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Structure of ultrathin films of Co on Cu(111) from normal-incidence x-ray standing wave and medium-energy ion scattering measurements

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Applications of the techniques of normal-incidence x-ray standing wave (NIXSW) and medium-energy ion scattering (MEIS) to the elucidation of the structure of an ultrathin metallic film, Co on Cu(111), are reported. NIXSW and MEIS are shown to yield valuable and complementary information on the structure of such systems, yielding both the local stacking sequence and the global site distribution. For the thinnest films of nominally two layers, the first layer is of entirely fcc registry with respect to the substrate, but in the outermost layer there is significant occupation of hcp local sites. For films up to 8 monolayers (ML) thick, the interlayer spacing of the Co layers is $0.058 \pm 0.006 \text{ \AA}$ smaller than the Cu substrate (111) layer spacing. With increasing coverage, the coherent fraction of the $(\bar{1}11)$ NIXSW decreases rapidly, indicating that the film does not grow in a fcc continuation beyond two layers. For films in this thickness range, hcp-type stacking dominates fcc twinning by a ratio of 2:1. The variation of the $(\bar{1}11)$ NIXSW coherent fraction with thickness shows that the twinning occurs close to the Co/Cu interface. For thicker films of around 20 ML deposited at room temperature, medium-energy ion scattering measurements reveal a largely disordered structure. Upon annealing to 300 °C the 20-ML films order into a hcp structure.

I. INTRODUCTION

Many methods exist for the determination of the structure of surfaces and ultrathin films. Many of these, such as low-energy electron diffraction (LEED), rely upon the long-range order of the system and in fact preferentially reveal information about well-ordered regions of the surface. Other techniques, such as surface extended x-ray-absorption fine structure (SEXAFS) investigate local structure, but are poorly directionally dependent and rely on analysis of weak scattering from second and third nearest neighbors to provide information about stacking sequences. Two examples of techniques that have aspects that are sensitive to both long-range order and local structure are normal-incidence x-ray standing wave (NIXSW) and medium-energy ion scattering (MEIS). In this paper, applications of both methods to the investigation of an example of the growth of an ultrathin metallic film, Co on Cu(111), are reported. Analysis protocols for both techniques are reported that enable the determination of both global site distributions (in NIXSW) and local stacking sequences (in MEIS).

The growth of Co on Cu(111) is an interesting and important example of metal-on-metal epitaxy. The technological motivation for studies of this system is the use of (111) textured Co and Cu multilayers in magnetic devices utilizing the giant magnetoresistance effect.¹ The thermal deposition of Co onto Cu(111) at room temperature has been studied using x-ray photoelectron diffraction,²⁻⁴ low-energy ion scattering,⁵ SEXAFS,⁶ LEED,^{7,8} scanning tunneling micros-

copy (STM),⁹⁻¹¹ and backscattered secondary electron imaging.¹²

It has been shown that the growth of Co on Cu(111) is not layer-by-layer and the current consensus is that the growth mode is complex. Below 2 monolayers (ML), the film forms triangular islands⁸ that have a height of two atomic layers above the surrounding surface¹¹ and may have one subsurface layer. The structure of the growing Co films and the registry relative to the Cu substrate have both been the subject of some controversy. It is generally believed that the first two layers continue the fcc structure^{6-8,10} and have fcc registry,⁶ i.e., both layers adopt the same registry as the next two Cu layers would have in an extended bulk crystal, although it has been suggested that some fraction of these islands are twinned⁹ (i.e., the stacking sequence of the layers is inverted at the Co/Cu interface as would occur in a Cu/Cu twin). It should be noted, of course, that for only two atomic layers in isolation there is formally no distinction between fcc and hcp so the distinction for the first two layers is only meaningful if one regards these as an epitaxial extension of the Cu substrate. Upon increasing thickness, the film has been reported to undergo a transition to hcp structure, but the abruptness of this transition is not clear. Films of between 10 and 20 ML have been reported to be hcp, but with some disorder.^{2,10} Low-energy ion scattering⁵ and CO titration measurements¹¹ have indicated that the island structure is not stable at room temperature, with Cu diffusing around and onto the islands.

The x-ray standing-wave technique^{13,14} is an established

method for the determination of the structure of adsorbates on metal and semiconductor surfaces. It exploits the fact that at an x-ray Bragg reflection condition, the incident and reflected waves interfere to form an x-ray standing wave with a periodicity in intensity equal to that of the atomic scatterer planes. As one scans through the finite range of total reflectivity, this standing wave shifts in phase in a predictable fashion, and the absorption profile of any atom through this range is characteristic of the position of the atom relative to the scatterer planes. Traditionally, this experiment was conducted at an arbitrary (often grazing) incidence angle by varying this angle, and the "rocking curve" width is extremely narrow, rendering the method only applicable to very perfect crystals. At normal incidence to the scatterer planes, however, mosaicity is not such a problem and metal crystals may be used.^{14,15} When applied to the (111) reflection of a (111) oriented crystal, the method provides information about the layer spacing of an adsorbate relative to the extended bulk scatterer plane positions. By performing a second measurement using the $\bar{1}\bar{1}\bar{1}$ reflection, a simple geometric triangulation also allows determination of the adsorption site.

Medium-energy ion scattering (MEIS) is a real-space technique that allows the determination of surface and near-surface structures.^{16,17} Elastic binary collisions between incident ions and ion cores in the surface lead to (incident) shadowing and (outgoing) blocking phenomena, and by analyzing the angular locations of the outgoing blocking dips at fixed incident directions one can determine the relative positions of near-surface atoms. The utility of the technique is enhanced by the ability to separate out scattering from lower layers from that from the surface layer, owing to the inelastic processes that reduce the energy of the ions by an amount proportional to path length through the surface region. This gives MEIS the unique ability to investigate structures with a depth resolution close to that of a single atomic-layer thickness.

In this paper, the application of both NIXSW and MEIS to the elucidation of the structure of ultrathin films of Co on Cu(111) is reported. NIXSW is sensitive to the location of Co atoms in the films relative to the positions of an extended bulk Cu substrate, and reveals that there is a rapid loss of coherence of the film with the substrate with increasing thickness in the 2–8-ML region. MEIS, on the other hand, is more sensitive to specific *local* stacking sequences and indicates that the film is rapidly dominated by hcp-type stacking, but contains a significant fraction of local fcc or fcc twin type coordination. For films around 20 ML, the outermost layers are largely disordered, but can be ordered into hcp stacking upon annealing to 300 °C.

II. EXPERIMENT

The experimental measurements reported in this work were made using CLRC central facilities based at Daresbury Laboratory, UK. The NIXSW measurements were made using station 6.3 (Ref. 18) on the Synchrotron Radiation Source (SRS) and the MEIS experiments were made using the national MEIS facility.¹⁹ In each case, a Cu(111) crystal was prepared *ex situ* using the usual methods. *In situ* sample preparation consisted of Ar⁺-ion bombardment and anneal-

ing to produce a clean and well-ordered surface as judged by Auger electron spectroscopy (AES) and LEED. Cobalt films were deposited using a small *e*-beam evaporator in which a wire feedstock was heated by electron bombardment from a hot filament. In both systems, the Co feedstock was maintained at a high potential so there was a possibility of Co ions impinging on the substrate in addition to the neutral species. Any such ion current was below the limits of detection. The coverage of Co was estimated using AES for both the NIXSW and MEIS measurements. The attenuation lengths of the Auger electrons in the film were obtained from the universal curve,²⁰ and the values for the Cu 920-eV *LMM* transition and the Co 656-eV *LMM* transition were used to determine the film thickness to an accuracy of 0.5 ML using published sensitivity factors. The more usual 774-eV Co transition overlapped a Cu transition. This determination was cross-compared with that from neighboring Co and Cu transitions and in every case the thickness determination was within the estimated experimental uncertainty. In addition, for the MEIS experiments, the thickness was *also* estimated by using ion energy loss to measure the depth of structural transitions beneath the surface. These two methods were found to agree within 0.5 ML and therefore there is a high degree of confidence in the thickness estimates.

Beamline 6.3 on the SRS is a dedicated line for NIXSW and SEXAFS measurements that is equipped with a double-crystal Ge(111) monochromator capable of delivering x rays in the energy region of the normal-incidence Cu(111) Bragg reflection (2965 eV at room temperature). The system is equipped with a concentric hemispherical electron energy analyzer that was used to detect the $2p_{3/2}$ photoemission from both Cu and Co to monitor the absorption of the x rays as the photon energy was scanned through the Bragg energy. Owing to the long time scales of the NIXSW measurements, Co was deposited with the sample at room temperature, but this was then cooled to liquid-nitrogen temperatures to limit Cu and Co diffusion. This cooling was found to shift the (111) Bragg energy to 2971 eV. A subset of the measurements was also made at room temperature to facilitate comparison with the MEIS data, but no differences between the low-temperature and room-temperature data were detected.

The MEIS system is equipped with a preparation chamber for sample cleaning and film evaporation, and a scattering chamber for the ion scattering experiments. Sample cooling was not possible in this system at the time of the measurement. The scattering chamber contains a rotatable toroidal sector ion energy analyzer fitted with a two-dimensional position-sensitive detector that allows a range of ion energies and emission angles to be measured simultaneously. Adjusting the angular position and applied potentials can join several 2D "tiles" of this kind together to give more complete coverage of both energy and angular parameters. After transfer of the sample to the scattering chamber, scattered ion intensity data were collected using 50-keV H⁺ ions incident in the $[00\bar{1}]$ direction with the analyzer in the plane of incidence. This ion energy was selected to maximize depth resolution at the expense of mass resolution. At the typical scattering angle of 57°, this gave a depth sensitivity of 82 eV/Å, whereas the energy separation of ions scattered from Co and Cu atoms due to the mass difference was 55 eV. The analyzer had a resolution of 66 eV, giving a depth resolution of

FIG. 1. The NIXSW data from Co on Cu(111). Examples of the absorption profile of Co, as measured by monitoring the emission from the Co $2p_{3/2}$ state, from (a) the (111) and (b) the $(\bar{1}\bar{1}1)$ reflections for various coverages, are shown with the best fits from XSWfit superimposed. The accuracy of the determination of film thickness is ± 0.5 ML.

0.8 Å at the surface, but which degrades with increasing depth owing to straggling. The data tiles were reduced to blocking curves (plots of scattered ion intensity from a specific range of depths as a function of scattering angle) using a polygon procedure to account for the variation of elastic energy loss with scattering angle and the effect of path length on inelastic energy loss. The polygons were used to isolate data corresponding to particular layers of the structure estimated using stopping powers calculated by the SRIM code.²¹ In this way, the scattering originating from the Co overlayer and the Cu substrate could be separated despite their individual elastic scattering signals not being energetically resolved. However, it should be borne in mind that the scattering from the Co and Cu atoms will not be fully separated if there is any intermixing between film and substrate. This is discussed later in the paper.

III. RESULTS AND DISCUSSION

A. Normal incidence x-ray standing wave

NIXSW has been used to investigate films of cobalt on Cu(111) with effective coverages up to 8.5 ML. Examples of the absorption profile of Co as measured by monitoring the emission from the Co $2p_{3/2}$ state are shown in Fig. 1. It can be seen that the shape of the profiles from the (111) reflection changes little with coverage, as would be expected if the growing Co layers occupied spacings relative to the substrate that are rather similar to those of the Cu substrate. Notice,

FIG. 2. The values of the coherent positions obtained from fits to the Co NIXSW absorption profile from both the (111) (filled circles) and $(\bar{1}\bar{1}1)$ (open circles) reflections of Cu(111) vs coverage. The solid line is a linear fit to the values of the coherent position for the (111) reflection.

however, that the Cu substrate and Co film layer spacings are not expected to be identical, so as the film thickens, the cumulative effect is to shift the outer layers further from the extended substrate scatterer plane positions. This accounts for the evident reduction in modulation amplitude for the data from the 6–8.5-ML films, as will be discussed below. The $(\bar{1}\bar{1}1)$ reflection, however, shows completely different behavior. As the thickness of the overlayer increases, the absorption profile undergoes a clear shape change towards one that is more consistent with the reflected intensity, implying a complete loss of coherence. XSW data can be fitted using two structural parameters, the coherent position D and the coherent fraction f_{co} ,¹³ and Fig. 1 also shows the best fits to the data using the XSWFIT routine.²² Figure 2 shows the values of the coherent position used in these fits to the Co absorption profiles, as a function of average film thickness, in units of the Cu(111) substrate layer spacing (2.087 Å). While $D(\bar{1}\bar{1}1)$ stays largely constant, though with increasing scatter of the values, $D(111)$ decreases systematically with Co coverage. Previous workers^{7,8} have observed a decrease in the Co film layer spacing relative to that of bulk Cu(111) to around 2.03 Å over the first three layers, consistent with a Co fcc structure. In the measurements presented here, the monotonic decrease in the coherent position reflects the way that NIXSW measures the layer spacing averaged across the entire film thickness relative to the atomic scatterer plane positions of an extended substrate, so that each successive Co layer position is displaced further from the nearest extended substrate plane. Figure 2 shows a linear fit to $D(111)$; this gradient is equal to half of the value of the difference between the film atomic-layer spacing and the substrate layer spacing, so the linear fit shown implies a value for this difference of 0.058 ± 0.006 Å.

The values obtained for the Co coherent fractions as a function of film thickness are shown in Fig. 3. The value of $f_{co}(111)$ is more or less constant with coverage, perhaps

FIG. 3. The values of the coherent fractions obtained from fits to the Co NIXSW absorption profile from both the (111) (filled circles) and $\bar{1}\bar{1}\bar{1}$ (open circles) reflections of Cu(111) vs coverage. The lines show calculations for the expected behavior of $f_{co}(\bar{1}\bar{1}\bar{1})$ for several different stacking sequences.

with a weak trend to decrease with increasing coverage. This behavior implies that the growth of the first few layers (at least) is unlikely to be truly layer-by-layer. If one did have layer-by-layer growth at this stage, the NIXSW from a single layer would see all Co atoms at the same layer spacing relative to the substrate and so should yield a high (near-unity) coherent fraction. Adding the second layer would then introduce a mixture of two different local layer spacings relative to the extended substrate planes and lower the coherent fraction. Adding further layers would continue this decline, but the effect would become less and less pronounced as the film thickness became comparable with the sampling depth of the photoelectrons used to monitor the NIXSW.

By contrast to the approximately constant value of $f_{co}(111)$, $f_{co}(\bar{1}\bar{1}\bar{1})$ falls towards zero with increasing coverage. To understand this in detail, recall the formalism used to obtain the values of the coherent fraction and coherent position when summing over several different atomic positions in NIXSW.¹⁴ This is given by

$$f_{co} \exp(2\pi i D/d) = \sum f_j \exp(2\pi i z_j/d), \quad (1)$$

where the summation is across all the different sites sampled (in the present case all the different layers in the film), d is the substrate layer spacing, and z is the local layer spacing of each absorber relative to the extended substrate scatterer plane positions. Notice that f_j is the product of the fractional occupation number of each z value (normalized to have a sum of unity) and the coherent fraction associated with this single site. A convenient way to perform the summation is via an ARGAND diagram.²³ The contribution from each site (i.e., each term in the summation on the right-hand side of the equation) can be expressed by a vector of length equal to f_j and angle $2\pi z/d$ (Fig. 4). Successive Co layers always involve local occupation of a hollow site relative to the layer below, but depending on the stacking sequence the possible

FIG. 4. The vectors representing the three high-symmetry sites on the argand plane. The angle of the vector from the real axis relates to the coherent position for the $\bar{1}\bar{1}\bar{1}$ reflection and the length of the vector relates to the coherent fraction.

sites relative to the substrate continuation are fcc, hcp, and atop. It should be emphasized that the “sites” as determined by NIXSW in an extended film do not refer to the local adsorption site relationship between one layer and the one below it, but rather to the global adsorption site relationship with the layer that would have been below if there had been a perfect fcc continuation of the substrate. Notice, therefore, that while one normally defines these three sites, fcc, hcp, and atop, as corresponding to atop a third-layer, second-layer, or top-layer atop, respectively, on an fcc crystal, in the present case these positions are relative to the extended bulk rather than the actual atomic planes below. If the usual *ABCABC...* notation for the stacking sequence of the fcc substrate planes is used, with lower case for the overlayer, then for a single atomic overlayer fcc, hcp, and atop sites would correspond to *ABCa*, *ABCb*, and *ABCc*, respectively. Of course, this last sequence would not place the overlayer in a hollow site and is clearly not expected to occur for Co in Cu(111).

Consider, however, a three-layer film. A stacking of *ABCabc* would give “fcc” sites in each atomic layer in the film. If the stacking were *ABCacb*, however, the sites for the three layers of the film would be “fcc,” “hcp,” and “atop,” respectively, even though local coordination is in a hollow site in each case. The layer spacings perpendicular to the surface, and thus the z values of these sites in the (111) XSW, will all be the same (ignoring the small contraction with thickness). However, the z values relative to the $\bar{1}\bar{1}\bar{1}$ scatterer planes are very different. Simple geometry²³ shows that if the layer spacing of a particular site relative to the (111) scatterer planes is z_{111} , then relative to the $\bar{1}\bar{1}\bar{1}$ planes the appropriate z values for atop, hcp, and fcc are $z_{111}/3$, $(z_{111} + d_{111})/3$, and $(z_{111} + 2d_{111})/3$, respectively. The value of the $\bar{1}\bar{1}\bar{1}$ substrate layer spacing is the same as that (d_{111}) of the (111) planes, so the ARGAND diagram vectors represented by these three sites are separated by an angle of $2\pi/3$ (see Fig. 4). If the three sites are equally occupied, the resultant gives a coherent fraction of zero. Combining only two of these sites, on the other hand, leads to a resultant vector of finite (but reduced) length (coherent fraction) but with some intermediate direction (and thus with a coherent position different from that expected for the fcc site alone). Thus, if one starts with an occupation of fcc sites and in-

TABLE I. Local sites relative to a fcc continuation for the three stacking positions as a function of layer number.

Layer	<i>a</i>	<i>b</i>	<i>c</i>	Substrate continuation
1	fcc	hcp	atop	A
2	atop	fcc	hcp	B
3	hcp	atop	fcc	C
4	fcc	hcp	atop	A
5	atop	fcc	hcp	B
6	hcp	atop	fcc	C
7	fcc	hcp	atop	A
8	atop	fcc	hcp	B
9	hcp	atop	fcc	C
10	fcc	hcp	atop	A

creases the film thickness, it is quite possible for the coherent position to stay at unity, while the coherent fraction falls; this occurs if equal numbers of global “hcp” and “atop” sites become occupied in addition to fcc sites. However, if a structure grows in which hcp is favored over atop or vice versa, then the coherent position would also change.

Returning to the data in Fig. 2, the ($\bar{1}11$) coherent position does initially fall, but the fall does not continue with increasing thickness (for the thicker films the very low coherent fractions lead to increased scatter in the coherent position values). The initial fall is not surprising, because if the film were not to follow entirely fcc stacking (as for a simple bulk continuation), then the “hcp” site is the only other one that is initially available. Stacking atop is not possible for the first faulted layer; however, it can occur in subsequent layers above a hcp registered layer, as will be shown below. The fact that the fall in coherent position does not continue after the first faulted layer implies that the growing film does not have a mismatch in the number of “hcp” and “atop” sites beyond this thickness.

In Fig. 3, the falling value of $f_{co}(\bar{1}11)$ shows that the site selection of the Co atoms loses coherence with the substrate. Ideal substrate continuation would show a constant high value of f_{co} with all atoms in “fcc” sites. If the substrate terminates with a stacking pattern of ...ABC, then the NIXSW site description in terms of layer and “a,” “b,” or “c” type stacking is given in Table I, where layer 1 is the first layer of the film, etc. Table II shows several different possible layer growth sequences starting with the expected fcc registry, including the effects of fcc growth with a twin boundary at the second layer and hcp growth with two different stacking patterns, and the implied XSW global sites. Using these ideas, calculations for the expected behavior of $f_{co}(\bar{1}11)$ for several different growth sequences have been made and are also shown in Fig. 3. The various stacking patterns assume a first layer of Co in the “a” (fcc) site as indicated by other investigators. It can be seen that the rapid fall of f_{co} indicates that significant fractions of the twin ...ABCacacb or a hcp pattern ...ABCAacacac are present, as both give reduced numbers of fcc sites after a small increase in coverage. In fact, no stacking sequence starting ABCac within a combination of stacking patterns can be ruled out.

For a more detailed insight into the data, they have been

TABLE II. Some possible growth sequences and the local site implied by XSW assuming a fcc registry with the substrate.

Layer	Substrate continuation	twinned			
		fcc	fcc	hcp (1)	hcp (2)
1	A	<i>a</i> = fcc	<i>a</i> = fcc	<i>a</i> = fcc	<i>a</i> = fcc
2	B	<i>b</i> = fcc	<i>c</i> = hcp	<i>c</i> = hcp	<i>b</i> = fcc
3	C	<i>c</i> = fcc	<i>b</i> = atop	<i>a</i> = hcp	<i>a</i> = hcp
4	A	<i>a</i> = fcc	<i>a</i> = fcc	<i>c</i> = atop	<i>b</i> = hcp
5	B	<i>b</i> = fcc	<i>c</i> = hcp	<i>a</i> = atop	<i>a</i> = atop
6	C	<i>c</i> = fcc	<i>b</i> = atop	<i>c</i> = fcc	<i>b</i> = atop
7	A	<i>a</i> = fcc	<i>a</i> = fcc	<i>a</i> = fcc	<i>a</i> = fcc
8	B	<i>b</i> = fcc	<i>c</i> = hcp	<i>c</i> = hcp	<i>b</i> = fcc
9	C	<i>c</i> = fcc	<i>b</i> = atop	<i>a</i> = hcp	<i>a</i> = hcp

reexpressed in terms of site occupations using the routine ARGAND,²⁴ and these are shown in Fig. 5. The site occupations shown for any layer are not the fractions of atoms in each site in that layer but the averages across all layers between the start of the film and that layer. The figure shows that the first two layers, if bilayer islands were initially present, would have approximately $80 \pm 10\%$ in the “fcc” site and $20 \pm 5\%$ in the “hcp” site (the fraction of atoms in atop sites is less than 5%). An explanation of the fraction of “hcp” sites is that the second layer has partial occupation of a “c” type site, i.e., some fraction of the film grows in the form ...ABCac while the remainder has the ...ABCAb sequence expected for the fcc continuation. Corroboration for this is provided by the MEIS measurements as reported in the next section. The “fcc” site occupation falls with coverage, owing to increasing departure from fcc growth. Similarly, “hcp” site occupation and then “atop” site occupation increases with coverage. By 8 ML, there is equal occupation of all three sites.

In summary, the NIXSW (111) measurements show that the *d* spacing of the Co layers is smaller than that of the

FIG. 5. Reexpression of the NIXSW data in terms of site occupations vs coverage for Co on Cu(111). The site designations are relative to the ideal substrate lattice continuation rather than to the local coordination.

substrate by $2.8 \pm 0.3\%$. The $(\bar{1}11)$ measurements show that although a fcc registry is favored for the first layer, there is a rapid deviation from fcc continuation stacking with increasing thickness and the initial Co islands (probably two to three layers thick) are definitely not dominated by fcc continuations. Moreover, the deviation from this ideal behavior cannot be explained by only a small density of stacking faults as previously reported.^{7,8} The rapid appearance of “hcp” sites shows that stacking in the second layer has a large fraction of atoms in this site, and the rapid drop in $f_{\text{Co}}(\bar{1}11)$ together with the appearance of “atop” sites below 3 ML shows that twinning occurs at low coverages. Beyond 3 ML, the site occupation changes more slowly towards equal occupation of the three high-symmetry sites.

B. Medium-energy ion scattering

MEIS has been used to investigate films of cobalt on Cu(111) with nominal coverages of 1.7, 4.8, 8.2, and 20.2 ML. For each data set comprising several two-dimensional energy/scattering angle data tiles, blocking curves of the scattered ion intensity as a function of exit polar angle relative to the surface normal were extracted for specific ranges of scatterer depths by integrating over energy within polygonal regions of the tiles. Blocking curves extracted in this way from the data for the three thinner films are shown in Fig. 6. These scattering signals are shown as the actual number of integrated counts, so the role of Poisson noise can be evaluated directly. The substrate scattering signal shown was obtained by integration over the energy range estimated to correspond to scattering from atoms in layers 9–15 below the surface using the data taken with an 8.2-ML Co film on the Cu(111) substrate. For the 1.7-ML film, ion scattering from the film alone is shown. For the 8.2- and 4.8-ML data, the counts originating from the outermost two layers have been removed so that scattering from the lower three and five layers, respectively, is shown. The angular positions of the dips in the substrate scattering signal have been used to correct the angular scale of the data to within 0.5° , which is a standard procedure for this instrument.¹⁹ The strong dip in this data range corresponds to the $[\bar{1}11]$ blocking directions that is expected to be at 70.5° exit angle.

Inspection of the data in Fig. 6(a) shows that the scattering from the 1.7-ML film is qualitatively similar to that from the fcc substrate, except that the $[\bar{1}11]$ blocking dip is broadened and displaced to higher exit angle. However, the data from 4.8- and 8.2-ML films shown in Fig. 6(b) differ radically from the substrate signal, indicating a deviation from fcc growth. A particularly strong feature is the blocking dip between 63° and 67° that is indicative of stacking of the form “aba” or “aca” and originates from blocking by an atom that, relative to the scattering atom, is two layers higher and is displaced by two atomic sites laterally. In a bulk hcp lattice, this would be a $[20\bar{2}1]$ -type direction.

Figure 6(b) also shows the blocking curve collected from the 8.2-ML structure, but with the sample rotated azimuthally by 60° so that the ion beam is incident in the $[1\bar{2}2]$ direction. This curve is essentially identical to that collected in the original scattering plane demonstrating that the film is sixfold symmetric, and not threefold symmetric as is ex-

FIG. 6. The MEIS blocking curves from various effective overlayer thicknesses of Co on Cu(111). The data were collected using 50-keV H^+ ions incident in the $[00\bar{1}]$ direction. (a) Comparison of the blocking curve from the 1.7-ML overlayer of Co with that from the Cu(111) substrate. The VEGAS simulations for “ab” and “ac” stacking (assuming that the substrate stacks ...ABC) are shown and the best fits to the overlayer structure and the substrate are superimposed on the data. (b) The blocking curves from 4.8 and 8.2 ML and from 8.2 ML with the substrate rotated azimuthally by 60° .

pected for a fcc (111) surface. This sixfold symmetry has been reported in previous studies⁴ and may arise from equal areas of the two possible hcp terminations or from equal areas of fcc and twinned fcc films.

To achieve a quantitative analysis of the data, simulations for various growth sequences have been calculated using the VEGAS code.^{25,26} For comparison with the data, the simulations have been multiplied by a cubic polynomial background, using a procedure that is standard for this instrument to account for variation of detector sensitivity across the angular range. It was also found to be necessary to add a small constant offset to the simulation to account for the effect of disorder in the film. The solid line through the substrate data

FIG. 7. The MEIS blocking curve from the top five layers of 1.7 ML of Co on Cu(111) compared with the four possible VEGAS simulations starting *ABC...*. The best fit to the data is shown as a solid line imposed on the data.

in Fig. 6(a) is the result of the VEGAS simulation for Cu (111) oriented crystal fitted to the data by optimizing the background and ion yield.

Also shown in Fig. 6(a) are the results of simulations for two-layer structures having the stacking sequence *ab* and *ac* relative to the underlying bulk *ABC* structure. The *ab* pair follows the ideal fcc stacking of the substrate and shows a blocking dip near 70°, like the bulk crystal. The *ac* pair (for which the second “c” layer has local hcp registry) has a much stronger dip near 75°. A mixture of these two clearly offers a way to account for the experimental data collected from the 1.7-ML film, for which we have already remarked upon the very broad blocking dip covering this angular range. Fitting this experimental curve by a mixture of these two two-layer structures yields the good quantitative fit shown by the full line in Fig. 6(a), and corresponds to 77% *ab* stacking and 23% *ac* stacking, with an uncertainty in each figure of 10% of the total. This corresponds to films in which three-quarters of the bilayers follow fcc stacking and one-quarter are twinned fcc. Notice, however, that MEIS does not distinguish between Cu and Co in the mode employed here. Previous workers⁸ have reported Cu atoms in a twinned structure atop Co islands. Some fraction of the *ac* stacking that is observed by MEIS may originate from Cu rather than Co, but the presence of *ac* stacking in the Co is unambiguously demonstrated by the element-specific NIXSW measurements.

To determine the registry of the 1.7-ML film relative to the underlying substrate, the integrated scattering intensity originating from the top five layers (i.e., including three substrate layers) has also been “sliced” from the raw experimental data. The resulting blocking curve is shown in Fig. 7 together with the results of the VEGAS simulations for the

FIG. 8. (a) The blocking curves from 4.8 and 8.2 ML of Co on Cu(111) with the best fit superimposed. The best fit was obtained by combining two pairs of three-layer VEGAS simulations representing hcp (*abc* and *aca*) and fcc twin (*aba* and *acb*) and (b) the VEGAS simulations of the four possible three-layer structures.

four possible structures beginning “*ABC...*” It can be seen that the two structures with the “b” site occupied in the fourth layer [i.e., with the first Co layer occupying hcp sites on the Cu(111) surface] have dips near 65° and 67°, where there are no dips in the data, so the registry of the first layer of the film must be completely fcc. The quantitative fit to the data shown by the solid line confirms this hypothesis. This best fit is obtained with 76% *ABCab*, 24% *ABCac*, 0% *ABCba*, and 0% *ABCbc*, with estimated uncertainties of 10% of the total. This relative occupancy of the two contributing growth sequences agrees well with that obtained from fitting the blocking curve for the two layers of the film alone [Fig. 6(a)] discussed above, and confirms the perfect fcc registry of the first layer of the film.

The blocking curves obtained from the 4.8- and 8.2-ML films are very different from those expected for a fcc continuation. Figure 8 compares these data with the results of simulations of scattering from the lower layer of the four possible three-layer stacking sequences: *aba*, *abc*, *aca*, and *acb*. Three-layer models have been selected because they

contain most of the information about the layer stacking sequence on the fcc (111) surface and create the strong dips that dominate a MEIS blocking curve. Simulations of the 16 possible stacking patterns in a five layer film were also investigated, but the fits were found to be sensitive to the starting parameters as the simulations contain a high redundancy of information of the stacking in the films. For example, a dip originating from an atom in an “*a*” site two layers above another “*a*” could occur in either the third, fourth, or fifth layer of the film and a similar quality of fit can be achieved using various mixtures of five-layer simulations containing similar three-layer patterns but in different orders.

The three-layer simulations indicate that the dips between 60° and 72° are the most informative in establishing the layer stacking sequence. A hexagonal structure corresponding to “*aba*” or “*aca*” stacking introduces a dip between 63° and 67° , whereas a fcc twin structure has “*acb*” stacking that gives a dip between 66° and 70° . In the experimental geometry used in this work, MEIS is largely insensitive to pure fcc “*abc*” stacking, owing to shadowing of “*a*” atoms by “*b*” atoms and so on. The dominant dip in the experimental data from both the 4.8- and 8.2-ML films is the one associated with hcp stacking between 63° and 67° . The dip that is characteristic of twinning between 66° and 70° is present, but is much weaker. Thus, both types of deviation from the ideal fcc structure are present, but hexagonal stacking dominates. Quantitative assessment of the stacking sequences in the 4.8- and 8.2-ML films has been made by fitting the simulations from the three-layer models to the data. Although the simulations in Fig. 8(b) show that the experiment is relatively insensitive to *aba* and *abc* stacking, the fact that the 8.2-ML film is sixfold symmetric indicates that these sequences must be present in the film in similar fractions to *aca* and *acb*, respectively. The blocking curve obtained from *aca* in the original geometry is identical to that obtained from *aba* following rotation by 60° , and similarly the blocking curve obtained from *acb* in the original geometry is identical to that obtained from *abc* following rotation by 60° . A quantitative fit to the data has been made as follows. The simulations for the *abc* and *acb* stacking sequences have been added to give the blocking curve expected for a fcc twin. Similarly, the simulations from *aba* and *aca* have been added to give the curve expected for hcp stacking. Using these two pairs of sequences, a quantitative fit to the data has been made as shown as a solid line in Fig. 8(a). This fit corresponds to $68 \pm 9\%$ hcp stacking for the 8.2-ML film and $65 \pm 9\%$ for the 4.8-ML film; the remainder being fcc twin. Care must be taken in the interpretation of this fraction, as these three-layer simulations do not completely account for the level of illumination of the scattering atoms and, more importantly, the weight that should be given to each layer in the structure. The topmost layers of the films will contribute more to the data, so the fit unintentionally weights the top of each film more highly than the lower layers. The fits show that the structure cannot be dominated by fcc and fcc twin domains to 5 ML and greater, and demonstrate that hcp is a more appropriate description by the third to fifth layer of the film.

Thicker films of Co on Cu(111) have also been investigated. Figure 9(a) shows the data from a film of Co of 20.2-ML thickness collected using the same incidence angle as previously, but with take-off angles closer to normal emis-

FIG. 9. MEIS blocking curves from 20.2 ML of Co on Cu(111) collected for 50-keV H^+ ions incident in the (a) $[00\bar{1}]$ direction (filled symbols) and (b) with the sample rotated azimuthally by 60° (unfilled symbols). Data from the substrate and the upper and lower 10 ML are compared with (c) the VEGAS simulations calculated for the four main stacking patterns with the beam incident in the $[00\bar{1}]$ direction.

sion in order to increase sensitivity to more deeply buried structures. For this thicker film, separate blocking curves are shown extracted from energy integrations corresponding to the upper and lower 10 ML of the film. The data collected following an azimuthal rotation of the sample by 60° are shown in Fig. 9(b). The experimental geometry that was selected for the majority of the experiments was one in which a pure fcc structure would be poorly illuminated owing to shadowing of the bulk by near-surface layers. This geometry was selected to maximize sensitivity to any deviations from pure fcc stacking. Upon rotating the experimental scattering

plane by 60° , however, the shadowing of lower layers is reduced and, therefore, the illumination increased. This effect can be seen quite clearly by comparing the blocking curve from the substrate for incidence in the $[00\bar{1}]$ direction with that following azimuthal rotation by 60° . The substrate data collected in the latter geometry have been multiplied by a factor of 0.2 in Fig. 9(b) to counteract the increased signal caused by the greater degree of illumination, to allow easier comparison of the curves. It should be noted that the structure of the fcc lattice rotated by 60° is the same as that created by twinning, so this increase in signal is a good illustration of the sensitivity of our original experimental geometry to twinning. Figure 9(c) shows VEGAS simulations from extended lattices with the four possible bulk stacking patterns.

Inspection of Fig. 9 reveals that the film exhibits sixfold symmetry as the blocking curves obtained in the two different azimuthal scattering planes are similar. The film has poor order as evidenced by the weak blocking dips relative to the background. The lower 10 ML of the film shows evidence of blocking dips near 36° and 48° . The first of these is expected in all structures but the latter is characteristic of hcp stacking. The upper 10 ML of the film is less well ordered but still shows a poorly defined blocking dip at 36° . Although this thick film is sixfold symmetric, the MEIS data show clearly that the upper 10 ML has little long-range order.

Figure 10 shows the effects of a 300°C anneal on the film. The annealing process improves the ordering in the structure, particularly in the upper 10 ML as shown by the increased definition of the blocking dips and the reduction in the absolute scattering signal owing to improved channeling. Following annealing, the whole film is hcp and sixfold symmetric. Strong blocking dips are now present near 36° and 48° . The strength of the dips compared with the background, particularly that at 48° , demonstrates the large improvement in order.

In summary, the MEIS measurements show that the low coverage (nominal bilayer) islands have fcc registry in the first layer, but that the outermost layer has a large fraction of atoms in the ‘hcp’ hollow sites. Films of 4.8 and 8.2 ML are dominated by hcp stacking, but both exhibit a partial fcc twinned structure. Thicker films (~ 20 ML) are disordered, but following a brief anneal to 300°C they order into a hcp structure.

C. Comparison of NIXSW and MEIS

When comparing the results of NISXW and MEIS, it is important to realize that the two techniques measure different things. NIXSW is element-specific and the absorption profile studied provides information that represents an average over all the Co atoms that are present; these data contain no information on the Cu substrate. Our MEIS data, on the other hand, do not distinguish between Co and Cu in the experimental mode employed here, as their atomic masses are too similar to be separated at the small scattering angles used and with the available instrumental resolution. When an energy slice of the MEIS data is taken, scattering from all Co and Cu atoms within the relevant depth range is included. This point is particularly important for the Co on Cu(111) system, as it is known that the initial growth is in islands and there is evidence for Cu floating on top of these Co islands.

FIG. 10. The effect of annealing on the 20.2-ML film. MEIS blocking curves are shown for (a) the upper 10 ML of the film and (b) the lower 10 ML of the film, both as deposited at room temperature (circles) and following an anneal to 300°C (triangles). The filled symbols are for incidence in the $[00\bar{1}]$ direction and the unfilled for the sample rotated by 60° to the $[1\bar{1}2]$ direction.

Bearing in mind these differences in the techniques, we can compare and evaluate their results to obtain a clearer view of the structure of the Co films grown on Cu(111). The MEIS data show unequivocally that the registry of the first Co layer is 100% in fcc sites. Understanding the registry of the second needs more careful consideration. MEIS indicates that there is a 23% deviation from fcc stacking in the *top* layer of the 1.7-ML coverage, whereas NIXSW indicates that 20% of the *atoms in the whole* film are in ‘hcp’ sites. Thus, if all the atoms in these global ‘hcp’ sites are in the second layer of bilayer islands, the NIXSW data would imply the fraction occupying this site is 40%, significantly greater than the 23% deduced from MEIS. This apparent inconsistency can be understood as a consequence of the island growth known to occur from other studies. With island growth, even given at our incidence angle of 54.7° , a fraction of the MEIS scattering signal is derived from areas of clean (fcc) Cu(111). The true fractional deviation from fcc stacking in the top layer of the film, therefore, will be higher than indicated by

the fits to the MEIS data. There remains the question of whether the initial growth is by bilayer or trilayer islands. Our experiments do not address this question directly. However, the results of the two techniques for the 1.7-ML film can be reconciled most easily if the initial growth is by trilayer islands. For a film of this average thickness, bilayer islands would leave only 15% of the surface uncovered, and this low contribution of clean surface contribution to the MEIS scattering from the outermost layers (actually reduced by the aspect ratio for the grazing incident ion beam) would make a full reconciliation of the outer-layer hcp site occupation marginal. If trilayer island growth occurs, however, both MEIS and NIXSW results are consistent with deviation from fcc stacking only in the top layer. This conclusion is implicit in the results of the VEGAS simulation of the MEIS data from the 1.7-ML Co film. In addition, the NIXSW data from the thinnest films show partial occupation of "atop" sites relative to the extended bulk structure, which can only occur in films that are three or more layers thick. A further important conclusion for the thinnest films derived from NIXSW is that a large fraction of the Co atoms show deviation from *abc* stacking in the initial islands. This conclusion contrasts with that of previous investigations by LEED,^{7,8} a method lacking clear element specificity, which states that the growth of these thin films is dominated by ideal fcc stacking.

For thicker films, both MEIS and NIXSW are qualitatively in agreement, although here too there are complementary aspects to the conclusions to be drawn from the two methods. Both methods sample the whole film, but with a bias towards the upper layers, caused by shadowing of lower layers in MEIS, and by inelastic scattering of the photoelectrons in NIXSW; the attenuation length for these electrons is estimated to be about eight layers in both reflection geometries. The thickness dependence of the site registries obtained from NIXSW (Fig. 5) shows clearly that coherence with the substrate in terms of predominance of continuing ideal fcc growth falls rapidly over about five layers. This observation *could* be interpreted solely in terms of twinning (see also Table II), and indeed other workers have reported evidence of twinning.⁹ However, the MEIS data show clearly that beyond the first two or three layers, the growth is *not* predominantly in the form of a twin. For both the 4.8-ML and the 8.2-ML data, the blocking dip corresponding to that found in simulations of twinning is much weaker than the dip that indicates hcp-type stacking. However, a growth mode in which fcc twinning occurs within the first three layers, followed by a transition to hcp growth in subsequent growth to greater thicknesses, is entirely consistent with both the MEIS and NIXSW data.

IV. SUMMARY

Developments to the techniques NIXSW and MEIS that facilitate the study of the structure ultrathin metallic film on single-crystal surfaces have been reported. It has been shown that NIXSW and MEIS reveal valuable complementary information about the atomic stacking sequence and local structure of ultrathin metal films grown epitaxially on single crystal surfaces. We have shown that NIXSW can be used to quantify the onset of stacking faults relative to the extended underlying bulk crystal in a relatively straightforward way. By contrast, MEIS has been used to determine the *local* structures and stacking patterns within the film. Both techniques provide information on the initial registry of the film to the substrate.

The deposition of Co onto Cu(111) has been investigated in the 2–8-ML regime using NIXSW and MEIS. NIXSW has been used to determine the interlayer spacing of the Co layers to be 0.058 ± 0.006 Å smaller than the Cu(111) bulk layer spacing. With increasing coverage, the coherent fraction of the ($\bar{1}11$) NIXSW decreases rapidly, indicating that the film does not grow in a fcc continuation beyond the first one to two layers. The number of global "fcc," "hcp," and "atop" sites (relative to the bulk continuation) becomes comparable at around 8 ML. In the first two layers, there is a ratio of 80:20 of fcc to hcp sites; if this initial growth is in trilayers, as we propose, this implies that 60% of the third layer occupies hcp sites. If the growth is initially in bilayers, as has been suggested by some earlier work, our result implies that 40% of the second layer has hcp registry.

MEIS measurements indicate an entirely fcc first-layer registry, but with a significant fraction of the outermost layer atoms in the thinnest films in local hcp sites, consistent with the NIXSW measurements. For 4.8- and 8.2-ML films, hcp-type stacking dominates but a fraction of fcc twinning is present. The ratio of hcp to twinned fcc of 2:1 is fully consistent with the NIXSW ($\bar{1}11$) coherent fraction and with twinning near to the interface followed by hcp growth.

For thicker films of around 20 ML deposited at room temperature, MEIS measurements reveal a largely disordered structure with poorly defined hcp blocking features. Upon annealing to 300 °C, the films order into a well-defined hcp structure.

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