEED/AES observation implying a strong compositionally modulated Cu/Fe single crystal structure comparison of *in situ* photoemission measurements with self-consistent band structure and photocurrent calculations show that a true SL structure has *not* been imposed. Our results support the idea of non-ideality in the growth mechanism of Fe on Cu(100) possibly in the form of Fe cluster formation.

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