Structure Determination of Metastable Cobalt Films

Y. U. Idzerda, W. T. Elam, B. T. Jonker, and G. A. Prinz
Naval Research Laboratory, Washington, D.C. 20375
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The bulk atomic structure of cobalt films deposited on GaAs has been unequivocally determined to be the body-centered-cubic metastable phase. A comparison of the conversion-electron x-ray-absorption fine structure of Co films deposited on GaAs(110) with similar measurements for the stable phases of hcp Co, fcc Cu, and bcc Fe establishes the Co bcc phase with a lattice constant of 2.82 ± 0.01 Å. Furthermore, this first application of the technique to single-crystal epitaxial films shows it to be a most powerful procedure for establishing their crystal structure.

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The generation and stabilization of thermodynamically metastable crystal structures for studies of their material properties is the first step in crucial tests of a new class of total-energy calculations.[1] True metastable phases (a local minimum of the total energy under conditions of zero pressure or applied field) should be differentiated from forced structures which are externally maintained, for example, by interfacial energies which force registry with an underlying substrate surface net. Although metastable phases may be initially stabilized by deposition onto a suitable substrate, because of the nonequilibrium nature of the growth process additional deposition leads to the formation of a true metastable, stress-free film. Each arriving atom finds it energetically more favorable to assume the metastable structure than to locally distort the surrounding atoms into the more stable phase. For forced structures, the interplay between interfacial energies and bulk strain energies generally results in some form of crystal distortion and a thickness-dependent lattice constant which "relaxes" with increasing thickness toward the equilibrium bulk value. This variation in lattice spacing is accommodated by generation of crystal dislocations and is often accompanied by a variation in the material's properties.[2] These shortcomings are absent in metastable crystal structures which maintain a single atomic spacing with no variation in material properties. Also, the excess energy of the metastable phase above the thermodynamically stable structure should be manifest by interesting magnetic and electronic behavior, making the phases more technologically interesting and scientifically valuable than their more stable counterparts.

The body-centered-cubic (bcc) phase of cobalt is an especially interesting example of a metastable phase. Although not present on the known thermodynamic phase diagram, it can be concluded on general grounds that it should exist as a metastable phase. The electronic band structure for bcc Co was first calculated by Bagayoko, Ziegler, and Callaway[3] using a density-functional method and assuming a range of bcc lattice constants based upon a Wigner-Seitz radius consistent with other Co phases (i.e., a near constant atomic density regardless of the crystal structure). The first prediction of the true lattice constant[4] was based upon metallurgical data from the Fe-Co alloy system,[5] and provided the guidance for its first synthesis by epitaxial growth upon GaAs.[4] Subsequent total-energy calculations[6] showed the bcc phase to be metastable and occur at an equilibrium energy slightly higher (0.06 eV/atom) than the calculated minimum for the fcc phase and at an atomic spacing in close agreement with the observed value. Other total-energy calculations[7] then showed that the minimum of the fcc phase was only 0.03 eV/atom higher in energy than the minimum for the hcp phase, which is the lowest-energy phase. The calculated band structure for bcc Co shows it to possess a spin-resolved electronic structure which is unique, containing only a very few unfilled electron states of majority-spin character.[3,8,9] This band-saturated electronic structure and the large exchange splitting have been exploited in this material for the clear observation of fundamental electron spin-flip transitions (Stoner excitations) and for the first observation of multiple structures in these spin-flip spectra.[10]

Although several investigations of the properties of Co/GaAs films have been performed, with additional experiments forthcoming, no *direct* confirmation of the bcc structure of the bulk phase has yet been published. Since many intriguing and controversial conclusions rely on the assumed bcc structure, it is extremely important that the atomic structure of the examined films be determined. The cubic nature of these films was inferred by electron diffraction [reflection high-energy electron diffraction (RHEED)],[5] and the symmetry properties investigated by vibrating-sample magnetometry and ferromagnetic resonance,[5,11] and through a variety of x-ray diffraction studies.[12] However, the complete atomic description has remained inconclusive. (Initial growth studies indicate that the first stages of film growth are characteristic of bcc formation,[13] but additional deposi-

tion may result in the development of hcp or fcc phases.) The difficulty in unambiguously establishing the film structure is a consequence of the fact that the resulting Co lattice parameter very nearly matches half that of GaAs. Any long-range-order probes of the Co/GaAs films (such as diffraction) will produce a signal which is submerged in the much larger signal produced by the substrate. Hence, these films needed to be examined using an element-specific, local-order probe which is unaffected by the presence of the substrate.

We have confirmed the bcc structure of these metastable films through the use of such a probe—conversion-electron x-ray-absorption fine structure.[14,15] This is a recently developed modification of the more typical extended x-ray-absorption fine-structure (EXAFS) technique in which the electrons emitted by the sample, due to Auger decay of the core hole produced during x-ray absorption, are detected in a He-gas ionization chamber.[16] A diagram of the apparatus is shown in Fig. 1, with the relevant voltages and signals as configured for this work. Note that the sample itself serves as part of the signal collection electrode. The sample current has been shown[15,16] to directly reflect the x-ray-induced core-hole creation and therefore a determination of the local structure of the material can be made by analysis of the variations in the sample current with changing photon energy as is done for EXAFS. The spectra were measured using the NRL materials analysis beam line (X23B) at the National Synchrotron Light Source. The properties of this beam line relevant to x-ray spectroscopy have been presented elsewhere.[17]

For comparative purposes, the conversion-electron extended fine structure (EFS) above the K edge of four closely associated materials was recorded. The extended fine structure of a 357-Å Co film deposited on the (110) surface of GaAs (believed to be in the metastable bcc phase) was compared to three standard samples of well-known atomic structure; a rod of polycrystalline hcp Co (the stable room-temperature phase of bulk Co), a foil of fcc Cu, and a film of polycrystalline bcc Fe which had been deposited onto a clean glass slide. The Co film was grown by molecular-beam-epitaxy techniques under ultrahigh-vacuum conditions. Details of the Co growth have been presented elsewhere.[5] All samples were exposed to air for an extended period prior to the EFS measurement.

A direct comparison can be made between the Co-film data and the data for the hcp Co, the fcc Cu, and the bcc Fe standards. The bcc Fe is used because it is only reduced by 1 in atomic number from Co and therefore generates an EFS which is nearly identical to the spectrum anticipated for bcc Co. Similarly, fcc Cu is only slightly different in atomic number from Co and can be used to obtain an fcc EFS reference spectrum. The measured electron current of the four samples versus photon energy is shown in Fig. 2. The spectra are displayed with the incident photon energy referenced to the energy of the excitation edge. These reduced energies therefore reflect the photoelectron energy within the media and can be directly compared. A linear background is removed from the measured electron current which is also

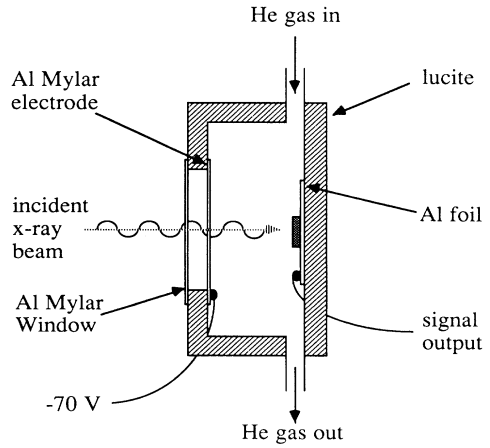

FIG. 1. Conversion-electron x-ray-absorption fine-structure apparatus. Sample is mounted inside a He-gas ionization detector.

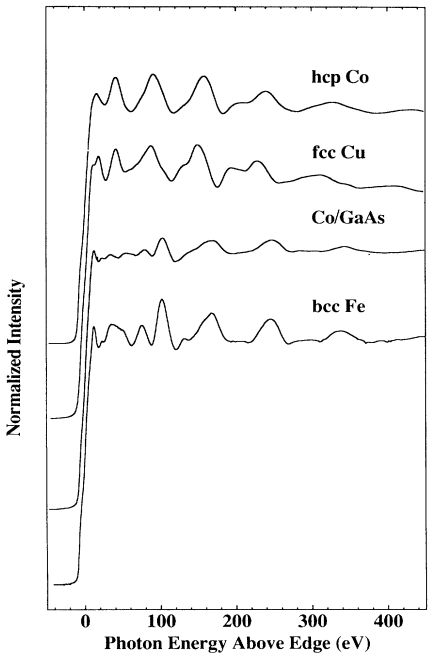

FIG. 2. Conversion-electron x-ray-absorption fine-structure spectra for a polycrystalline hcp Co rod, an fcc Cu foil, a Co film deposited on GaAs(110), and a thick film of bcc Fe deposited on a glass slide. Incident photon energies referenced to K edge of material. Spectra have a linear background removed, are normalized for unity step height, and are vertically offset for clarity.

normalized for a unity excitation step height. Two small, sharp current spikes associated with Bragg reflections from the single-crystal sample (film and substrate) have also been removed from the Co/GaAs data. The resulting spectra are vertically offset for clarity. Although the structural comparison is most easily performed after a Fourier transform, it is clear that the EFS of the Co thin film deposited on GaAs more nearly resembles the structure in the bcc Fe spectra than those of the other spectra.

Following the standard EXAFS analysis procedure,[18] the EFS of each spectrum is isolated, transformed from energy space to wave-number space, and Fourier transformed to obtain the radial distribution functions (RDF's), shown in Fig. 3. The wave-number range used in these transforms is $3.0\ \text{Å}^{-1} \leq k \leq 10.8\ \text{Å}^{-1}$. A direct comparison of the RDF's for the four samples clearly shows that our initial conclusion that the Co film is a bcc structure is now completely established. All major and minor peaks in the bcc Fe RDF are reproduced with the correct relative positions and nearly the same relative intensities (within the uncertainties established by the background subtraction) in the Co/GaAs RDF. (The small peaks at < 1.5 Å are not real and represent residuals of the background subtraction.) The RDF of the fcc structure is similar to the hcp RDF with additional variations in the third main peak and is easily distinguished from the bcc signature.

Because the transforms used here purposely do not include the electron phase shifts associated with the backscattering process, the radial coordinate of Fig. 3 does not represent the actual interatomic distances. To accurately determine the bcc Co lattice spacing, application of the EXAFS ratio method[19,20] is made to the EFS associated with the first major peaks of the RDF for the bcc Co film and the other materials. In this analysis technique, the EFS from a single coordination shell of a standard material with known structure is isolated and compared with the similarly isolated coordination shell for the measured EFS of the unknown. In this way, the bcc Co nearest-neighbor spacing is determined to be 2.44 ± 0.01 Å, corresponding to a bcc lattice constant of 2.82 Å. This compares very favorably to the lattice constant (explicitly assuming a bcc structure) determined by RHEED[5] and x-ray diffraction[12] of 2.825 Å and to the predicted bcc spacing.[6] A comparison of the relative disorder of the first coordination shell of the Co/GaAs and bcc Fe can be made. Utilizing an extension of the ratio method employing a cumulant expansion,[21] we find that the disorder is small and slightly asymmetric and can be characterized by a small increase in a Debye-Waller-type coefficient of 0.0011 Å^2 (with an additional small third term).

One remaining anomaly is the overall factor of 2 reduction in the Co/GaAs RDF intensity in comparison with the other spectra. This intensity reduction is also evident in the EFS data of Fig. 2. The reduction cannot be due to multiple phases in the film since the detailed analysis finds no evidence for additional phases (detection limit $< 10\%$). The analysis also finds no indication of significant interdiffusion at the Co/GaAs interface or of substantial oxidation of the Co surface. [The interdiffusion which does occur has been found to involve only ~ 20 Å of material at the (110) interface.[13]] Similar intensity reductions are observed in EXAFS mea-

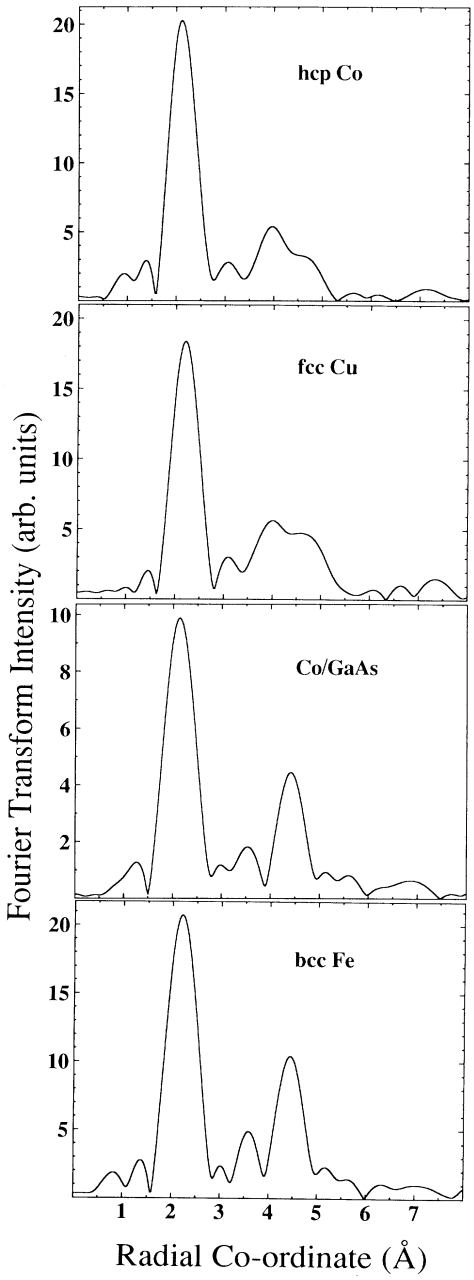

FIG. 3. Fourier transform of isolated fine structure for the polycrystalline hcp Co rod, an fcc Cu foil, a Co film deposited on GaAs(110), and a thick film of bcc Fe. Radial coordinate does not correspond to actual atomic spacings (see text).

surements of nanocrystalline materials which have approximately equal numbers of atoms at grain-boundary and interior crystal sites,[22] and in bcc Mn/Ag superlattice films where a significant tetragonal distortion of the Mn bcc structure exists.[23]

In conclusion, we have used conversion-electron EXAFS to unambiguously determine the structure of a metastable phase of Co grown on (110) GaAs. This demonstrates the first use of this technique to determine the structure of an epitaxially grown single-crystal thin film. In addition to clarifying the existence of this artificial phase, this work establishes a new and powerful approach to structural characterization of epitaxial films. This approach is especially important since, unlike diffraction techniques, it is element specific and can readily distinguish between film and substrate.

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