Formation and microstructural analysis of co-sputtered thin films consisting of cobalt nanograins embedded in carbon

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(Received 20 March 1997; accepted for publication 29 May 1997)

Cobalt–carbon thin films were deposited with a carbon concentration ranging from 27 to 57 at.% at different substrate temperatures. The morphology and phases of as-deposited films were investigated by transmission electron microscopy and x-ray diffraction. The effect of annealing on the microstructure is reported. Under particular conditions of substrate temperature, carbon concentration, and subsequent annealing, a granular morphology consisting of nanocrystalline cobalt grains embedded in graphitelike carbon was obtained. The cobalt grains were uniform in size. The particle size could be controlled in the range from 4 to 7 nm by varying the carbon concentration. The cobalt phase was found to depend on the carbon concentration and substrate temperature. The hexagonal close-packed cobalt phase was observed only via the formation of the metastable carbide δ' -Co₂C and its subsequent decomposition upon annealing. Otherwise the cobalt phase has a heavily faulted close-packed structure or a random stacking structure. (© 1997 American Institute of Physics. [S0021-8979(97)04417-4]

I. INTRODUCTION

Films with a nanogranular morphology have received much attention partly due to their potential applications as high-resistive soft magnetic materials,^{1,2} hard magnetic materials,³⁻⁵ and materials with giant magnetoresistance properties.^{6,7} The granular morphology is generally obtained via co-deposition of two nonmiscible materials, one magnetic and the other nonmagnetic, e.g., Co-Cu and Fe-Ag. Under particular deposition conditions, magnetic grains embedded in a nonmagnetic matrix can be obtained. The Co-C system has also been tried.⁸⁻¹¹ Until now, Co-C film phases have been studied, and metastable carbide phases reported.^{10,12,13} Magnetic properties have also been reported.^{8,9,11} However, data on the film morphology in conjunction with the film phases is lacking. In this article, we report on the microstructural properties of co-deposited Co-C thin films. The insulation of the magnetic grains in their nonmagnetic matrix and the crystal structure of the magnetic grains, which are particularly important for further applications, are described.

The experimental part of this work is reviewed in Sec. II. The results concerning the microstructure of as-deposited films are reported in Sec. III as a function of the carbon concentration and substrate temperature. Also, the modification of phases and morphology as a result of annealing are studied in Sec. IV.

II. EXPERIMENT

Co–C thin films were prepared by the co-deposition ion beam sputtering method. The geometry of the sputtering system is shown in Fig. 1, together with the Co–C target arrangement. The carbon concentration of the deposited films can be varied by moving the boundary between the Co and C plates relative to the ion beam center, thus the target area exposed to the ion beam determines the surface ratio of Co to C. The chemical compositions of the films were assessed by Auger electron spectroscopy. In this study, the carbon concentration was varied from 27 to 57 at. %. Sputtering was carried out under an argon pressure of 0.20 mTorr. A Kaufmann-type ion beam source was used,¹⁴ and the Ar ion beam had an energy of 1.5 keV and a diameter of 30 mm. The substrate temperature was varied between 100 and 300 °C. The deposition parameters are summarized in Table I.

Glass and NaCl cleaved in air were used as substrates. The glass substrates were cleaned prior to deposition by being dipped into a supersonic bath with ethanol, then methanol, and finally exposed to methanol vapor. Before the deposition of Co–C films and during the same run, an amorphous carbon layer was deposited on both substrates (the cleaved NaCl and glass). The purpose of this carbon underlayer was to equalize the surface conditions of the two substrate types; indeed on a NaCl substrate, epitaxial growth could be observed. Thus, the carbon underlayer ensured that the two types of substrates had films with the same microstructure. It also provided a clean surface for further deposition. The carbon underlayer was amorphous and \sim 5 nm thick.

Co–C thin films deposited on cleaved NaCl were floated in pure water, and the resulting free-standing thin films were put onto a holey carbon film supported by a copper mesh. The free-standing thin films together with their holey carbon film and copper mesh were used for transmission electron microscopy (TEM) observations. A Hitachi H9000 with an acceleration voltage of 300 kV was used. Selected area diffraction (SAD) patterns were recorded; differences in the phase due the deposition conditions and changes in phase with subsequent annealing of the samples were observed. X-ray diffraction (XRD) patterns were measured on glass substrates; a glancing angle of 1° was used and the direction 2θ was scanned. Cu $K\alpha$ radiation was used, and the average wavelength was taken to be 1.5418 Å. The estimated preci-

2200 J. Appl. Phys. 82 (5), 1 September 1997

0021-8979/97/82(5)/2200/9/\$10.00

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FIG. 1. Deposition chamber geometry, together with the Co–C target and ion beam arrangement. The target is moved across the ion beam, thus varying the Co/C geometric ratio which changes the carbon concentration of the film.

sion on 2θ was $\pm 0.04^{\circ}$, whereas the accuracy was about $\pm 0.1^{\circ}$ due to the nonresolved K_{α_1} and K_{α_2} radiation. The accuracy on the calculated lattice parameters was then ± 0.005 Å.

The grain morphology of the free-standing films was studied with TEM. Annealing of the samples, on glass substrates and on copper meshes, was performed in a lamp furnace under vacuum with a pressure of less than 10^{-5} Torr. The time sequence of the annealing treatment was as follows: 1/2 h to reach the annealing temperature Ta, followed by a plateau of 1 h at Ta. For each new sequence, Ta was

TABLE I. Sputtering conditions.

Targets	Co plate, 99.9% purity, 60 mm \times 60 mm
~ .	C plate, 99.9% purity, 60 mm×60 mm
Substrates	0211 Corning glass, cleaved NaCl
Target-substrate distance	50 mm
Ion beam	Ar ions (99.9999% purity), 1.5 kV, 10 mA
Base pressure	10^{-8} Torr
Total pressure	0.2 mTorr
Substrate temperature	100–300 °C
Film thickness	30-40 nm

increased by a 50 °C step; the first annealing temperature was Ta = 300 °C. The subsequent annealings were all carried out on the same samples (not on different pieces of the same samples).

III. RESULTS OF AS-DEPOSITED FILMS

A. Effect of the carbon concentration

Three films were deposited with carbon concentrations of 36, 46, and 57 at. %, having a deposition rate ranging from 2 to 3.5 nm/min; the other parameters were kept constant at 200 °C for Ts and 35 nm for the film thickness. Figure 2 shows bright-field TEM plane views of the as-deposited films, together with their SAD patterns.

In the case of 36 at. % carbon concentration, the film had a crystalline phase, as can be seen from the diffraction



FIG. 2. TEM plane views and SAD patterns of as-deposited Co–C films with carbon atomic concentrations of 36, 46, or 57 at. %. All film thicknesses are within 35 ± 5 nm; Ts=200 °C. In the diffraction pattern, the rings are indexed with $(hkl)_{orth}$ and $(hkl)_{hcp}$ for the orthorhombic carbide and the hexagonal cobalt, respectively.

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pattern of Fig. 2(b). By reviewing the Co–C system, it was possible to index this diffraction pattern as the MS II phase found by Konno and Sinclair.¹⁰ This metastable phase is composed of an orthorhombic cobalt carbide (δ' – Co₂C) and hcp cobalt. The easily recognizable rings of the carbide are the innermost (011)_{orth}, the (110)_{orth}, and the (111)_{orth}, the latter having the strongest reported intensity. As for the hexagonal cobalt, the (100)_{hcp} and (101)_{hcp} rings can be indexed; but the (002)_{hcp} is too close to the (021)_{orth} to be clearly distinguished. All rings of the diffraction pattern could not be indexed precisely, but there is an overall agreement with the MS II pattern for this carbon concentration.

The TEM observation of Fig. 2(a) reveals that the film has a granularlike morphology : the grains being defined by a difference in contrast in the image. The darker areas indicate a high Z element-rich phase. The grains have a cobaltrich phase and are separated from the neighboring grains by a boundary layer of a carbon-rich phase. In the inset of the TEM plane view, a higher magnification image shows lattice images. In this inset, the observed grain region, which is dark, has lattice images corresponding to (110)_{orth}. Thus, with the results of electron diffraction and lattice image observation, we conclude that the grain phase included the δ' – Co₂C carbide and the hexagonal cobalt (MS II phase). The bright area of the inset corresponds to a grain boundary found to have a larger d spacing than that of the grains, roughly corresponding to $(011)_{orth}$, which has a d spacing of 3.18 Å.¹⁰ The boundary thickness is too small to ensure that its contribution to SAD has been correctly detected in this case. Indeed, the main contribution to the SAD comes from the grain; so the diffraction rings of the boundary phase may overlap with the $\delta' - \text{Co}_2\text{C}$ and may not be distinguished (e.g., if the boundary phase is graphite). It is therefore difficult to reach a conclusion for the boundary phase.

At this carbon concentration [Figure 2(a)], the cobaltrich grains were not well insulated from their neighbors by the carbon-rich phase. Some of them were large without clear boundaries. Roughly, the grain size ranged from 5 to 20 nm and the boundary layer was ~ 2 nm thick.

When the carbon concentration was increased to 46 at. %, the diffraction rings of [Figure 2(d)] became very broad, indicating an amorphouslike phase. The innermost ring corresponded roughly to the (002) ring of graphite, but had a low contrast. The second ring was very broad and may consist of several unresolved rings. In this case, the film phase cannot be described precisely. However, this will become possible upon annealing the sample (see Sec. IV).

From the TEM plane view of Fig. 2(c) and the atomic number effect, we found that the morphology of the film was granular, although the separation between the grain and its boundary was not well defined. Thus, the film was composed of cobalt-rich nanograins, separated by carbon-rich boundaries.

The high-resolution image in the inset of Fig. 2(c) shows grains with imperfect lattice images having an ~ 0.2 nm spacing and boundaries with 0.3–0.4 nm spacing. The grains were nearly round and the average diameter of the grains was estimated to be 7 nm. The uniformity of the grain was clearly

improved by increasing the carbon concentration from 36 to 46 at. % at this substrate temperature.

At 57 at. % carbon concentration, the diffraction rings of Fig. 2(f) were narrower than those of Fig. 2(d). They also differed from the 36 at. % C case: the $(110)_{orth}$ ring was missing and the innermost ring shifted toward a larger *d* spacing value (from 3.2–3.4 Å). The innermost ring position corresponds approximately to the (002) graphite ring, and the center of the second broad ring of the pattern corresponds to the $(002)_{hep}$ or $(111)_{fcc}$ of the cobalt phase.

The TEM plane view of Fig. 2(e) shows that the morphology was granular, with an estimated grain size of 4 nm. The grain boundary was ~ 2 nm thick. In the high-resolution image in the inset, lattice images of the grains can be distinguished. These had a spacing of ~ 0.2 nm, which corresponds to the broad cobalt ring in the diffraction pattern. The lattice images also show that the grains had a poor crystal perfection. In the boundary region, lines with a much larger spacing can be recognized; these correspond to the innermost ring of the diffraction pattern, the position of which was close to the (002) graphite. Thus, the film mainly consisted of cobalt-rich grains with poor crystal perfection embedded in graphitelike carbon.

In conclusion, it can be stated that increasing the carbon concentration changes the film phase and morphology. The phase changes from a crystalline MS II phase (hcp Co plus $\delta' - \text{Co}_2\text{C}$ carbide) to a cobalt-rich phase plus graphitelike carbon (the results on the observed phases are summarized in Table II). A granular morphology with a uniform grain size was obtained for a carbon concentration larger than 46 at. % at Ts = 200 °C, and the grain size decreased with increasing the carbon concentration.

B. Effect of the substrate temperature

Next we varied the substrate temperature Ts while keeping the other parameters constant; i.e., the carbon concentration was fixed at 27 at. %, the deposition rate was 15 nm/ min, and the film thickness was fixed at 30 nm. Three films were deposited at Ts = 100, 200, and 300 °C. Figure 3 shows TEM plane views of the as-deposited films, together with their corresponding SAD patterns.

For the sample deposited at $Ts = 100 \,^{\circ}C$, the diffraction rings of the SAD shown in Fig. 3(b) are too broad to be indexed precisely. However, the diffraction pattern has some resemblance to the MS II phase [Fig. 2(b)]: there is a $(110)_{\text{orth}}$ ring and a brighter ring at the $(111)_{\text{orth}}$ or $(002)_{\text{hcp}}$ positions. But the innermost ring is shifted toward a smaller *d* spacing compared to that of the MS II phase.

The TEM plane view of Fig. 3(a) reveals small grains having a regular rounded shape with a diameter of 5 nm. The dispersion of the grain size was small. Also, the separation between the grain and its boundary was not very well defined. The inset of the TEM view shows lattice images from a grain of this film. No lattice image could be observed in the grain boundary region.

Hence, the observed broadening of the SAD rings must be due to the crystallite size effect. Therefore, the film phase contained a crystalline carbide close to the MSII phase. The

TABLE II.	Summary of	f crystallographic	data as	obtained	from SAD.	Graphitelike	carbon i	s abbreviated	in	graphite
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Carbon concentration (at. %)	Grain size (nm)	As-deposited $Ts = 200 \ ^{\circ}\mathrm{C}$	$Ta = 300 \ ^{\circ}\mathrm{C}$	<i>Ta</i> =350 °C	$Ta = 400 \ ^{\circ}\mathrm{C}$
36 at. %	5-20	grain: MS II phase (δ' - Co ₂ C+hcp Co) boundary: (?)	grain: MS II phase $(\delta' - Co_2C + hcp Co)$ boundary: (?)	grain: hcp Co boundary: graphite	grain: hcp Co boundary: graphite
46 at. %	7	amorphouslike	grain: heavily faulted Co boundary: graphite +little carbide	grain: heavily faulted Co boundary: graphite	no data
57 at. %	4	grain: poor Co crystal boundary: graphite	grain: poor Co crystal boundary: graphite	grain: crystalline Co boundary: graphite	grain: crystalline Co boundary: graphite

film consisted then of crystalline carbide and/or cobalt grains embedded in an amorphous boundary. Thus, lowering *Ts* expands the C concentration region found in Section III A (Ts = 200 °C and $C \ge 46$ at. %), for which a granular morphology can be obtained.

At $Ts = 200 \circ C$, the diffraction pattern [Fig. 3(d)] can be indexed as the MS II phase. The film morphology, as inferred from the TEM image of Fig. 3(c), was polycrystalline. In this case, crystallites were not separated by a boundary region of a different phase with a significant thickness. The crystallite size ranged from 20 to 40 nm. At the substrate temperature, $Ts \le 200$ °C, the crystallite size was governed by the temperature dependency of the nucleation density; that is, the crystallite size increased with Ts.¹⁵

The sample deposited at $Ts = 300 \,^{\circ}C$, had a SAD pattern [Fig. 3(f)] that can be indexed as hcp Co, fcc Co, and a rather broad graphite (002) ring. The rings indexed as belonging to the cobalt phase had the following characteristics:

(a) the ring with the strongest intensity was $(002)_{hcp}$ instead of $(101)_{hcp}$, which in a randomly oriented hcp phase is the strongest,



FIG. 3. TEM plane views and SAD patterns of as-deposited Co–C films with substrate temperatures Ts of 100, 200, or 300 °C. All film thicknesses are within 30 ± 5 nm; the C concentration is 27 at. %.

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FIG. 4. Small-angle x-ray diffraction pattern of Co–C film deposited at Ts = 300 °C and 27 at. % C concentration. Arrows indicate the positions of the diffraction peaks with their Miller indices. The film thickness was 60 nm.

- (b) two broad rings at (101)_{hcp} and (200)_{fcc} were obtained, and
- (c) the $(102)_{hcp}$ and $(103)_{hcp}$ rings were missing.

This film was further investigated by XRD taken at a glancing angle $\theta = 1^{\circ}$; the measured XRD pattern is shown in Fig. 4. This pattern has one diffraction peak close to the (002) plane of the hcp Co structure, and other peak intensities of $(100)_{hcp}$, $(101)_{hcp}$, and $(200)_{fcc}$, are very low but were detected. The $(002)_{hcp}$ peak position corresponds to a *d* spacing of 2.035 Å, which is in agreement with that of the standard data for hcp Co (Ref. 18) within the measurement accuracy.

An examination of both diffraction results shows that the most intense (002)_{hcp} diffraction found in both patterns [Fig. 3(f) and Fig. 4] cannot be explained by the existence of a crystallographic texture, since the two patterns were measured using two different geometries. The SAD patterns missing the $(102)_{hcp}$ and $(103)_{hcp}$ rings indicate a heavily faulted hcp phase; generally the (h,k,l) rings with h-k $=3 n \pm 1$, where n is an integer and l is not 0, are broadened or even eliminated by the presence of a high density of stacking faults.¹⁶ Finally, all of the above characteristics can be explained by a random close-packed phase; that is, a phase having a random stacking of close-packed planes: e.g. ABABCBABC... instead of the ABAB sequence for hcp, or ABCABC sequence for fcc. In the random stacking case, an intense reflection was found at the (002)hcp position, and two broad reflections were observed at the $(101)_{hcp}$ and $(200)_{fcc}$ positions.¹⁷ The inset of the TEM image of Fig. 3(e) provides a direct illustration of an almost random stacking sequence in the film; it shows the details of a cobalt grain having stacking faults every three to six stacking planes. Therefore, the film consisted of a cobalt phase with a structure of nearly randomly stacked close-packed planes plus graphitelike carbon.

The TEM plane view [Fig. 3(e)] shows that the structure obtained at this substrate temperature had particles that were not well insulated. Combining the diffraction and lattice image results, it can be concluded that this film consisted of cobalt grains with a random stacking structure embedded in



FIG. 5. Schematic diagram of Ts vs the C concentration, recapitulating the conditions for the fabrication of the nanogranular microstructure.

graphitelike carbon. The grain-size distribution was broad, and in some places the boundaries were not well defined. Most of the grain sizes ranged from 5 to 30 nm. Some particles a few nanometers in size were also detected.

To summarize the effect of the substrate temperature, two types of granular microstructures have been found:

- with a low *Ts* deposition, the granular morphology had a small grain-size dispersion and the grain phase was a carbide;
- (2) with a high *Ts* deposition, the granular morphology had a broad grain-size distribution and consisted of cobalt grains with a random stacking structure embedded in graphitelike carbon.

The results of the influence of the carbon concentration and Ts on the film morphology are outlined in Fig. 5. As regards the film phases, high Ts (\geq 300 °C) promoted the formation of cobalt grains with a highly faulted/randomly stacked close-packed plane structure, whereas in the case of low Ts (\leq 200 °C) a metastable carbide and an amorphouslike phase were obtained. In the following, an investigation of the effect of subsequent annealing of the films deposited at Ts = 200 °C (the previous carbon concentration series of Sec. III A, for which a metastable carbide and an amorphouslike phase were found) is reported. Phase and morphology changes are described.

IV. RESULTS OF ANNEALED SAMPLES

The films shown in Fig. 4, which were deposited at Ts = 200 °C with a carbon concentrations of 36, 46, or 57 at. %, were annealed at Ta = 300, 350, and 400 °C. The TEM plane view images and SAD patterns of the annealed films are shown in Figs. 6 and 7, respectively.

For a C concentration of 36 at. %, annealing of the sample at Ta = 300 °C did not change the phases [Fig. 7(a)] or the morphology [Fig. 6(a)] of the as-deposited film [Figs. 2(a) and 2(b)]. That is, the film consisted of grains having the MS II phase not perfectly embedded in a carbon-rich phase. However, in the SAD pattern of the annealed film, the rings corresponding to the hcp Co were more intense than those of the as-deposited film; this means that the $\delta' - \text{Co}_2\text{C}$ carbide



FIG. 6. TEM plane views of Co–C films (Ts = 200 °C) with an annealing temperature Ta of 300, 350, and 400 °C (except for 46 at. %C for which Ta was 500 °C instead of 400 °C). The carbon concentration is shown in the figure.

phase started to decompose at this annealing temperature. When annealing was performed at Ta = 350 °C, the phase changed to hcp Co and graphitelike C as indicated by the innermost (002) ring [Fig. 7(b)]. The carbide was completely decomposed at this temperature since no carbide diffraction ring can be found in the SAD. With regard to the cobalt phase, the most intense ring was $(101)_{hcp}$, followed by $(002)_{hcp}$ and $(100)_{hcp}$, was unlike the random stacking case that occurred when deposited at $Ts = 300 \degree C$ [Fig. 3(f)]. Also the $(102)_{hcp}$ and $(103)_{hcp}$ rings can be seen, whereas they were absent in the random stacking case. These properties indicate that a pure hcp Co phase was obtained. However a small intensity (200)_{fcc} ring was also detected in the SAD of Fig. 7(b), and few stacking faults can be observed in the TEM image. Thus, the cobalt phase mainly consisted of hcp with few stacking faults, and probably short sequences of fcc can be found locally. The TEM image in Fig. 6(b) shows that the grains have a lattice spacing of ~ 0.2 nm, whereas it is 0.3-0.4 nm for the boundary regions. Thus it can be concluded that the grains have a hcp Co phase and that their boundaries are graphitelike C. The morphology was changed by annealing in that the grains became better insulated from each other by the graphitelike C boundaries. Subsequent annealing at Ta = 400 °C, also changed the morphology of the film [Fig. 6(c)], but not the phases [Fig. 7(c)]. It is found that the cobalt grains coalesced to form larger grains and that the boundary layer thickness increased in some places.

For this C concentration of 36 at. %, XRD patterns were observed to ensure the lattice parameters of the hcp Co; we also tried annealing the sample at higher temperatures. XRD patterns measured at Ta = 400, 500, and 600 °C are shown in Fig. 8, and the corresponding results are reported in Table III. For Ta = 400 °C, the peak positions were in general agreement with the hcp Co powder standard data,¹⁸ which confirms the SAD results. When Ta was increased to 600 °C, the peak positions were not affected. Probably no phase transition (hcp Co-fcc Co) took place at these annealing temperatures, because the austenitic temperature, which lies around 440 °C in the case of pure bulk Co,¹⁹ is shifted to a higher value in the Co-C system.¹³ The full width at half maximum (FWHM) of the $(101)_{hcp}$ peak increased with Ta from 0.75° to 1°. Other hcp peak FWHMs were not significantly changed. The broadening of the (101)_{hcp} peak is related to the presence of staking faults in the hexagonal closepacked structure.¹⁶ Also the integrated intensity of the $(002)_{hcp}$ peak is increased with Ta relative to the other peaks; this is also in agreement with the presence of an increasing number of stacking faults as observed in the extreme case of a random staking structure.



FIG. 7. SAD patterns of Co–C films (Ts = 200 °C) with an annealing temperature Ta of 300, 350, and 400 °C (except for 46 at. %C where Ta was 500 °C instead of 400 °C).

At 46 at. % carbon, the film phase was changed by annealing at Ta = 300 °C. The SAD pattern of Fig. 7(d) is the same as the pattern obtained at $Ts = 300 \circ C$ [Fig. 3(f)], which represents a cobalt random stacking phase plus a graphitelike carbon phase. An additional ring was observed at the position corresponding to the $(110)_{\text{orth}}$ ring of the δ' $-Co_2C$ carbide. At Ta = 300 °C the film phase included a carbide, presumably $\delta' - \text{Co}_2\text{C}$. The carbide ring disappeared at the higher annealing temperature of 350 °C, as can be seen from the corresponding SAD of Fig. 7(e). Thus at Ta = 350 °C, the film consisted of a cobalt phase that was a heavily faulted close-packed structure or had a random stacking structure of close-packed planes, plus a graphitelike carbon phase. Since the lattice images of the grains had a smaller spacing than that of the grain boundaries, the film microstructure at Ta = 350 °C consisted of cobalt grains with a random stacking structure embedded in graphitelike C. Further annealing at $Ta = 500 \,^{\circ}\text{C}$ drastically altered the morphology: the grains coalesced to form larger particles and were separated by a graphitelike region of unequal dimensions.

For 57 at. % C, the SAD pattern of Fig. 7(g) taken at Ta = 300 °C had two more rings, whose positions corresponded to $(110)_{hcp}/(220)_{fcc}$ and $(112)_{hcp}/(311)_{fcc}$. The SAD patterns were not significantly changed by annealing at a higher temperature, Ta = 350-400 °C [Figs. 7(h) and 7(i)].

The broadening of the diffraction rings caused by the small size of the cobalt-rich crystallites (\sim 4 nm) rendered the phase determination difficult. However, these patterns cannot be explained by one of the carbide phases reported in refer-



FIG. 8. Small-angle x-ray diffraction patterns of the Co–C film deposited at Ts = 200 °C and 36 at. %C. The data were obtained after annealing at Ta = 400, 500, and 600 °C.

TABLE III. Results of XRD pattern analysis of Co–C thin films, deposited at a carbon concentration of 36 at. % and Ts = 200 °C, with annealing temperatures of Ta = 400, 500, and 600 °C. The lattice parameters and integrated intensities of hcp Co (a = 2.505 Å and b = 4.060 Å) and fcc Co (a = 3.5447 Å) are taken from Powder Diffraction Standards.^a Angular positions 2θ , d spacings, FWHM(s), and integrated intensity ratios $I_{(hkl)}/I_{(h'k'l')}$ of Bragg peaks are given. A Cu K α averaged wavelength of 1.5418 Å was used and the accuracy of the calculated d spacings is ± 0.005 Å.

	Phases and Miller indices	2 <i>θ</i> (deg)	d spacing (Å)	FWHM (deg)	Integ. intens. ratio (%)
Co hcp ^a	hcp(100)	41.72°	2.165		$I_{(100)}/I_{(101)} = 0.2$
	hcp(002)	44.63°	2.030		$I_{(002)}/I_{(101)} = 0.6$
	hcp(101)	47.61°	1.910		
Co fcc ^a	fcc(111)	44.25°	2.047		$I_{(200)}/I_{(111)} = 0.4$
	fcc(200)	51.57°	1.772		
C: 36 at. %	hcp(100)	41.7°	2.165	0.8°	$I_{(100)}/I_{(101)} = 0.4$
$Ta = 400 \ ^{\circ}\mathrm{C}$	hcp(002)	44.6°	2.030	0.7°	$I_{(002)}/I_{(101)} = 0.8$
	hcp(101)	47.6°	1.910	0.75°	(***)
C: 36 at. %	hcp(100)	41.8°	2.160	0.8°	$I_{(100)}/I_{(101)} = 0.4$
$Ta = 500 ^{\circ}\mathrm{C}$	hcp(002)	44.7°	2.030	0.9°	$I_{(002)}/I_{(101)} = 1.1$
	hcp(101)	47.6°	1.910	0.9°	(***)
C: 36 at. %	hcp(100)	≈41.7°	2.165	≈1°	$I_{(100)}/I_{(101)} \approx 0.7$
$Ta = 600 ^{\circ}\mathrm{C}$	hcp(002)	44.6°	2.030	0.7°	$I_{(002)}/I_{(101)} = 1.3$
	hcp(101)	47.7°	1.905	1°	,,

^aSee Ref. 18

ences 10,12 and 20. Furthermore, the $(100)_{hcp}$, $(002)_{hcp}$, $(101)_{hcp}$, $(111)_{fcc}$, and $(200)_{fcc}$ SAD rings were not resolved for this crystallite size, making it impossible to determine the phase of the cobalt-rich grains. Also the lattice images of the cobalt-rich grains became clearer after annealing at Ta = 350 °C, as seen in the inset of Fig. 6(h). Thus, the film most likely consisted of crystalline cobalt grains embedded in graphitelike C at this annealing temperature. On the other hand, the granular morphology was not changed by annealing at Ta = 300-400 °C [Fig. 6(g)-6(i)]. It should be noted that the behavior of the film on its mesh and on the glass substrate might be different, particularly regarding stress and the grain coalescence caused by annealing. However, it was possible to demonstrate that the coalescence of grains takes place on the glass substrate as well, by observing the changes in XRD. The crystallites in this sample were too small to be observed by XRD; but a diffraction pattern similar to Fig. 4 was observed after annealing at Ta =500 °C. Thus, the cobalt crystallites rapidly grew in size at *Ta*>500 °C.

To summarize this section, the annealing influence on the phase changes and morphology is found to depend on the carbon concentration. For a C concentration of 36 at. %, the MS II phase of the as-deposited sample transformed upon annealing at Ta = 350 °C into hcp Co plus graphitelike C. At 46 at. % C, the phases became a heavily faulted close-packed Co or a random stacking Co, plus graphitelike C. The results of the phase changes are shown in Table II. The granular morphology was maintained after annealing, if Ta is lower than 400 and 500 °C for 36 and 57 at. % C, respectively. When Ta exceeded these values, the grains coalesced and the morphology was drastically modified.

V. DISCUSSION

The as-deposited films had a crystalline phase (e.g., $Ts = 200 \degree C$ and C ≤ 36 at. %) or an amorphouslike phase (Ts

=200 °C and C≥36 at. %). Although Konno and Sinclair reported that films become amorphous as soon as the carbon concentration exceeds 5 at. %,¹⁰ this difference is very likely to be due to the difference in the substrate temperatures: in the quoted reference, samples were deposited at room temperature, whereas in this work, where Ts = 200 °C, Ts acts as a driving force for crystalline phase formation. Oda et al. have reported that Co-C films have an amorphous phase for C≥5 at. % when deposited at $Ts = 160 \degree C.^{\frac{1}{8}}$ However, this conclusion was based on the broadening of the XRD peak, which also depends on the crystallite size (not reported). Further, the film phase is most likely to be a metastable carbide, which has many diffraction peaks that are difficult to resolve by XRD in the case of small crystallites. Therefore, it is difficult to be sure that these films have an amorphous phase in the 5-20 at. % C range by using XRD only.

Concerning the formation of the metastable carbide δ' – Co₂C under the conditions Ts = 200 °C and $27 \le C \le 36$ at. %, and its decomposition into hcp Co plus graphitelike C at $Ta \approx 350$ °C, the present results agree well with Ref. 10. Relatively low formation temperatures ($T \le 500$ °C) for the metastable carbides (Co₃C and Co₂C) are also reported in references 8, 9, 12, and 13.

Within the ranges of Ts and C concentration that were evaluated, the hcp Co phase was obtained only via the decomposition of the $\delta' - \text{Co}_2\text{C}$ carbide. When the metastable carbide was not formed due to the C concentration and/or the Ts being too high, the cobalt phase resulted in a heavily faulted close-packed structure or a random stacking structure, which were stable at room temperature. The presence of a large number of stacking faults was possible because they induced a small variation in the free energy. Indeed, only a small variation in the free energy is necessary for the phase transition from hcp Co to fcc Co.²¹ In the case of bulk Co, the metastable cubic phase is often present in samples at room temperature.¹⁹ It should be possible to avoid the for-

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mation of stacking faults (equivalent to short sequences of the fcc phase) to some extent by alloying cobalt with a material that will increase the temperature of the phase transition from hcp to fcc (e.g. rhenium²² or ruthenium).

The metastable carbide $\delta' - \text{Co}_2\text{C}$ has been found to decompose into hcp Co plus graphitelike C, as reported in Ref. 10, which further stated that the formation of a graphite phase is possible only via a metastable carbide phase formation. However graphitelike C was also found in the film with a C concentration of 57 at. % ($Ts = 200 \,^{\circ}\text{C}$), for which no carbide phase was found. The graphitelike C may form via cobalt-mediated crystallization of the carbon phase. Also graphitelike C was formed at $Ts = 300 \,^{\circ}\text{C}$ with 27 at. % C. At this substrate temperature, Co and C segregate and a Co crystalline phase and a graphitelike phase are obtained. Again this may occur via Co-mediated crystallization of the carbon phase.

A granular morphology consisting of uniform particles of Co with low size dispersion was obtained. The particle diameter can be controlled between 7 and 4 nm by adjusting the C concentration in the 46–57 at. % range at Ts=200 °C. The insulation of the cobalt grains by graphitic carbon was good with a boundary thickness of about 2 nm. Annealing retained the granular morphology when Ta did not exceed a certain value at which Co diffuses through the carbon boundaries and the grains start to coalesce. The Ta limit, at which the morphology starts to change, depends on the carbon concentration: the higher the carbon concentration, the higher the annealing temperature must be for coalescence to take place. At 36 at. % C, the coalescence of the grains can be attributed to the poor grain insulation, and at 46-57 at. % C to the many imperfections of the graphitelike boundaries.

VI. CONCLUSIONS

Co–C films were deposited with a carbon concentration in the range of 27–57 at. % and a substrate temperature in the range of 100–300 °C. Granular films consisting of nancrystalline cobalt particles, with a sharp distribution of the particle sizes, embedded in graphitelike C were obtained at Ts = 200 °C, C=46–57 at. %, and after subsequent annealing at Ta = 350 °C. The grain size could be controlled in the range of 4–7 nm by varying the carbon concentration. Under these conditions, the cobalt phase had a heavily faulted close-packed structure or a random stacking structure. The metastable carbide $\delta' - \text{Co}_2\text{C}$ was formed at $27 \leq \text{C} \leq 36$ at. % and $100 \leq Ts \leq 200$ °C. The $\delta' - \text{Co}_2\text{C}$ decomposed into hcp Co and graphitelike C at Ta = 350 °C. At the C concentrations and Ts values used, the hcp Co phase was obtained only via the formation and subsequent decomposition of the metastable carbide $\delta' - \text{Co}_2\text{C}$. Graphitelike C was formed at the grain boundaries through the decomposition of the metastable carbide, but it was also formed when no carbide phase was found (Ts = 200 °C and C>46 at %, and Ts = 300 °C and C=27 at. %). In the latter case, the graphitelike C may have formed through cobalt-mediated crystallization of the carbon phase.

A detailed investigation of the magnetic properties of the investigated thin films is now being prepared.

ACKNOWLEDGMENTS

The authors wish to thank K. Ichikawa, E. Sato, and H. Takenaka for their valuable contributions in the various stages of the experiments carried out.

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