Evidence for a strain-stabilized bct phase of cobalt deposited on Pd{100}: An x-ray photoelectron diffraction study

Hélène Giordano, Andrea Atrei, Marco Torrini, and Ugo Bardi*
Dipartimento di Chimica, Università di Firenze, Via G. Capponi 9, 50121 Firenze, Italy

Michael Gleeson and Colin Barnes
Dublin City University, School of Chemical Sciences, Dublin 9, Ireland
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The structure of cobalt layers grown on a Pd{100} single-crystal surface has been studied by scanned angle x-ray photoelectron diffraction. At room temperature the cobalt layers grow in a structure related to the bulk cobalt fcc phase characterized by a large expansion of the in-plane lattice parameters and a corresponding contraction of the interlayer spacing ($\sim$10%). This structure persists to coverages greater than 30-layer equivalents, and can be interpreted as a metastable body-centered-tetragonal (bct) phase. [S0163-1829(96)06339-4]

I. INTRODUCTION

The growth of thin layers of a magnetic metal on a non-magnetic substrate is of interest because of its potential application in the development of data storage devices.[1,2] A great deal of attention has been focused on the growth of cobalt on either palladium or platinum substrates, because these overlayers exhibit properties which are considered particularly suited to such applications.[3,4] Since the magnetic properties of the overlayer can be significantly affected by the substrate, it is important to study the structural properties of these systems at atomic level. Apart from the magnetic properties, there is a great deal of interest in the growth of metal films on substrates where a large lattice mismatch exists, because lattice distortion may alter the chemical and physical properties of the overlayer.

The growth of a metal on a crystal with larger lattice parameters can result in overlayers with expanded in-plane parameters and, as a consequence, a large in-plane strain. This strain can be relieved, in part, by a contraction of the interlayer spacing.[5] An extreme example of such a distortion was suggested by Bain,[6] whereby a large biaxial expansion of a fcc lattice in the {100} plane causes the stabilization of a stable bct (body-centered-tetragonal) phase. Such an effect could be envisaged to occur as a result of overlayer growth on a fcc {100} substrate with larger surface lattice parameters. Recent papers have proposed the existence of a stable bct phase of Cu both theoretically[7] and experimentally for growth on Pd{100},[8,9] although doubts have been raised about the validity of the theoretical results.[10]

In the present work we report x-ray photoelectron diffraction (XPD) results which show that cobalt grows on Pd{100} in a bct phase that can be seen as deriving from a distortion of the fcc structure involving a compression of the lattice along the direction parallel to the surface plane, and an expansion of the in-plane lattice spacing. This structure persists to relatively high cobalt coverages (>30-layer equivalents). The structural parameters of the cobalt phase are consistent with the hypothesis of a ''Bain transition'' (fcc→bct) taking place in a manner similar to that proposed for Cu and on Pd{100}. We propose that the existence of such a metastable phase is the only explanation consistent with the persistence of such a large distortion at high coverages. We will also show that upon annealing, partial alloying takes place at the interface, causing the migration of the cobalt atoms in the palladium lattice and a relaxation of the strain.

II. EXPERIMENT

All measurements were carried out in an UHV chamber with a base pressure in the low 10^{-8}-Pa region. The chamber was equipped with a multichannel hemispherical electron–ion-energy analyzer, an x-ray source with Al and Mg anodes, a quadrupole mass spectrometer, and three-grid low-energy electron-diffraction (LEED) optics. An acceptance cone of half angle 2.5° was used for all XPD measurements. The angle between the x-ray source and the analyzer was 55°. The Pd single crystal, cut and polished along the {100} plane, was mounted on a manipulator with motorized azimuthal and polar motion.

Sample cleaning involved cycles of Ar^+-ion bombardment and annealing to $\sim$900–1000 K. During the initial stages of cleaning, residual carbon on the surface was removed chemically by oxygen treatment. Subsequently, a clean surface could be routinely obtained by bombardment and annealing cycles. Surface cleanliness was monitored by x-ray photoelectron spectroscopy (XPS) at normal emission. No contaminants were detectable above the noise level on the clean surface. Reproducible formation of a well-ordered palladium surface was confirmed by LEED. Cobalt was evaporated using an electron-beam evaporator located in the analysis chamber. In all tests reported here, the substrate was kept at room temperature during deposition. Carbon contamination after evaporation was estimated from the XPS data to be never higher than 0.1 ML. In many cases no C $1s$ signal was detected above the noise level after cobalt evaporation.

The cobalt coverage on the surface was estimated from

the attenuation of the Pd $3d$ XPS emission intensity relative to the intensity from the clean surface. An inelastic mean free path of ~ 18 Å was used, taken as an average of the values calculated by the methods of Seah and Dench[11] and Tanuma, Powell, and Penn.[12] In the present work the estimated coverages are quoted in layer equivalents (LE's), corresponding to the amount of Co required to form a perfect monolayer. Since the growth of cobalt on Pd{100} is known to be in three-dimensional islands,[13] the quoted values are expected to underestimate the actual Co coverage.

All XPD measurements were made at room temperature using nonmonochromatized Al $K\alpha$ radiation ($h\nu = 1486.6$ eV). Polar angles were measured with respect to the surface normal. Curves were acquired by monitoring the electron intensity at a kinetic energy corresponding to the maximum emission from a suitable atomic core level (Co $2p_{3/2}$ at ~ 700 eV; Pd $3d_{5/2}$ at ~ 1145 eV). Background normalization was done by monitoring the electron intensity at a point on the high kinetic-energy side of the respective core-level emission peaks. The anisotropy of the XPD curves is defined here as $(I_{\max} - I_{\min})/I_{\max}$, and in the figures its value is reported in parentheses near the plotted data.

Angle-resolved XPD curves measured from a lattice structure at high outgoing electron kinetic energies (>500 eV) are characterized by strong forward focusing peaks.[14] These peaks occur at positions approximating the interatomic directions between an emitting atom and the scattering atoms of the surrounding lattice. Peaks due to scattering by atoms within the immediate vicinity of the emitter are strongest, with peak intensities attenuating rapidly as the distance of the scatterer from the emitter increases. Polar XPD curves can be considered as a direct monitor of the local geometric arrangement of atoms in a lattice structure, and hence information can be obtained directly from XPD plots by observing the positions of the main forward focusing peaks.

Calculations of the diffracted intensities were performed on the basis of the single-scattering cluster model,[14] taking into account the spherical wave correction according to Ref. 15 (SSC-SW model). The atomic scattering was described in terms of phase shifts derived from the atomic potentials. The cluster radius was limited, assuming a maximum electron path from the emitter atom. The attenuation of the electron flux as a function of the path was described by mean free paths calculated according to Ref. 12. It is well known that the SSC approximation does not provide a completely quantitative description of the experimental XPD data, since neglecting the influence of multiple-scattering effects results in an overestimation of the forward-scattering enhancement factor for the peaks corresponding to the nearest-neighbor chains. Nevertheless we found that the SSC-SW theory reproduced well the position of the experimental peaks in the Co-Pd{100}, system and that in all cases the results of the calculations agree with the simple qualitative identification of the forward scattering directions.

III. RESULTS

In a previous paper,[13] we used low-energy ion scattering and x-ray photoelectron spectroscopy to determine that cobalt grows initially on Pd{100} in three-dimensional islands. We also reported that a good agreement could be found in
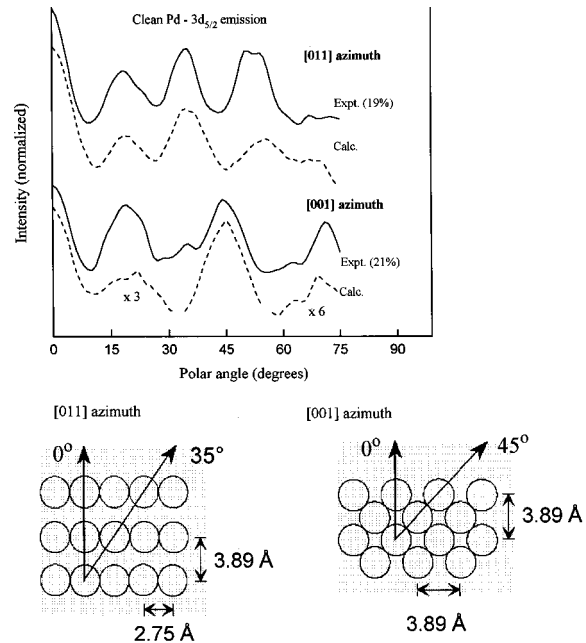

FIG. 1. Polar XPD curves measured from the clean Pd{100} surface using Pd $3d_{5/2}$ emission at ~ 1145 eV (solid curves) along the [001] (bottom) and [011] (top) azimuths. The relative anisotropies $(I_{\max} - I_{\min})/I_{\max}$ are shown in parentheses. The dashed curves are SSC-SW calculation for a bulk Pd{100} cluster. Note that sections of the calculation for the [001] azimuth are shown at a magnified intensity. The models (right) represent cross-sectional cuts of a Pd{100} bulk crystal along the two azimuths. The origin of the primary forward-focusing peaks is indicated.

the azimuthal XPD data by means of a simple model that assumed a fcc structure for the cobalt layer with the {100} plane parallel to the substrate surface. However, the question remains as to what extent the lattice parameters, both in-plane and interlayer, of the cobalt film are affected by the interaction with the Pd substrate.

Figure 1 shows polar XPD curves for the Pd $3d_{5/2}$ emission for the clean surface measured along the high-symmetry [001] and [011] azimuths. The accompanying models represent cross-sectional cuts of the Pd crystal along these azimuths. The main forward-focusing peaks occur at a polar angle of $\sim 45°$ along the [001] azimuth, and at $\sim 35°$ along the [011] azimuth. The peak at normal emission ($0°$), which occurs in polar scans along any azimuth, is due mainly to scattering between first and third layers. Other peaks on the experimental curves can also be attributed to forward-scattering directions, but are not illustrated on the model.

Also included in Fig. 1 are SSC-SW calculations for emission of Pd $3d_{5/2}$ electrons from a bulk Pd{100} lattice structure. The calculated pattern along the [011] azimuth reproduces the peak positions and relative intensities quite well. The calculation for the [001] azimuth also reproduces the peak positions. However, in this case the curve is dominated by the peak at $45°$. This is due to the well-documented overestimation of the forward-focusing peak intensity by single-scattering theory.[14] For this peak, the probable reason for the especially strong overestimation is the short emitter-scatterer separation along the [011] direction which enhances multiple-scattering effects. For this reason, in Fig. 1 the re-
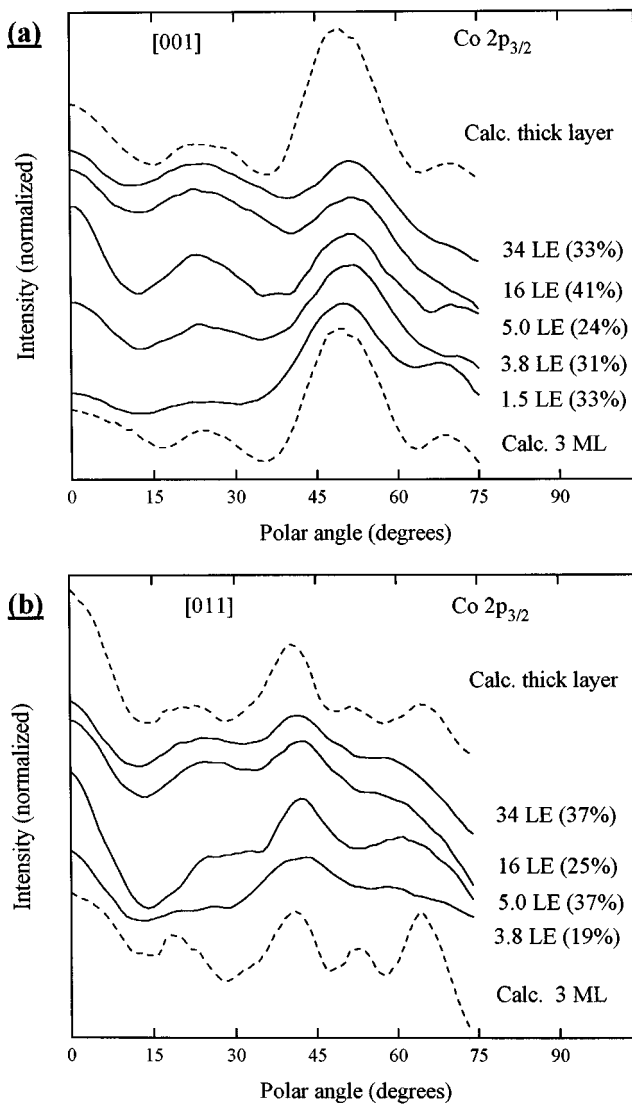
FIG. 2. Polar XPD curves measured for a range of Co coverages on Pd{100} using Co $2p_{3/2}$ emission at ~700 eV (solid curves) along the [001] (a) and [011] (b) azimuths. Coverages are quoted in layer equivalents (LE's, see text for details). SSC-SW calculations (dashed curves) are shown for a 3-ML Co film on bulk Pd{100} cluster (bottom) and a thick Co layer without substrate (top). In both cases the in-plane interatomic distance was taken as 2.75 Å and the interlayer separation (d_z) 1.6 Å.

maining structure is shown at a magnification of its calculated value.

In Fig. 2, we show XPD polar curves measured for emission from the Co $2p_{3/2}$ core level as a function of the amount of deposited cobalt. The cobalt coverages have been estimated as described in Sec. II. At 1.5 LE, a strong forward-focusing feature is already visible at ~50° along the [001] azimuth. In addition, peaks corresponding to scattering between first and third layers are visible, although weak. This is evidence that islands at least three layers in height already exist on the surface, a result that confirms those reported in Ref. 13. By a coverage of five LE's, all XPD features are fully formed along both azimuths.

As reported in Ref. 13, XPD azimuthal curves show that the structure of the cobalt film is related to the fcc bulk

structure of pure cobalt. However, compared with the positions of the forward-focusing peaks from clean palladium, the peak positions for the cobalt overlayer are substantially shifted to higher polar angles. The corresponding positions of the peaks measured at ~45° ([001]) and ~35° ([011]) from the clean Pd are ~51° (±1°) and ~41° (±1°), respectively, for the cobalt overlayer. At the energies involved in these measurement (~700 eV) the electron mean free path can be estimated as of the order of ~15 Å, hence the XPD curves reflect the structure of several atomic planes. The simplest model that can be derived from these data is a contraction of the fcc structure along the direction perpendicular to the surface to form a bct (body-centered-tetragonal) phase.[6] We can rule out the formation of different cobalt phases; for instance, a hcp phase could not give rise to the observed fourfold symmetry in the azimuthal curves.[13] We can also consider it highly unlikely that alloying takes place during deposition. Cobalt and palladium form bulk alloys over the whole range of compositions;[16] however, surface alloying at bimetallic interfaces at room temperature has normally been observed to be very slow, or not detectable at all.[17] In the present case, the fact that the positions of the Co XPD features remain constant from low to high cobalt coverages (when the Pd XPS signal has been effectively eliminated) is strong evidence against alloying during the initial stages of growth. Finally, recent results of an XPS study for the Co-Pd{111} system[18] show that the results obtained at low temperature (~100 K) are essentially identical to those at room temperature.

In the hypothesis that the measured angles correspond exactly to the interatomic directions shown on the models in Fig. 1, purely geometric consideration are sufficient for a direct determination of the ratio of the lattice constant perpendicular to the surface plane (c) to the in-plane lattice constant (a) of the bct lattice. The resulting c/a ratios are 1.14 and 1.15 from the data measured for the [011] and [001] azimuths, respectively. The corresponding ratio for an fc crystal is 1.41. This result clearly indicates that the Co lattice is strongly distorted from its bulk fcc values. Perhaps the most surprising result is the absence of any significant relaxation of the forward-focusing peaks back toward bulk Co values at high coverages.

Considerations based solely on forward scattering permit the determination of the c/a ratio, but not the absolute values of the overlayer lattice parameters. However, it is possible to impose a lower limit on these parameters by considering that in bulk fcc cobalt the shortest Co-Co interatomic distance is 2.503 Å,[19] a value which we can treat as the minimum possible separation. Using this assumption, we can calculate the interatomic distances in the distorted lattice, obtaining $a = 2.75$ Å and $c = 3.16$ Å (interlayer spacing along the c direction, $d_z = 1.58$ Å), respectively. These values correspond to a 10.7% contraction of the interlayer spacing along the [100] direction with respect to bulk fcc cobalt. Conversely, the value obtained for a corresponds to an expansion of 9.9%. The latter value matches very well the lattice parameter of palladium, and this result is a strong indication that cobalt grows as a pseudomorphic layer. This result is also in agreement with LEED observations[13] of a 1×1 periodicity in the whole range of coverages examined.

These considerations can be confirmed on the basis of

SSC-SW calculations. Several structural models were examined, but the only one that provided a reasonable qualitative agreement with the whole set of experimental data was that of a fcc cobalt lattice contracted along the $\langle 100 \rangle$ direction, assumed to be perpendicular to the substrate surface. In Fig. 2 we show calculations for the Co $2p_{3/2}$ emission (~ 700 eV) from three-layer slab of Co on a Pd{100} substrate, and from a cluster containing a number of layers several times larger than the electron mean free path. In both cases the in-plane parameter was 2.75 Å and the interlayer spacing (d_z) was 1.6 Å, approximately the values calculated from the simple geometrical model described above. The calculations for the [011] azimuth are structurally richer than those for the [001] azimuth, but the agreement with the experimental curves is worse, and it appears that in the experimental curves the features are broadened and have merged with each other. This is an indication of some degree of disorder within the lattice structure, resulting in a variety of local scattering geometries and a range of possible lattice parameters. However, in both azimuths the forward-focusing peak maxima remain at a constant position with coverage, indicating that a favored mean lattice structure exists. Calculations for variable values of d_z are shown in Fig. 3. In all cases, the best agreement is found for values of the interlayer spacing of 1.5–1.6 Å close to that determined from geometrical considerations. This is most clearly obvious for the [011] azimuth, but is also evident for the [001].

In all these calculations the interlayer distances in the cobalt overlayer are kept to the same value, but we also performed tests where they were varied independently, in particular assuming that the first interlayer distance was shorter than the remaining ones. The comparison with the experiment shows that it is not possible to rule out slightly variable interlayer distances; however, we found that a strong contraction of all the interlayer distances is a necessary condition in order to obtain a good agreement with the experimental data. The contraction of the the first layer only is not sufficient, even assuming physically unrealistic values.

We also performed calculations where the in-plane lattice parameters were varied, still maintaining the values of the lattice parameters in such a way that the c/a ratio remained 1.15. The results are shown in Fig. 4 along with the 5.0-LE experimental curve for comparison. The agreement between theory and experiment is worse for $a < 2.75$ Å, most clearly obvious by the shift in the peak at $\sim 40°$ along the [011] azimuth. For values of $a > 2.75$ Å the level of agreement is approximately constant, and a reliable distinction cannot be made. Though not conclusive, the results favor a Co in-plane lattice parameter equal to that of Pd, as there would be no reason for the overlayer to assume a lattice parameter larger than that of the substrate.

We also observed that annealing affects the lattice parameters of the surface. A cobalt layer deposited at room temperature for a coverage of approximately 3.7 LE's was annealed in two stages at ~ 670 K: an 8-min anneal period followed by a 12-min period. After annealing, the XPS spectrum showed a significant reduction in the cobalt signal, indicative of alloying. Figure 5 shows the evolution of the XPD polar curves for both Co $2p_{3/2}$ and Pd $3d_{5/2}$ emission along the [001] azimuth. For cobalt, along the [001] azimuth the peak at $\sim 51°$ shifts to $\sim 47°$, whereas along the [011]
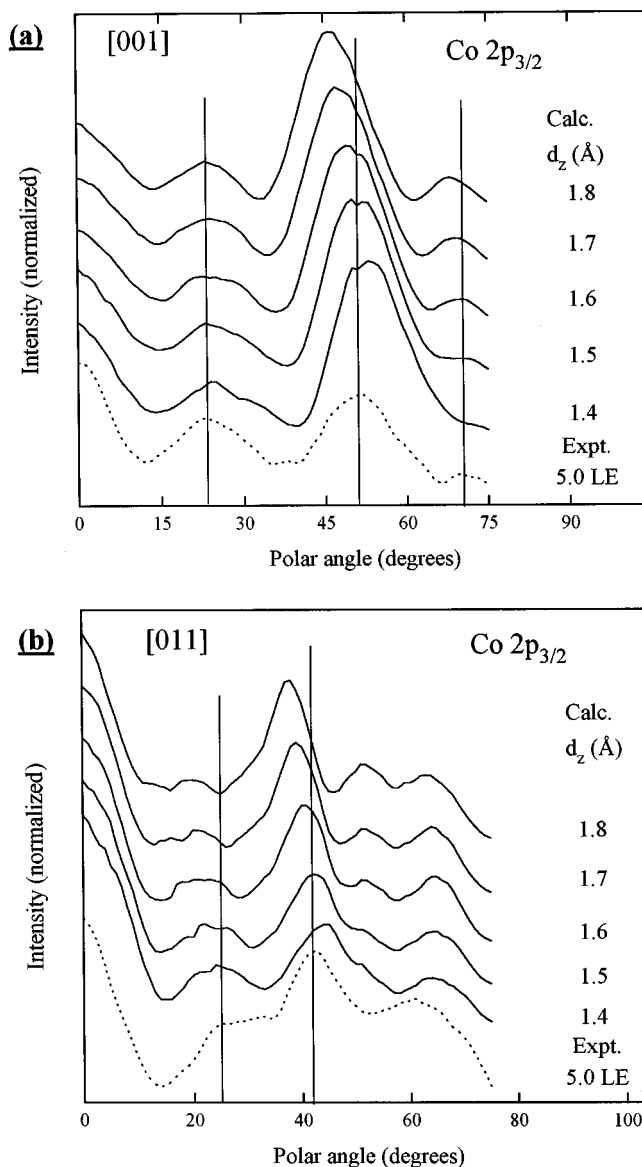

FIG. 3. SSC-SW calculations for a thick Co cluster (no Pd substrate) using Co $2p_{3/2}$ emission (solid curves) along the [001] (a) and [011] (b) azimuths. The structural model is derived from the fcc lattice with the in-plane interatomic distance of 2.75 Å and d_z (interlayer spacing) varied from 1.4–1.8 Å. The polar XPD curves measured from the five-LE Co overlayer is also shown (dashed curve).

azimuth the peak at $\sim 41°$ shifts to $\sim 37°$. The shift in peak position back toward those of bulk Pd is a natural consequence of the incorporation of the Co atoms within a bulk Pd lattice structure. However, the position of the diffraction peak due to forward focusing between first and second layers along the [001] azimuth ($\sim 47°$) indicates that some contraction in the lattice parameter is still present. In the case of the Pd $3d_{5/2}$, the same qualitative considerations apply; note also the rapid attenuation of intensity of the Pd signal for the ''as-deposited'' cobalt film, expected if most palladium is located below the surface. These considerations can be quantified by SSC-SW calculations, also shown in the same figures. The best agreement was found for a cobalt interlayer spacing of 1.8 ± 0.05 Å.
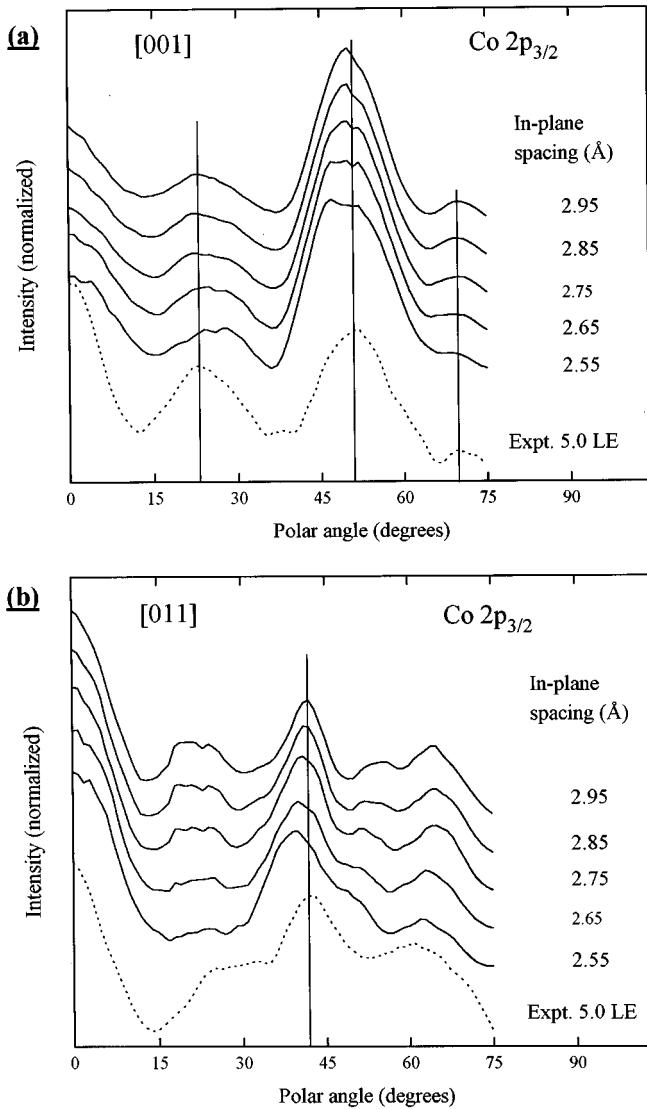
FIG. 4. SSC-SW calculations for a thick Co cluster using Co $2p_{3/2}$ emission (solid curves) along the [001] (a) and [011] (b) azimuths. In the structural model, the in-plane interatomic distance is varied in the range 2.55–2.95 Å. In each calculation, the inter-layer spacing perpendicular to the surface is varied in such a way to maintain constant the measured c/a ratio (1.15). The experimental curve measured from the five-LE Co overlayer is also shown (dashed curve).
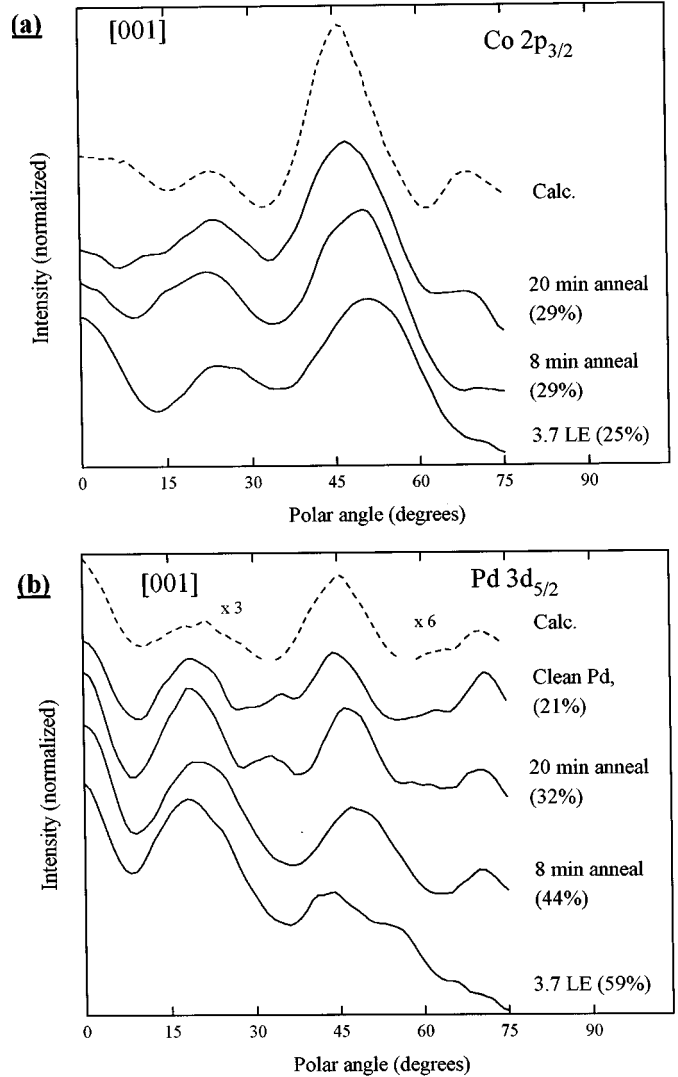

FIG. 5. Polar XPD curves measured along the [001] azimuth using Co (a) and Pd (b) emission. The experimental curves were measured following deposition of 3.7 LE of Co, after annealing to 670 K for 8 min and after reannealing to 670 K for a further 12 min. The polar XPD curve measured from clean Pd is included in (b) for comparison. The dashed curve corresponds to a SSC-SW calculation from a cluster where cobalt atoms are randomly dispersed in the palladium lattice. Note that sections of the calculated Pd curve are shown at a magnified intensity.

IV. DISCUSSION

A model illustrating the basic results obtained in the present study is shown in Fig. 6. The distortion of the cobalt lattice is certainly high in comparison to the results reported in the literature so far, and it is important discussing the possible sources of error affecting the measurement. Assuming an uncertainty of the order of ±1° in the determination of the forward-focusing peak, we can set an error bar to the measured value of the contraction of approximately ±3%. Hence, even in the hypothesis of an experimental overesti-mation of the angle, the lattice contraction remains large, at least of the order of 8–9 %. If we were to assume that the contraction is not the same for all layers, the average value

should still be around 10% and some of the layers should be even closer to each other. Refraction by the surface at these energies is generally small ($\sim$0.5°),[14] and would have only a minor effect. Other angular effects, such as the characteristic drop in intensity at grazing emission ($>$50°), are accounted for by the background normalization, and in any case the effect of this drop is to shift peaks toward normal emission, hence to underestimate the effect. Regarding the possibility of partial alloying affecting the structure of the overlayer, as discussed earlier on, it is unlikely to occur in any appreciable extent at room temperature. In any case, the results of Fig. 5 show that deliberate alloying has the effect of reducing the distortion and of bringing the lattice perameters closer to those of bulk fcc.
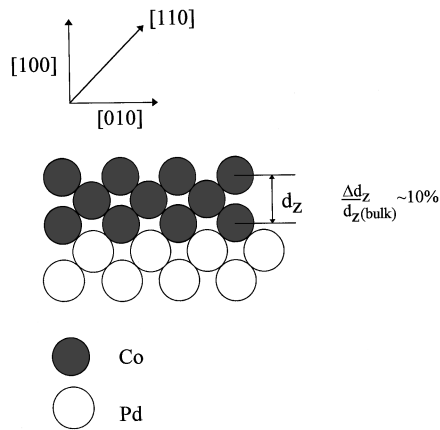
FIG. 6. Schematic model of the Co-Pd{100} interface as it results from the measurements performed in the present work.

The high values of the contraction find some support from the data reported in the literature for similar systems. Considering pure cobalt surfaces, in crystallographic LEED studies no detectable contraction in the first- to second-layer distance was reported for the densely packed Co(111) and Co(0001) surfaces.[20] However, a contraction was observed for more ''open'' Co{100} surfaces: 4% for the Co(100) surface[21] and 8.8% for the Co(11$\bar{2}$0) surface.[22] The last result indicates that contractions of the order of 10% in the interlayer distances in cobalt are possible, especially considering that in the present case the contraction does not involve a reduction of the Co-Co nearest-neighbor distance.[23] The expansion of the cobalt lattice to match the parameter of the substrate is also not unrealistic when compared with the literature data. In the case of the Co-Pt system, where the lattice mismatch is approximately the same as for the Co-Pd one, it has been demonstrated by LEED crystallography that on the Pt(111) face cobalt adopts the in-plane parameter of the substrate.[24] Our results can also be compared with those reported for the case of copper on Pd{100}, where a metastable bct phase of copper has been theoretically suggested[7] and observed experimentally.[8,9] This phase represents a local-energy minimum of the distorted fcc lattice structure. The lattice parameters determined for Cu on Pd{100} were $a=2.75$ Å and $c=3.1$ Å ($d_z=1.55$ Å).[10] These yield a c/a ratio of 1.13, a value very similar to the ratio determined in the present work for the Co-Pd system (1.14–1.15).[25] Finally, we can note how in the case of the Cu-Pt(100) system, where the lattice misfit is 8.7%, a pseudomorphic Cu layer exhibiting a strain of about 9% in the {001} plane was reported to form up to a coverage of 10–15 atomic layers.[25] It can therefore be concluded that, although there is some uncertainty on the exact value of the lattice parameters, in any case the model of a cobalt bct lattice (Fig. 6) agrees with all the experimental results available and is not physically unrealistic.

The stabilization of the bct structure can be explained in terms of the relaxation of in-plane strain due to a lattice expansion by a contraction of the interlayer spacing. An estimation of the expected contraction for a given in-plane expansion can be obtained using the Poisson module of cobalt ($\nu=0.31$). The expected contraction of the interlayer spacing

(Δd_z) for a given in-plane expansion (Δa) is related to the Poisson module by the well-known formula[5]

$$\frac{\Delta a/a}{\Delta d_z/d_z}=\frac{1-\nu}{2\nu},$$

where a and d_z are bulk lattice parameters of the material. Assuming that the cobalt in-plane lattice parameter expands to match that of the palladium, the Poisson equation yields an interlayer contraction of ~0.16 Å (8.9%). The contraction determined in Sec. III on the basis of the forward-scattering peak position (0.19 Å) corresponds to a Poisson module of 0.35. The two values can be said to be in acceptable agreement considering the uncertainty associated with applying the Poisson formula to a single-crystal material

In general, it would be expected that the high strain associated with the lattice expansion to match the overlayer-substrate parameters to be partially relieved by the growth of defects within the overlayer structure.[23] The presence of defects should allow the relaxation of the lattice parameters back toward bulk values as the cobalt coverage increases. The coverage required for relaxation to occur is dependent on the percentage misfit between the lattice parameters of the substrate and the adsorbate. Clearly, the results reported here are at odds with this general picture. The large in-plane mismatch involved (9.9%) should not allow good epitaxial growth, and relaxation to bulk lattice values would be expected to occur at low (<10 LE) Co coverages. In this respect we should note that XPD, as all diffraction-based techniques, is sensitive to ordered phases only, and we cannot rule out that a significant fraction of the cobalt present on the surface is in a random oriented or disordered phase that gives no detectable feature in XPD. Nevertheless, the constancy of the Co XPD features with coverages clearly indicates that at least a fraction of the overlayer film forms a bct phase, stable up to a coverage of about 30 LE. It appears that the persistence of this phase for relatively large coverages can only be explained assuming that it represents a local-energy minimum of the structure obtained compressing the fcc lattice along the ⟨100⟩ direction.

V. CONCLUSION

Cobalt overlayers grown on Pd{100} at room temperature form a bct structure that can be interpreted as resulting from the deformation of a fcc structure characterized by a large in-plane lattice expansion, coupled with a contraction of the interlayer spacing. The experimental curves are found to be most consistent with an in-plane lattice parameter of 2.75 Å (pseudomorphic with the Pd substrate) and an interlayer spacing of 1.5–1.6 Å. This structure persists to Co coverages of greater than 30 LE. Annealing of a cobalt overlayer on Pd{100} to 670 K results in alloying at the interface and in a reduction of the lattice strain at the interface.

*Electronic address: Bardi@Cesit1.unifi.it

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