Fourfold anisotropy and structural behavior of epitaxial hcp Co/GaAs(001) thin films

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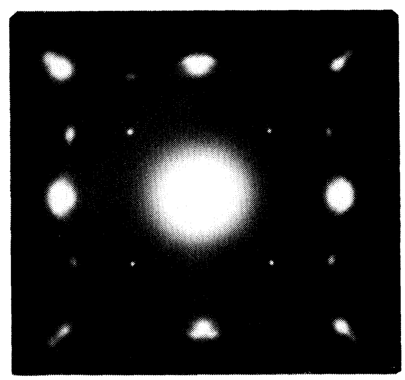
Thin Cr-capped Co films (thickness 50–150 Å) have been grown epitaxially on GaAs(001) single-crystal substrates by molecular-beam epitaxy. In contrast to other investigations, transmission electron diffraction reveals that the epitaxial Co films have a hexagonal-close-packed (hcp) structure with the epitaxial relationships $(\bar{1}2\bar{1}0)[0001]$Co$\|(001)[110]$GaAs and $(\bar{1}2\bar{1}0)[0001]$Co$\|(001)[\bar{1}10]$GaAs, i.e., the *c* axis of each crystallite is assigned to either the in-plane [110] or the $[\bar{1}10]$ direction of the GaAs(001) substrate. In-plane magneto-optical Kerr-effect hysteresis loops and Brillouin light-scattering measurements show that the thinnest epitaxial hcp Co film (50 Å) has a dominant fourfold anisotropy with easy axes along the in-plane $\langle 100 \rangle$ directions and that a uniaxial anisotropy becomes dominant with increasing film thickness. We are able to account for the magnetic anisotropy properties of these epitaxial Co films in terms of their oriented hcp microstructure.

Epitaxial magnetic films supported by oriented semiconductor substrates have attracted substantial interest.[1–3] Their novel structural and magnetic properties permit fundamental studies in magnetism and offer possibilities for a range of device applications. One of the most interesting topics to emerge from this increasingly active field is the question of precisely what crystal structure may form according to the substrate and growth conditions. Since the magnetic metals often occur in several different crystallographic phases and each of these different crystallographic structures will possess different magnetic properties, the structural characterization of magnetic films is especially important in the interpretation of their magnetic properties. A typical example in this field is the epitaxial growth of Co films. At room temperature bulk Co is in the hexagonal-close-packed (hcp) structure, and above 700 K it undergoes a martensitic transition into the face-centered-cubic (fcc) structure. Using the technique of molecular-beam epitaxy, Prinz demonstrated that it is also possible to grow the body-centered-cubic (bcc) phase of Co, which does not occur in nature, epitaxially on GaAs(110) substrates.[1] The epitaxial growth of Co on GaAs(110) substrates has been studied in a number of laboratories.[1,4,5] Recent theoretical calculations showed that the bcc Co is not a metastable phase but a forced structure stabilized by the interaction with the substrate.[6] Thus, it is expected that the epitaxial growth of bcc Co depends strongly on the substrate and substrate preparation. Although it was thought that Co could also be stabilized in the bcc phase on GaAs(001) substrates, the detailed structural characterization of epitaxial Co/GaAs(001) films especially for thicker epitaxial Co films ($\gtrsim 50$ Å) in which a large magnetocrystalline anisotropy develops remains controversial.[2,7,8] It has been reported that the reconstructed surface of GaAs(001) cannot provide a template as suitable as is the (110) GaAs surface for driving Co atoms into a bcc phase.[2,8] Furthermore, previously reported magnetic anisotropy properties of Co/GaAs(001) films cannot be related satisfactorily with the suggested bcc structure. For example, as bcc Co has a negative cubic anisotropy constant,[1,9] for epitaxial bcc Co/GaAs(001) films, an in-plane fourfold magnetocrystalline anisotropy with easy axes along the in-plane $\langle 110 \rangle$ directions is expected. However, to our knowledge, such anisotropy properties have never been reported. In our previous work on Co/GaAs(001), an in-plane fourfold anisotropy was indeed observed.[8] However, the easy axes of this fourfold anisotropy were found to be parallel to the $\langle 100 \rangle$ rather than $\langle 110 \rangle$ directions.

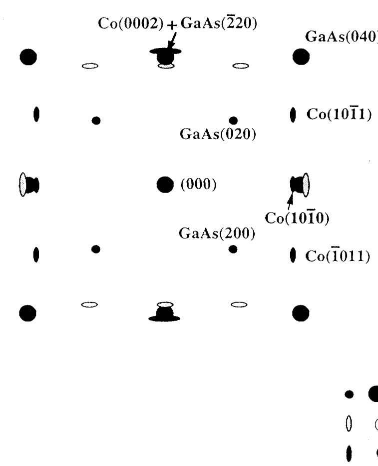
In this paper, by using the transmission electron diffraction technique, we demonstrate that the stable phase in epitaxial Co/GaAs(001) films is not a bcc but an oriented hcp with its $(\bar{1}2\bar{1}0)$ plane parallel to the GaAs(001). The magnetic properties of these Co films were measured by magneto-optical Kerr-effect (MOKE) magnetometry and Brillouin light scattering (BLS). Strong fourfold anisotropy was found for the thinnest epitaxial film (50 Å). It will be shown that the measured magnetic anisotropy properties of these Co/GaAs(001) films are consistent with the oriented hcp structure.

The Co films were grown in an UHV chamber. During growth, the pressure was less than 5×10^{-10} mbar. The surface structure and chemical compositions of the substrate and the Co films were monitored by low-energy electron diffraction (LEED) and Auger electron spectroscopy. A commercial Si-doped GaAs(001) wafer was used as a substrate. Both carbon and oxygen peaks were found in Auger spectra recorded before *in situ* substrate treatment. The surface oxide layer can be removed by heating the substrate to 600 °C for 1 h. It is found that all detectable contamination (O and C) of the GaAs surface can be removed by using Ar^{+}-ion (500-eV) bombardment. Since Ar^{+}-ion bombardment leaves a rough surface, selected bombarded substrates were then heated to 600 °C to smooth the surface and to desorb implanted Ar ions. The annealing also desorbs As atoms from the topmost layer and orders the substrate surface. The substrate prepared by Ar^+-ion bombardment followed by annealing at 600 °C gives rise to a LEED pattern showing a (4×6) reconstructed surface structure. From the LEED patterns the [110] and [$\bar{1}$10] directions of the GaAs substrate could be distinguished. Under identical deposition conditions, Co films were grown simultaneously on substrates treated by (i) annealing only and (ii) by Ar^+-ion bombardment followed by annealing at 600 °C. The substrate temperature of 140 °C and a deposition rate of 1.0 Å min^{-1} were used for the Co growth in all cases. It has been reported that Co diffusion into the GaAs(001) substrate starts at 325 °C, resulting in the formation of a ternary phase, Co_2GaAs.[10,11] Since our substrate temperature is much lower than this reaction temperature, the amount of Co diffusing into the GaAs substrate should be negligibly small. The LEED pattern from the substrate disappeared immediately after a few Å of Co had been deposited and during the entire Co growth process, LEED diffraction spots were not visible. This result suggests that from initial stage Co growth departs from an ideal layer by layer growth mode and the crystalline grains in the Co films are small (<200 Å).[12] Significant field-dependent MOKE (*in situ*) signal was observed only for film thicknesses greater than 10 Å, suggesting that As outdiffusion may occur.[2,7,8] During growth, the film thickness was monitored by a quartz microbalance calibrated by a Dektak profilometer. Finally, each completed Co film was capped with 12 Å of Cr, which, from electron energy-loss spectroscopy measurements, was found to be sufficient to prevent oxidiation of the films.[13]

Transmission electron microscopy (TEM) is a powerful technique for thin-film structural characterization. TEM can provide unambiguous and detailed structural information such as the grain size and the epitaxial relationship. In this work, the microstructural analyses of the Co films were carried out using a JEOL-2000 EX transmission electron microscope operated at 200 kV. The TEM specimens were prepared by both chemical etching and Ar^+-ion milling techniques. The TEM measurements show that the Co films grown on GaAs(001) substrates prepared only by annealing have a hcp polycrystalline structure. Such a Co film of thickness 50 Å has an average grain size of about 100 Å and its MOKE hysteresis loops are isotropic. The Co films grown on the GaAs(001) substrate prepared by Ar^+-ion bombardment followed by annealing show very different structural and magnetic properties. An electron diffraction pattern of such a Co film of thickness 50 Å is shown in Fig. 1(a). This TEM diffraction pattern can be indexed very well as a superposition of the single GaAs(001) orientation and two ($\bar{1}2\bar{1}0$)[0001]Co(hcp) orientations with the two [0001] directions perpendicular to each other as shown in Fig. 1(b). In this diffraction pattern, the double diffraction spots produced by the GaAs 220-type reflections can be seen and we observe that the hcp Co diffraction spots are elongated. Whereas the 200-type diffraction spots from the GaAs are very sharp, as overlapped by Co diffraction and double diffraction spots, the 220- and 400-type diffraction spots from the GaAs appear to be broad and elongated. The observed elongation of the hcp Co diffraction spots may be attributed to the shape of Co crystallites and the lattice distortion induced by the lattice mismatch between hcp Co and GaAs lattices, both can produce a rather broad minimum of the interfacial energy as a function of azimuthal rotation.[14] The ($\bar{1}2\bar{1}0$) plane of a hexagonal structure is shown in Fig. 2(a). The two-dimensional (2D) rectangular unit cell in this plane has sides of length 4.342 and 4.070 Å. From the diffraction pattern, it is deduced that in real space, the rectangular unit cell of the ($\bar{1}2\bar{1}0$) plane aligns with its *c* edge parallel to either the [110] or the [$\bar{1}$10] diagonal direction of the 2D GaAs mesh as shown in Fig. 2(b). In the diagonal direction the lattice mismatch between the 2D Co and GaAs cells ($D_{GaAs}=7.996$ Å) is 1.8% and in the orthogonal direction the mismatch is 7.9%. Since the Co nucleation occurs in two possible orientations, the film is not a continuous single-crystal film but rather a



(a)



(b)

FIG. 1. (a) A selected-area electron diffraction pattern of a Co(50 Å) film grown on a GaAs(001) substrate prepared by 500-eV Ar^+-ion bombardment followed by annealing at 600 °C. (b) A schematic indexed pattern corresponding to the diffraction pattern shown in (a).

structure of crystallites with two possible lateral alignments. Similar diffraction patterns have also been obtained for epitaxial Co/GaAs(001) films with thicknesses up to 150 Å, indicating that the hcp epitaxial growth can persist for thicker films. The Co films have also been characterized by nuclear magnetic resonance (NMR) spectroscopy. The NMR spectra were measured by a coherently detected spin-echo spectrometer at 4.2 K. For the above-mentioned 50-Å Co film grown on the GaAs substrate prepared by only annealing, the measured hyperfine field distribution has a main peak centered at 222.4 MHz. This result is consistent with the hcp polycrystalline structure deduced by TEM. However, it was found that for the epitaxial Co films grown on the GaAs substrates prepared by Ar^+-ion bombardment followed by annealing, the NMR frequencies are around 217.2 MHz. Since these Co films have an epitaxial hcp structure as shown by the TEM measurements, the NMR line shift towards lower frequencies is attributed to the in-plane strain induced by the lattice mismatch between the epitaxial hcp Co film and GaAs substrate.[15] A detailed discussion of the NMR spectra will be presented separately.

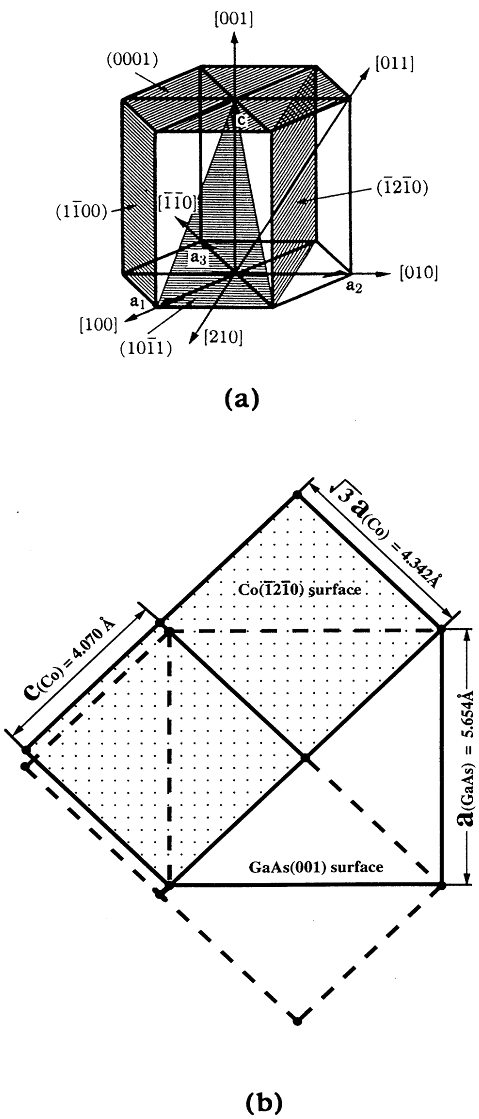


FIG. 2. (a) Schematic representation of the crystallographic structure of hcp Co. (b) The epitaxial relationship of the hcp Co cell to the GaAs(001).

The in-plane angle-dependent *M-H* hysteresis loops were measured *ex situ* at room temperature using a MOKE magnetometer.[16] The *M-H* hysteresis loops of the epitaxial hcp Co(50 Å)/GaAs(001) film with the field applied along the four principal crystallographic directions of the GaAs(001) substrate are displayed in Fig. 3. These hysteresis loops show that this film has a predominant in-plane fourfold anisotropy with the easy and hard axes corresponding to the in-plane ⟨100⟩ and ⟨110⟩ directions, respectively. Furthermore, from the hysteresis loops it can be seen that the coercivity for the field applied along the [$\bar{1}$10] direction is less than that for the field applied along the [110] direction, indicating that apart from the fourfold anisotropy there exists an in-plane uniaxial (twofold) anisotropy with the easy axis parallel to the [110] direction. MOKE measurements for thicker epitaxial hcp Co films revealed that by increasing the film thickness the easy axis orientation of the in-plane uniaxial anisotropy changes from the [110] direction to the [$\bar{1}$10] direction and the strength of this uniaxial anisotropy becomes increasingly large. The BLS measurements were performed in the standard backscattering geometry.[17] The sample holder was attached to a rotary amount so that a magnetic field up to 10 kOe could be applied in any direction in the film plane with an accuracy of better than 1°. In Fig. 4(a), the spin-wave mode frequency is plotted against the angle between the applied field and the [100] axis for the epitaxial Co(50

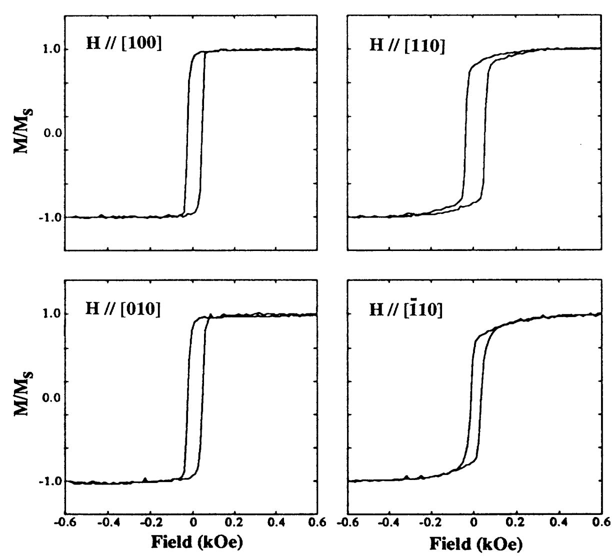


FIG. 3. MOKE hysteresis loops of the epitaxial hcp Co(50 Å)/GaAs(001) film for magnetic fields applied along the four principal in-plane axes of the GaAs(001) substrate.

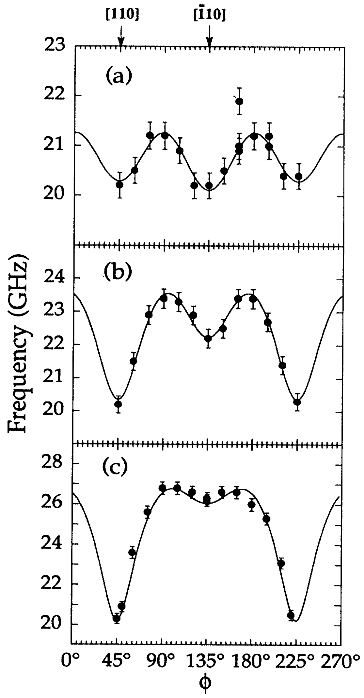


FIG. 4. BLS spin-wave mode frequencies are plotted for the epitaxial Co/GaAs(001) films of thickness (a) 50 Å, (b) 90 Å, and (c) 145 Å as a function of the angle φ between the applied magnetic field and the in-plane [100] direction. The solid lines show the fitted curves. The applied magnetic field strength was 3 kOe for all measurements.

Å)/GaAs(001) film. It can be seen that the frequency minima for the two $\langle 110 \rangle$ directions are almost equivalent, indicating a predominant fourfold anisotropy ($|K_{\text{eff}(2)}/K_{\text{eff}(4)}|=0.15$) with effective magnetic easy axes along the in-plane $\langle 100 \rangle$ directions. BLS data and fitted curves for thicker (90 and 145 Å) epitaxial hcp Co films are displayed in Figs. 4(b) and 4(c). By fitting the data, the ratios of the uniaxial anisotropy to the fourfold anisotropy ($|K_{\text{eff}(2)}/K_{\text{eff}(4)}|$) in these two films were determined to be 0.78 and 1.73, respectively. From Fig. 4 it can be seen that for thicker films the easy axis of the uniaxial anisotropy is parallel to the [$\bar{1}$10] direction of the GaAs(001) substrate and that the strength of this uniaxial anisotropy increases with film thickness. We find that the BLS results are consistent with the results of the MOKE measurements.

We next discuss how the magnetic anisotropy behavior of the epitaxial hcp films described above relates to the microstructure revealed by TEM characterization. It is known that hcp Co has a uniaxial anisotropy and that the c axis is its easy direction. The crystal anisotropy energy is written as

$$E=K_1\sin^2\theta_1+K_2\sin^4\theta_1+K_3\sin^6\theta_1+\cdots , \tag{1}$$

where θ_1 is the angle between the magnetization vector and the c axis of the hcp structure. For bulk hcp Co, K_1 ($+4.3\times10^6$ ergs/cm^3) and K_2 ($+1.2\times10^6$ ergs/cm^3) are comparable and K_3 and K_4 are negligible.[18] We assume that the grains in the epitaxial hcp Co films are strongly exchange coupled so that the magnetization vector is coherent over an area substantially larger than the grain size. If the two types of gains in an epitaxial hcp Co film occupy fractions f_1 and f_2, from Eq. (1), the net anisotropy energy of an epitaxial hcp Co/GaAs(001) film may be written in the form

$$E=f_1(K_1\sin^2\theta_1+K_2\sin^4\theta_1)+f_2(K_1\sin^2\theta_2+K_2\sin^4\theta_2) , \tag{2}$$

where θ_1 and θ_2 are the angles between the magnetization of film and the c axes of the two types of grains aligning parallel to the [110] and [$\bar{1}$10] directions of the GaAs(001) substrate. If the magnetization is confined to the film plane, for a coupled Co film the magnetization direction may be defined by the angle φ between the magnetization vector and the [100] axis. The anisotropy energy may then be rewritten in the form

$$E=(f_1+f_2)K_2\sin^2\varphi\cos^2\varphi +(f_2-f_1)(K_1+K_2)\cos^2(\varphi-\pi/4) . \tag{3}$$

We see that the form given above may always be modeled as a sum of a fourfold anisotropy and a uniaxial anisotropy with effective anisotropy constants

$$K_{\text{eff}(4)}=(f_1+f_2)K_2,\quad K_{\text{eff}(2)}=(f_2-f_1)(K_1+K_2) . \tag{4}$$

The easy axes of the fourfold anisotropy in Eq. (3) are parallel to the in-plane $\langle 100 \rangle$ directions since the K_2 is positive and depending on the values of f_1 and f_2, the easy axis of the uniaxial anisotropy can be parallel to either the [110] or the [$\bar{1}$10] direction of the GaAs(001) substrate. This is in agreement with the MOKE and BLS results. Furthermore, it can be seen that if the fractions of the two kinds of grains are nearly equal ($f_1\cong f_2$), the uniaxial anisotropy term is eliminated and then the film will show predominant fourfold anisotropy, as observed in the 50-Å epitaxial Co film. If we assume that the uniaxial anisotropy of the Co films results only from the difference in the fraction of the two kinds of grains and use the bulk hcp values for K_1 and K_2, then from Eq. (4) and the measured ratio of $K_{\text{eff}(2)}$ to $K_{\text{eff}(4)}$ it is possible to estimate the values of f_1 and f_2. On this basis we estimated that for the epitaxial Co(50 Å)/GaAs(001) film, the ratio f_2/f_1 is 0.95; i.e., for this film, the amounts of the two kinds of grains are almost the same. Increasing the film thickness results in an increase in the ratio f_2/f_1 (for the 90-Å Co film $f_2/f_1=1.4$ and for the 145-Å Co film $f_2/f_1=2.2$). This indicates that as the film becomes thicker the growth of grains oriented with their c axis parallel to the [$\bar{1}$10] direction seems to be favored.

In the above analysis, it has been assumed that the grains in the Co films are strongly exchange coupled so that the magnetizations of neighboring grains are aligned parallel to each other. This assumption is correct for most magnetic thin films.[19] However, it should be noted that in some magnetic thin films, magnetic grains may be well separated by nonmagnetic grain boundaries or voids.[20] Such microstructures lead to weak or perhaps nonexchange coupling between the grains.[21] In this case, the magnetic interaction between the grains is mainly due to magnetostatic coupling. The magnetic reversal processes of nonexchange coupled thin films have been simulated recently by using a micromagnetic model.[21] If each grain in a nonexchange coupled thin film is considered to be a single domain particle with a uniaxial anisotropy whose easy axis is randomly assigned to either one of the two given in-plane orthogonal directions, with a strong magnetostatic interaction between the grains, the simulation can give rise to a fourfold anisotropy similar to that found in our epitaxial hcp Co films.[22] However, both the simulation and the experimental results show that the coercive fields of nonexchange coupled films are much higher than those measured for the epitaxial hcp Co films. Moreover, from high-resolution TEM images of the epitaxial Co films, no voids were observed. These results suggest that the grains in the epitaxial hcp Co films should be strongly exchange coupled and that their magnetic anisotropy properties can be explained by the analysis presented in the previous section.

In conclusion, we have shown that the stable phase in our epitaxial Co/GaAs(001) films is not a bcc but an oriented hcp with its $(\bar{1}2\bar{1}0)$ plane parallel to the GaAs(001). MOKE magnetometry and BLS measurements show that the epitaxial hcp Co films have both in-plane uniaxial and fourfold anisotropies. The relative strength of the uniaxial and fourfold anisotropies is found to be a strong function of the film thickness. The anisotropy properties of these epitaxial Co films can be explained in terms of their oriented hcp structure. We have also shown that the in-plane strain that develops in these epitaxial hcp films can significantly shift the NMR frequency from that found in relaxed polycrystalline hcp films.

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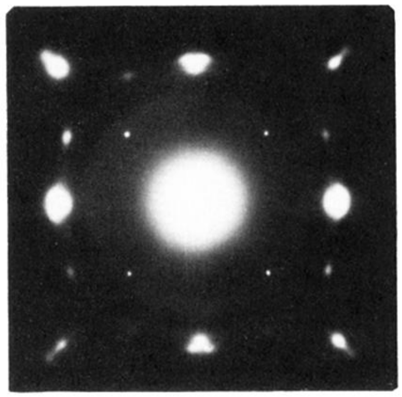
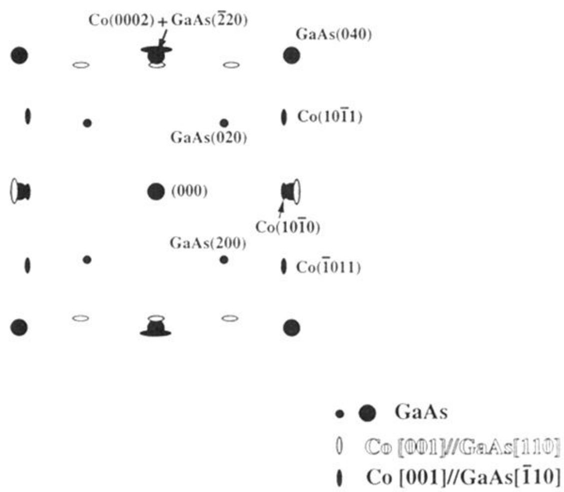


(a)



(b)

FIG. 1. (a) A selected-area electron diffraction pattern of a Co(50 Å) film grown on a GaAs(001) substrate prepared by 500-eV Ar^+-ion bombardment followed by annealing at 600 °C. (b) A schematic indexed pattern corresponding to the diffraction pattern shown in (a).