Molecular-beam-epitaxy growth and structural characterization of high-quality single-crystal Co/Cr(001) superlattices

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High-quality single-crystal Co/Cr(001) superlattices with layer thicknesses of 5–50 Å have been grown by molecular-beam epitaxy. In contrast to other investigations we found that hcp Co grows with its (11.0) plane parallel to Cr(001). The Co layers exhibit a remarkable expansion of $\approx 6\%$ perpendicular to the film plane, indicating a structural change in direction to the bcc phase. However, in-plane diffraction experiments confirmed that the hexagonal symmetry remains for Co layer thicknesses down to 4 Å.

Recent studies of magnetic metal multilayers and superlattices have attracted much interest for fundamental reasons as well as for applications as high-density magnetic and magneto-optical recording devices.[1] Especially the Co/Cr system has been intensively studied because of promising magnetic properties such as perpendicular anisotropy[2] and high coercive forces.[3] Most of the previous investigations have been limited to polycrystalline samples, making a microscopic understanding of the structural and magnetic properties difficult. An exception is Sato's study[2] of highly textured bcc-Co/Cr(110) superlattices. This orientation does not present difficulties in sample preparation because both growth planes, i.e., bcc(110) and fcc(111)/hcp(00.1) are most densely packed and therefore stable. More recently Vavra *et al.*[4] and Henry *et al.*[5] have analyzed the growth of Co/Cr(110) superlattices by reflection high-energy electron diffraction (RHEED) and found a competition between the Nishiyama-Wassermann and Kurdjumov-Sachs epitaxial relationship for bcc Cr(110) on hcp Co(00.1), resulting in two coexisting d spacings of the Cr layers. To the best of our knowledge, no (001)-oriented Co/Cr superlattice has yet been reported in the literature. This is because of the difficulties related to the growth process.

The (001)-oriented Co/Cr superlattices are of particular interest since a strong interlayer exchange coupling with short and long periodicities is expected.[6,7] The detailed arrangement of the Co atoms at the interface should be less important for the coupling,[8] but it seems to be essential that the Cr interlayer is (001) oriented, since in Co/Cr(110) multilayers the coupling is very weak[9,10] or could not be detected.[2]

In addition, the stabilization of the metastable bcc phase of Co in Co/Cr superlattices is another highly interesting challenge. The bcc phase of Co has been reported on GaAs substrates up to a Co film thickness of 357 Å.[11] In Co/Cr(110) superlattices it is still a matter of discussion[12,13] whether or not the bcc phase could be synthesized. As far as the Cr(001) surface is concerned, a recent study showed that the low-energy electron diffraction pattern did not change during evaporation of Co on a Cr(001) single-crystal surface until a deposition of 20-monolayer equivalents,[14] and therefore it was concluded, that bcc Co could be stabilized on Cr(001).

In this paper we report on the growth and structural characterization of high-quality Co/Cr(001) superlattices and show that the stable configuration of cobalt on Cr(001) is the hcp-(11.0) plane.

The samples were prepared in a conventional UHV chamber (base pressure $<10^{-10}$ Torr) which was designed for metal epitaxy. It is equipped with a RHEED electron gun working at 30 kV and the obtained RHEED patterns were analyzed with a charge-coupled-device camera and a real-time frame grabber card used in connection with a personal computer. High-quality sapphire Al_2O_3 ($1\bar{1}.2$) crystals were used as substrates. They were rinsed in acetone and isopropanol before loading into the introduction chamber, then annealed at 500 °C for 1 h, sputtered with Ar^+ (600 eV, 1 $\mu A/cm^2$) for 30 min, and then annealed again at 1100 °C in the preparation chamber. Co was evaporated by an e^- gun with an optical deposition controller, whereas Cr was heated in a Knudsen cell with a graphite crucible; the Cr flux was calibrated with a Bayard-Alpert gauge at the position of the sample. The deposition rates were typically 25 Å/min. Before the Co/Cr superlattice was grown, a 500-Å Nb layer was evaporated on the sapphire at a substrate temperature of 900 °C. It is well known that high-quality Nb layers with very small mosaic spreads grown on sapphire[15] are useful as buffer layers for a number of metal-metal epitaxy systems. On the Nb layer the first Cr layer was grown as thick as 500 Å at $T = 450$ °C, followed by a deposition of the Co/Cr superlattice at 300–350 °C. This method avoids the widely known problems with Cr single crystals as substrates such as bulk nitrogen surface segregation and long sputter-anneal cycles.[14]

The substrate temperature for the first Cr layer and the growth temperature for the superlattice have been optimized to obtain sharp streaks in RHEED patterns as well as strong superlattice peaks in x-ray scattering experiments. At lower temperatures an island growth of Co was observed, whereas disappearence of the superlattice peaks due to strong interdiffusion occurred above 400 °C.

All samples grown were characterized by x-ray scattering experiments. A medium resolution two-axis goniometer equipped with a graphite monochromator was

used for small- and high-angle out-of-plane x-ray scattering experiments. The radial and transverse resolutions in this configuration (using Cu $K\alpha$ radiation) were $\Delta 2\theta = 0.08°$ and $\Delta\theta = 0.11°$, respectively.

The in-plane structure has been analyzed by means of grazing incidence x-ray scattering techniques. The incident angle of the primary beam was fixed at the critical angle for the total reflection of x rays ($\approx 0.2°$), yielding a penetration depth of about 500 Å and a scattering vector in the plane of the sample. The surface x-ray diffractometer is equipped with a rotating anode generator operating at 60 kV and 300 mA. Mo $K\alpha$ radiation ($\lambda = 0.7107$ Å) was used for the in-plane scattering experiments.

Figure 1 shows low-angle x-ray reflectivity spectra of Co/Cr(001) superlattices for various Co and Cr layer thicknesses, t_{Co} and t_{Cr}, respectively. Strong satellite peaks and many film thickness oscillations are visible in spite of the weak contrast and strong absorption for Cu $K\alpha$ radiation. The data have been fitted using a dynamical Parrat-like model that treats interfacial roughness in the sense of Nevot and Croce.[16] We obtained a root-mean-square roughness of about 5 Å, indicating relatively sharp interfaces. The diffuse scattering of the x rays was found to be negligibly small (<10% of the specular intensity at 6°). We therefore believe that our quoted roughness parameters are rather accurate.

Figures 2(a)–2(d) show out-of-plane x-ray scattering spectra for some superlattices with different Co and Cr thicknesses. For large Cr and Co thicknesses strong satellite peaks are observable around the bulk bcc-Cr(002) and hcp-Co(11.0) positions. These profiles can be understood qualitatively as follows. We assume that the Co layers in our Co/Cr superlattices have hcp (11.0) orientation. The d spacing in Co $d_{Co}=1.25$ Å is much different from the one of the Cr layers $d_{Cr}=1.44$ Å. This leads to strong "satellite" peaks around the bulk Co(11.0) and Cr(002) positions, the fundamental peak

FIG. 2. $\theta - 2\theta$ scans of four different superlattices (a)–(d), a thin Co layer of 30 Å thickness (e), and a 500-Å Cr layer (f). The curves are shifted for clarity. (a) $[Co_{10\,Å} \cdot Cr_{21\,Å}]_{10}$; (b) $[Co_{19\,Å} \cdot Cr_{33\,Å}]_{10}$; (c) $[Co_{28\,Å} \cdot Cr_{43\,Å}]_{10}$; (d) $[Co_{32\,Å} \cdot Cr_{48\,Å}]_{10}$. The vertical lines denote the peak positions of bcc and hcp Co. Note the Cr-buffer peaks appear at 64.5°; all others are superlattice peaks.

being rather weak because of the destructive interference between both materials. With decreasing t_{Co} this feature becomes weaker, but a remarkable asymmetry is visible around the Cr(002) position at $t_{Co} = 10$ Å, indicating a change in d_{Co}. In rocking-curve measurements at the satellite peak positions we found very small mosaicities of about 0.5°. In addition we did not observe any other peaks belonging to orientations such as Cr(110) or hcp-Co(00.2)/fcc-Co(111); this can be taken as evidence for the single crystalline texture of our superlattices.

In Fig. 3 are plotted the d spacings d_{Co} and d_{Cr} as a function of the layer thicknesses as derived by the model calculations for the x-ray scattering spectra shown in Fig. 2. The kinematical model involves as fitting parameters d spacings of the pure layers and an assumed interface layer and layer thickness fluctuations. Typical
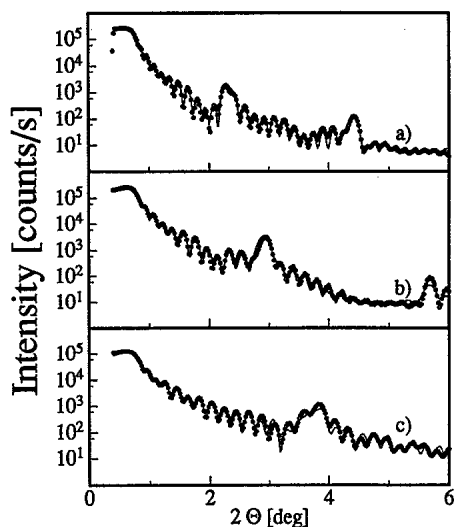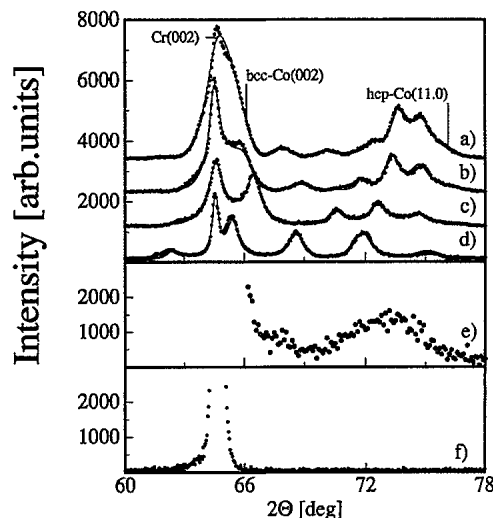

FIG. 1. Low-angle x-ray reflectivity spectra of Co/Cr(001) superlattices measured with Cu $K\alpha$ radiation. The curves are plotted on a logarithmic scale; the lines are fits to the data as descibed in the text. (a) $[Co_{12\,Å} \cdot Cr_{28\,Å}]_{10}$; (b) $[Co_{12\,Å} \cdot Cr_{20\,Å}]_{10}$; (c) $[Co_{12\,Å} \cdot Cr_{12\,Å}]_{10}$.
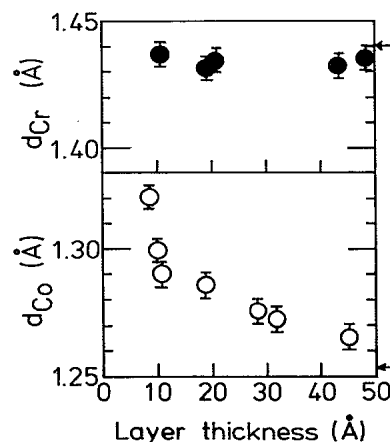

FIG. 3. The layer thickness dependence of the d spacings in Co (open circles) and Cr (full circles) layers. The arrows indicate bulk values.
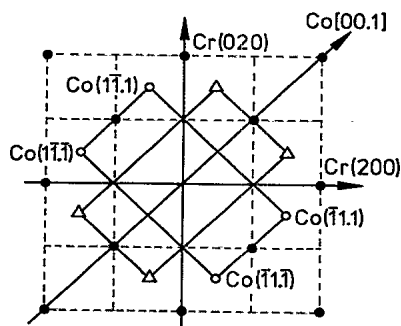
FIG. 4. In-plane diffraction spots observed in RHEED and grazing incidence x-ray scattering experiments. Filled circles indicate spots from both Cr and Co, while open circles and triangles are reflections only due to the hcp structure of Co.
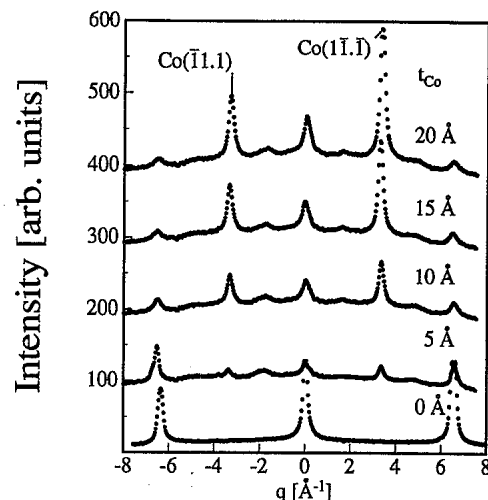

FIG. 5. Line scans perpendicular to RHEED streaks obtained from Co on Cr(001) for various thicknesses. Bottom: the one from the Cr buffer layer.

values of the layer thickness fluctuation, which broadens the superlattice peaks, are in the range of 10% of the individual layer thickness. The d spacings of the interface layer were always equal to the average of the pure Co and Cr layers, indicating the validity of the used model. The details of the modeling have been described in Ref. 17. The Co d spacing at t_{Co} =48.5 Å was found to be $d = 1.26$ Å which is in fact in good agreement with bulk hcp-Co(11.0) d=1.25 Å,[18] indicative of the hcp structure of the Co layers. With decreasing t_{Co}, the Co layers exhibit a remarkable expansion reaching d =1.32 Å for the thinnest $t_{Co} = 10$ Å grown in this study. This Co d spacing is too large to be explained by the Poisson expansion (2%) of Co layers induced by the epitaxial constrain of hcp-Co(11.0) on Cr(001), while it is too small to be taken as an evidence for the existence of a metastable bcc phase, whose d spacing is expected to be $d = 1.41$ Å.[11] The Co d spacings have been confirmed by x-ray scattering experiments in Cr/Co/Cr sandwich structures with the same Co thicknesses as in the superlattices. In Fig. 2(e) the x-ray spectrum of one sandwich structure ($t_{Co} = 30$ Å) is reproduced. It is quite clear from this plot that the broad peak at $2\theta = 73.2°$ originates from the Co layer by comparing it to the spectrum from a 500-Å-thick Cr(001) layer [Fig. 2(f)].

At the same time the d spacing of the Cr layers shows no layer thickness dependence and is in good agreement with the bulk lattice constant (1.44 Å), indicating the structural stability of the Cr layers; furthermore, d_{Co} does not significantly depend on the Cr thickness in the range $t_{Cr} > 10$ Å.

Figure 4 summarizes the in-plane diffraction spots observed in RHEED and grazing incidence x-ray scattering experiments. From the positions of the observed spots, we find that the c axis of hcp Co is parallel to Cr[110]. This orientation provides the smallest misfit of about -0.2% and $+6\%$ along the Co[00.1] and Co[11.0] axis, respectively. This epitaxial relation was predicted on the basis of geometrical considerations,[19] and was found

first in polycrystalline samples.[20] We observed this epitaxial relation for growth temperatures between 40 °C and 450 °C.

The additional peaks that appeared only in Co layers can be exclusively observed in hcp structures and are indexed as Co{1$\bar{1}$.1}, confirming the hcp structure of the Co layers. The intensity profiles of RHEED along this spot are shown in Fig. 5. It should be noted that this peak is not due to any surface reconstruction, since it is also clearly observed in grazing incidence x-ray scattering experiments which are sensitive to the signal from the entire film. The intensities of these spots decrease rapidly with decreasing t_{Co}, but they are still observable for Co layer thicknesses down to 4 Å. The asymmetry in the observed RHEED patterns is due to Kikuchi enhancements.

In summary, we have grown high-quality single-crystal Co/Cr(001) superlattices with sharp interfaces by means of molecular-beam epitaxy. The remarkable out-of-plane expansion of d_{Co} and the observed decrease in the intensity of the RHEED streaks indicate that the Co layers exhibit a continuous change of the crystal structure in direction to the bcc phase with decreasing thickness. However, our results show that a hexagonal symmetry remains at least for t_{Co} down to 4 Å.

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