Transmission electron microscopy investigation of Co thin films on GaAs(001)

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Transmission electron microscopy (TEM) observations of the microstructure of epitaxial Co thin films on GaAs(001) are reported. Cross-sectional TEM confirmed both bcc-Co and hcp-Co exist in a single 345 Å film. During film growth by molecular beam epitaxy, the epitaxial bcc-Co layer forms first at the GaAs interface, and hcp-Co islands subsequently form at the free surface of the bcc-Co layer when it reaches a thickness of about 145 Å. The bcc-Co film is single crystal at early stages of growth, but later may develop into multiple bcc crystals. The final hcp-Co grain size is roughly 15–20 nm, and selected area electron diffraction showed these grains are strongly textured. Four previously unreported variants of the hcp-Co/GaAs orientation relationship were observed in which the *c* axis of the hcp unit cell lies out of the plane of the film. [S0003-6951(99)02529-2]

The growth of ferromagnetic films on semiconductor substrates has received much attention over the past decade. The combination of the magnetism of the ferromagnetic layer along with the electronic properties of the underlying substrate offers the opportunity for innovative magnetotransport effects and devices to be realized. For example, the discovery of giant magnetoresistance (GMR) was made in an Fe/Cr superlattice epitaxially grown on GaAs.[1] In many GMR devices, cobalt plays an important role due to the high spin polarization of the carriers at the Fermi level.[2] Therefore, understanding the growth and microstructural evolution of Co on semiconductors, and how its crystal structure affects the magnetic and transport properties, is of technological interest. Furthermore, Co growth on GaAs is of special interest since the Co forms a crystallographic phase not found in bulk form for this element.

The low-temperature equilibrium structure of Co is hcp while the high-temperature phase is fcc. However, a nonequilibrium bcc structure, which does not naturally occur in bulk materials, was obtained by Prinz using epitaxial growth on GaAs(110) substrates.[3] The epitaxial growth of Co on GaAs serves as a model system in which equilibrium and metastable phases of Co can be examined both experimentally and theoretically. Researchers have grown and analyzed films of Co on both GaAs(110) and (001) substrates with varying results.[3–9] Theoretical calculations have suggested that bcc Co is not a true metastable phase but that it is a forced structure stabilized by the interaction with the GaAs substrate.[10] In addition, the presence of fcc-Co in these films has not previously been experimentally observed, but was suggested to coexist with hcp-Co and bcc-Co on 500-Å-thick films electrodeposited on GaAs(001).[11]

Stabilizing the nonequilibrium epitaxial phase of bcc Co is heavily dependent on processing conditions such as substrate surface preparation and various growth conditions, including temperature and deposition rate. Changes in these parameters may contribute to many of the discrepancies found in the literature. Since researchers have primarily relied upon indirect evidence to make conclusions concerning the microstructural evolution in such films, we have undertaken a transmission electron microscopy (TEM) study to examine in detail the microstructure of Co films on GaAs(001). This allows direct observation of the films and removes ambiguity associated with the surface diffraction techniques commonly employed.

A series of Co films ranging in thickness from 50 to 875 Å were grown by molecular beam epitaxy. The specifics of film growth have been described elsewhere.[3,5] The Co film structure was monitored *in situ* using reflection high energy electron diffraction (RHEED) and Auger spectroscopy. Samples were made for both plan view and cross-sectional TEM by dimpling and ion milling.[12] Conventional TEM was performed on a Philips CM30 at 300 KV and high resolution TEM was done using a Hitachi H9000 operating at 300 kV. Atomic force microscopy images revealed that the bare substrates were flat with an rms roughness of less than 5 Å.

Figure 1 shows representative RHEED patterns obtained during film growth. The first set of diffraction patterns shown in Fig. 1(a) are from the virgin GaAs substrate. These initial RHEED patterns show well-defined GaAs spots, indicating a high-quality single-crystal substrate surface prior to deposition of the Co film. During Co deposition, however, the RHEED patterns change quite drastically. RHEED patterns characteristic of a bcc structure are obtained for a 30-Å-thick Co film and shown in Fig. 1(b). The registry between the bcc-Co and the bare GaAs patterns is clearly seen, demonstrating the epitaxial growth of Co on GaAs. As the film thickness increases above 150 Å, the RHEED spots indicate a hcp structure as shown for a 200-Å-thick Co film. The diffraction patterns in Figs. 1(b) and 1(c) look quite different due to the change in crystal structure which is dependent upon only the layer thickness. It was also observed that the hcp-Co pattern remains for films well over 500 Å.

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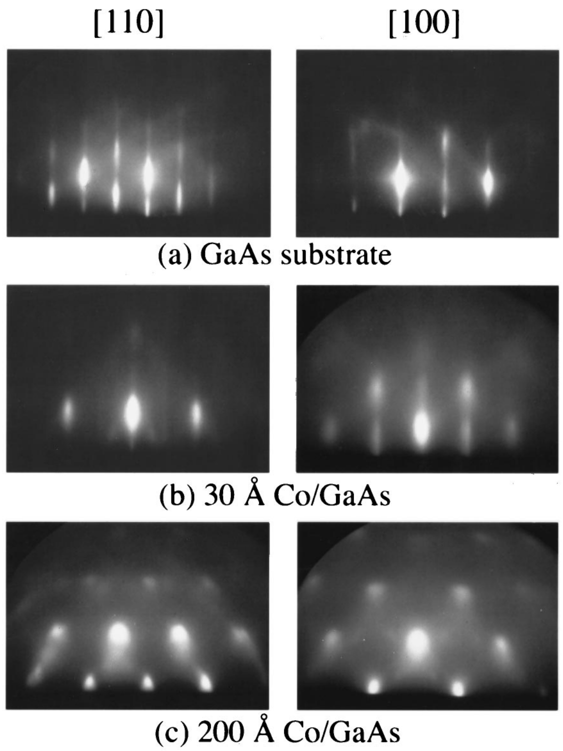

FIG. 1. RHEED patterns obtained along the [110] and [100] directions at various points in the Co film deposition: (a) the GaAs substrate, (b) a bcc 30 Å Co film, and (c) a hcp 200 Å Co film.

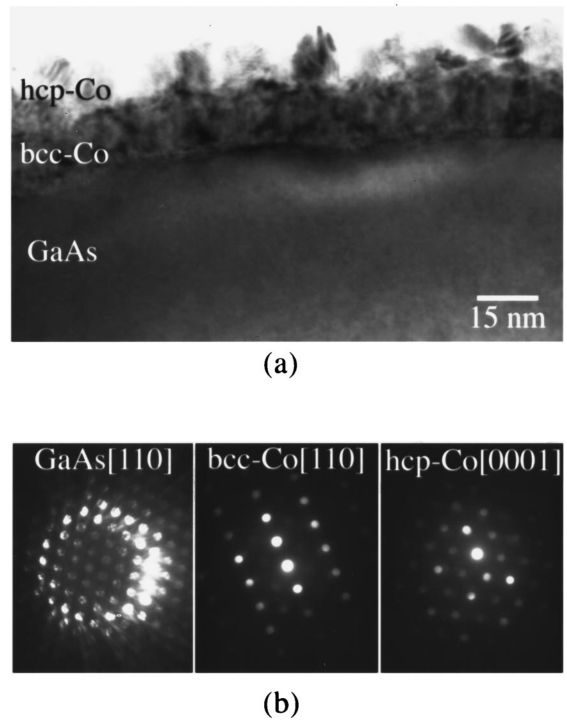

FIG. 2. (a) Cross-sectional TEM image of a 345 Å Co film showing two distinct layers (bcc and hcp) in the Co film. (b) Convergent beam electron diffraction patterns from the GaAs and the two layers of the Co film.

Although a range of film thicknesses was examined using TEM, the results reported here are from two thicknesses: 150 and 345 Å. Figure 2(a) shows a cross-sectional TEM image of the 345 Å Co film where two distinct layers are seen. The layer at the Co/GaAs interface is approximately 145 Å thick and its structure was determined to be bcc Co using convergent beam electron diffraction (CBED) [Fig. 2(b)]. Diffraction experiments indicate that the bcc-Co film is a single crystal when its thickness is 80 Å, but for a film thickness of 150 Å, multiple crystals may exist in the bcc layer. A cube:cube orientation relationship between the GaAs and the bcc-Co was observed, as indicated by the fact that the beam directions of the GaAs and the bcc-Co diffraction patterns are both $\mathbf{B}=[110]$ [Fig. 2(b)]. [The GaAs pattern in Fig. 2(b) is not exactly along the [110] zone axis which is due to foil bending in the TEM.] This result was verified by diffraction experiments from specimens in which the electron beam was parallel to $[100]_{GaAs}$.

As seen in Fig. 2(a), the interface between the Co film and the GaAs substrate is not smooth and this roughness could have developed during Co deposition. This is in agreement with the results of the RHEED patterns obtained in Fig. 1(b) where diffuse spots are indicative of surface roughness in the film which persisted throughout the deposition process.

The hcp-Co layer is not directly in contact with the substrate itself due to the presence of the bcc layer. The hcp grains are approximately equiaxed (not columnar) and details as to the development of this layer are provided by examination of a thinner film. A micrograph of the 150 Å film is shown in Fig. 3 where hcp-Co islands (marked by arrows) are observed at the free surface of the bcc-Co layer. The Co layer is approximately 140–150 Å when these hcp islands are first observed. Observations of films that are 100–120 Å thick show no evidence of hcp-Co island growth, while a continuous polycrystalline hcp-Co layer exists in the 345-Å-thick film (see above). These results indicate that the bcc-Co layer forms first on the GaAs substrate, then hcp-Co islands nucleate and grow upon the bcc-Co until they coalesce to form a continuous, polycrystalline hcp-Co layer. These results present no evidence of hcp-Co growing at the expense of bcc-Co. However, the bcc-Co layer in a thicker film (875 Å) was only 40–50 Å. Further experiments are underway to determine if this was a result of a variation in the film growth parameters or if the hcp-Co begins to consume the bcc-Co layer in thicker films.

As seen in plan-view TEM, the top layer of the 345 Å film is continuous polycrystalline hcp-Co with an average grain size of roughly 15–20 nm [Fig. 4(a)]. This grain size was observed to increase to 40–50 nm in thicker films. The

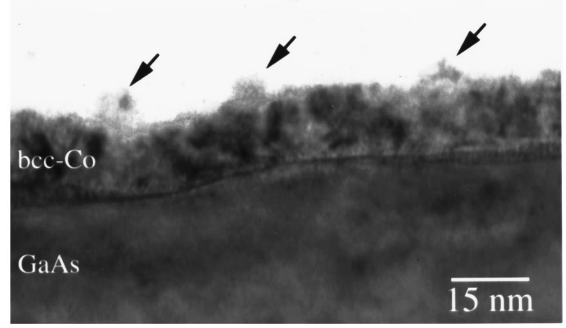

FIG. 3. Cross-sectional TEM image of 150 Å Co film showing formation of hcp-Co islands (arrowed) at the free surface of the bcc-Co layer.

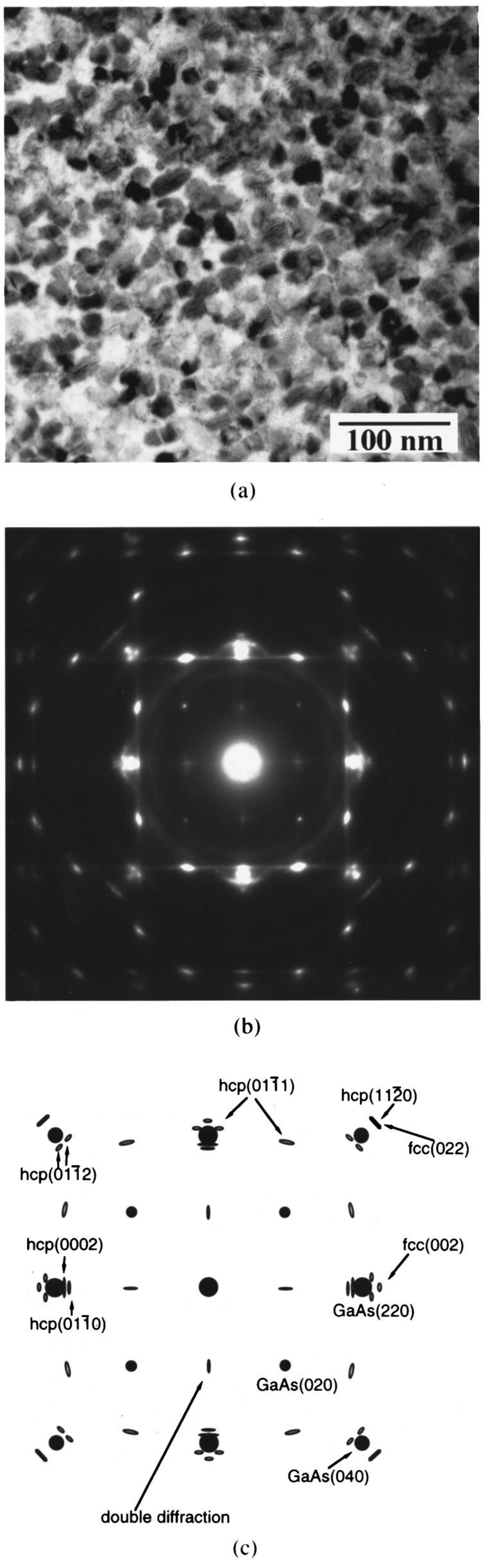

FIG. 4. (a) Plan-view bright-field TEM micrograph of polycrystalline hcp Co in a 345 Å film. (b) SAD pattern from Co and GaAs indicating strong texture of Co grains (presence of arcs rather than rings). (c) Schematic drawing of diffraction pattern showing variants of hcp-Co/GaAs orientation relationship and some fcc spots.

indexing of selected area diffraction (SAD) patterns [Figs. 4(b) and 4(c)] indicates the existence of both hcp-Co and some fcc-Co. The hcp-Co grains are highly textured and exhibit six variants of the following orientation relationship with the substrate: $[110]_{GaAs} \| [0001]_{hcp\text{-}Co}$, $(001)_{GaAs} \| (11\bar{2}0)_{hcp\text{-}Co}$. This orientation relationship is not exactly obeyed since the sample is polycrystalline, but the presence of well-defined arcs indicates that the grains are highly textured and exhibit only a slight deviation from the ideal relationship stated above. Only two variants, in which the *c* axis of the hexagonal unit cell lies in the plane of the film, have been previously reported.[8,9] The four variants observed here correspond to the hcp *c* axis lying out of the plane of the Co/GaAs interface. Although these variants have not been previously reported, they are consistent with published diffraction patterns in which all of the spots were not indexed.[8,9] As opposed to the cross-sectional TEM studies discussed above, SAD from plan-view specimens does not allow unambiguous identification of bcc-Co, since twice the ''predicted'' lattice constant of bcc-Co is only 0.2% less than that of the GaAs lattice.[3] Therefore, each bcc-Co diffraction spot has a GaAs reflection superimposed upon it, making it impossible to determine if bcc-Co exists by plan-view SAD.

In summary, direct observations have been made of the microstructure of Co films on GaAs(001). Two distinct layers, bcc-Co and hcp-Co, were observed in a 345 Å film. Bcc-Co forms first on the GaAs surface and is stable up to about 145 Å. The bcc-Co layer is single crystal in thin films, but may develop a polycrystalline structure at larger thicknesses. The hcp-Co layer subsequently forms at the free surface of the bcc-Co and is comprised of roughly equiaxed grains. The hcp-Co layer is highly textured, and four previously unreported variants of the hcp-Co/GaAs orientation relationship are present in which the *c* axis of the hcp unit cell lies out of the plane of the film. A small volume fraction of fcc-Co has also been observed in this film and is under further investigation.

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