Seeded epitaxy of metals by sputter deposition

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It is not generally appreciated that crystalline metallic thin film structures can be prepared using sputter deposition techniques by growth onto single crystalline substrates. Three systems, fcc Co/Cu(100), bcc Co/Cr(100), and hcp Co/Ru$(10\bar{1}3)$ multilayers are described in detail from a comprehensive study of more than 40 different systems. It is shown that the use of thin ''seed'' layers readily allows the preparation of different crystal structures and/or crystal orientations for the same substrate.

Sputter deposition growth techniques have recently played a central role in the exploration of the magnetic and transport properties of polycrystalline magnetic multilayers (see e.g., Ref. 1). Similar growth techniques have often been applied for the growth of single crystalline semiconducting or insulating films (e.g., oxides, etc.). It is not generally appreciated that the same techniques can be used to grow single crystalline metallic films even though, in recent years, crystalline Mo/V multilayers,[2] Fe,[3] Pt and Pt alloys,[4] Cu, Co/Cu and Fe/Cu multilayers,[5] and Fe/Cr multilayers[6] have been sputter deposited using oriented GaAs, MgO, Al_2O_3, and Si substrates as templates.

In this letter, we explore the epitaxial growth of metal films and multilayers via sputter deposition. A detailed discussion of three representative examples, fcc Co/Cu(100), bcc Co/Cr(100), and hcp Co/Ru$(10\bar{1}3)$ multilayers, selected from a larger study we have made of over 40 material systems/orientations is given. Of special interest is the use of seeded epitaxy, a technique developed in molecular beam epitaxy (MBE) deposition,[7] but also useful in sputter deposition (see e.g., Ref. 4).

All the films were deposited by magnetron sputter deposition, in 3.3×10^{-3} Torr Ar, in a chamber whose base pressure is $\sim2\times10^{-8}$ Torr. The deposition rate was 2 Å /s in all cases. To obtain epitaxy, it was found to be necessary to grow the first (buffer) layer at an elevated temperature, typically 500 °C. Subsequent layers were deposited at 100–150 °C.

As a first example, we consider a Co/Cu(100) superlattice. The complete structure is MgO(100)/Pd 50 Å/[Co 8 Å/Cu 7 Å$]_{40}$/Pd 30 Å. The Pd layer improves the crystalline quality of the subsequent multilayer. Figure 1(a) shows the specular θ–2θ x-ray scan. The multilayer is single orientation (100), showing only (200) and (400) diffraction features, and associated multilayer satellites. The (200) rocking curve full width at half maximum (FWHM) is only 1.7° [Fig. 1(b)]. This compares favorably with rocking curves from typical MBE metal superlattice structures[8] such as 0.5° for Co/Cu(111),[9] 1.4° for Co/Pt(111),[10] or 1.5°–2.5°[11] for Co/Ru(0001). The crystal structure of the Co is inferred from our own studies of thicker (1000 Å) films of Co/Cu(100) which show well-defined and separate Cu(200) and Co(200) features. Furthermore, the in-plane epitaxial relationship of the present film with the substrate [i.e., Co/Cu(010)—MgO(010)] has been confirmed with grazing-incidence x-ray diffraction.

One interesting property of magnetic/nonmagnetic multilayers is that the exchange coupling of adjacent magnetic layers usually oscillates between ferromagnetic (F) coupling and antiferromagnetic (AF) coupling, depending on the nonmagnetic layer thickness. Since its discovery,[12] this effect has received much attention. For example, exchange coupling in MBE multilayers of Co/Cu in various orientations has been closely studied.[13] But it has been found that crystalline quality can play a key role in determining whether or not such exchange coupling is observed.[14] Thus, as an im-

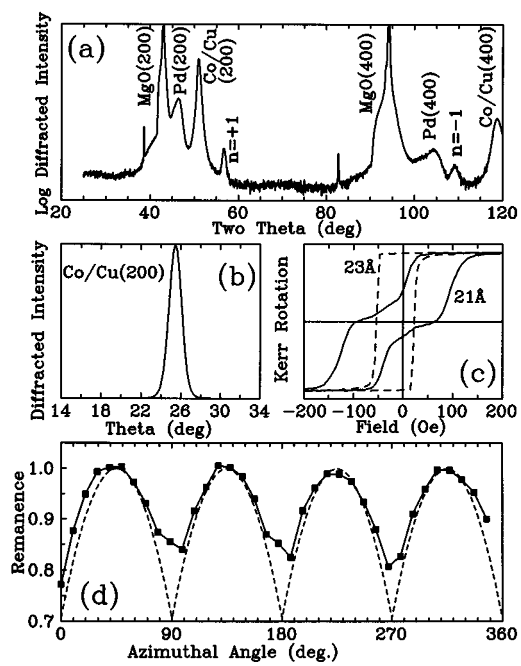

FIG. 1. Data from epitaxial Co/Cu(100) multilayers deposited by magnetron sputter deposition onto MgO(100). Specular x-ray diffraction (a) shows only the (100) orientation, as evidenced by the presence of only the (200) and (400) Bragg peaks, and associated superlattice features. The narrow rocking curve, (b), through the (200) indicates high crystallographic quality. Kerr magnetization loops, (c), indicate F or AF coupling depending on Cu layer thickness. A plot of remanent magnetic moment as a function of azimuthal angle verifies the *in-plane* epitaxial nature of these films.

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portant, albeit indirect characterization, we study the exchange coupling of the present multilayers in Fig. 1 (c). Here, in-plane easy-axis magnetization (Kerr) loops are displayed for two superlattices having different Cu layer thicknesses. The film with 23 Å Cu layers is ferromagnetically (*F*) coupled, as seen by the nearly full remanence it possesses in zero applied field. The remanence of the film with 21 Å Cu layers collapses in zero field, implying antiferromagnetic (AF) coupling. Related measurements of, e.g., magnetoresistance confirm the oscillatory nature of the exchange coupling.

As a final characterization, in Fig. 1(d) we use the magnetocrystalline anisotropy of these films to verify their epitaxial crystal structure. Choosing a single multilayer sample which displays *F* coupling, we plot its in-plane remanent magnetization as a function of azimuthal angle. The remanence then shows maxima (minima) along the easy (hard) magnetic axes of the film. In the present case, the remanence displays a fourfold anisotropy reflecting the symmetry of the fcc (100) surface. Overlaying this plot is a simple calculation of the idealized remanent response, which is proportional to the cosine of the angle between the measurement direction and the nearest easy-axis. The deviations of the real structure from this idealized response are due to finite coercivity (hysteresis) in the film. We note that the present anisotropy characterization is similar to one presented in Ref. 3.

The key to seeded epitaxy is that one can stabilize multiple crystal structures/orientations of a given element using a single substrate, by changing the initial buffer layer. In our second example, we begin again with MgO(100), but using a bcc Cr(100) buffer layer,[6] grow Co in a different crystal structure. The growth structure is MgO(100) / Cr 30 Å/[Cr 12 Å/Co 18 Å$]_{30}$. A previous MBE study of Co/Cr multilayers[15] (see epitaxial relationships therein) as well as our own further studies of the growth of Co/Cr(100) suggest that the Co (and Cr) in this multilayer have a strained structure intermediate between bcc(100) and hcp(11$\bar{2}$0), although the strain probably varies periodically throughout the structure. This is consistent with the specular x-ray diffraction, Fig. 2(a), which has five peaks associated with the multilayer. These peaks correspond to the $n=0$, ± 1, and ± 2, superlattice peaks Co/Cr multilayer. The $n=0$ feature, centered at 69.5°, is almost midway between the positions of bulk Cr(200) and bulk Co(11$\bar{2}$0) features. The rocking curve FWHM of the n=0 peak is 2.7° [Fig. 2(b)].

Easy-axis magnetization loops taken on two samples having Cr layer thicknesses of 12 Å and 10 Å are shown in Fig. 2(c). The 12 Å loop indicates *F* coupling, while the 10 Å loop indicates AF coupling. An azimuthal plot of the remanence on a *F* coupled sample shows the expected fourfold in-plane symmetry of the bcc(100) surface.

As a final example, consider epitaxial Co/Ru(10$\bar{1}$3), which has an hcp crystal structure. Instead of a many period multilayer, this is a wedged "sandwich" structure, nominally: MgO(110)/ Ru 220 Å/ Co 100 Å/ Ru t_{Ru}/ Co 100 Å/ Ru 30 Å. The thickness, t_{Ru}, of the central Ru layer was varied across the sample to allow measurement of the Co-Co interlayer coupling as a function of Ru layer thickness. The Ru is highly oriented, as seen in the specular x-ray diffraction [Fig. 3(a)], which shows only one Ru feature, the (10$\bar{1}$3) peak. This feature has a rocking curve FWHM of 1. 3° (not shown). The Co layers are also highly oriented, but because the surface normal does not coincide with an important set of atomic planes (for the Co), no Co diffraction features appear in this scan.

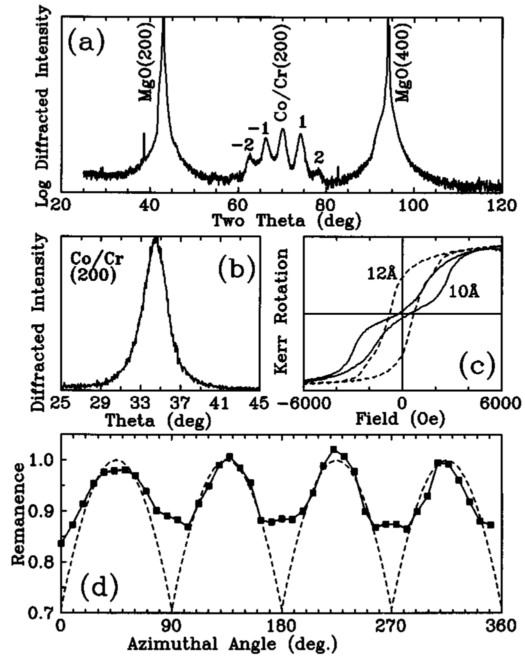

FIG. 2. Measurements analogous to Fig. 1, but for Co/Cr(100) multilayers.

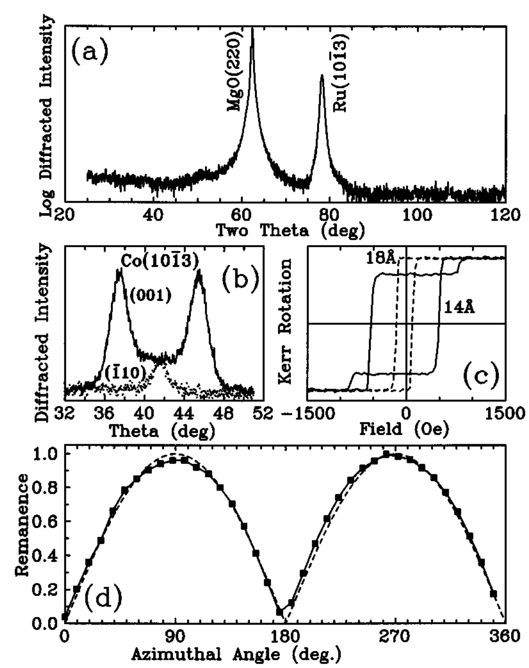

FIG. 3. Measurements analogous to Fig. 1, but from an hcp Co/Ru(10$\bar{1}$3) wedged multilayer film on MgO(110).

Assuming that the Co$(10\bar{1}3)$ feature is near the surface normal, we rocked the sample in the (001) and (011) planes of the MgO(110) substrate, keeping the x-ray detector set to the position of the Co(1013) feature. The resulting two rocking curves are presented in Fig. 3(b). Both the Co and Ru layers consist of two domains, with the [1013] axis canted toward either the [011] or [011] directions in the plane of the MgO(110). The two Co(1013) peaks are separated by $\sim 8°$ and centered about the surface normal. Because this splitting is much larger than the rocking curve FWHM (2.1°), no cofeature appears in the specular x-ray scan. For the Ru film, the (1013) peaks are separated by only 1.9°, which is of order the rocking curve FWHM. Hence the Ru peak appears in the specular scan. This is an example of ''tilted epitaxy,''[16] a well-known phenomenon in MBE, because the Co planes are nearly but not exactly parallel with the Ru planes.

Figure 3(c) displays easy-axis magnetization loops taken at different positions on this wedged sample, corresponding to different t_{Ru}. For $t_{Ru} \sim 18$ Å, the Co layers are *F* coupled, but for $t_{Ru} \sim 14$ Å they are AF coupled. Fig. 3(d) shows the remanent magnetization as a function of azimuthal angle for an *F* coupled region on this sample. The crystalline symmetry gives rise to a twofold magnetic anisotropy. The simple model of the remanent magnetization mentioned earlier is more accurate in this case since the magnetocrystalline anisotropy of hcp Co is about eight times larger than that of, e.g., fcc Co,[17] and hence dominates the coercivity of these films.

The above examples are typical of the epitaxial quality that can be achieved with a wide variety of materials. For example, we find that a 30 Å Pd buffer layer provides a good template for fcc Cu, Co, Ni, or Ag, in the (100), (110), and (111) orientations with the use of MgO(100), MgO(110), or Al_2O_3(0001) substrates, respectively. In a future paper, we will discuss the epitaxial growth of numerous other metal films using growth techniques similar to those discussed here.[18]

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