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CoZrNb amorphous thin films deposited by r.f. diode and d.c. triode sputtering: a comparative study

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The effects of the particular sputtering method on the structural and magnetic properties of amorphous CoNbZr thin films deposited by d.c. triode and r.f. diode sputtering are reported. A comparison has been made of the two kinds of films in terms of their local structures, stability, crystallization process and a number of magnetic characteristics. The structural investigations which are performed via the transmission electron diffraction pattern and by transmission electron micrographs showed that the local topological and chemical disorder is larger in triode sputtered films than in r.f. diode deposited ones. This result is related to the composition fluctuation in the first kind of film. Consequently, the structural relaxation and the crystallization process are also different in the two types of layer. At intermediate annealing temperatures one observes the formation of a higher chemical order in triode sputtered films. The difference in the structure does not affect the main characteristics of the *B–H* loops which are the same in the two sets of samples, but it does affect the characteristics of the ferromagnetic resonance spectra.

1. Introduction

The most widely used deposition methods for producing amorphous thin films are vapour deposition and ion sputtering. One of the main advantages of evaporation over sputtering is that during the deposition process the background pressure is much lower. On the other hand, the composition of sputter-deposited films is almost identical to the composition of the target so it is easier to obtain a chemically uniform alloy film by sputtering. Although there are several sputtering techniques, only a very few studies have, however, been performed in which the properties of the thin films deposited with different sputtering methods have been compared.

In a pioneering work Naoe *et al.* [1] made a comparative study of $Co_{1-x}M_x$ (M = Zr, W, Ta. . .) amorphous films prepared by r.f. sputtering, d.c. facing target sputtering and a dual ion beam sputtering, respectively. They observed that films prepared by r.f. sputtering are those which necessitate the lowest critical concentration in M to obtain an amorphous phase. This result was explained by the high energy of the deposited particles. A comparison of samples having the same concentration revealed that films deposited by ion beam sputtering generally exhibit the best soft ferromagnetic properties, a result attributed to the low effective substrate temperature characteristic of this deposition process.

Here we report on a study performed on CoZrNb amorphous thin films prepared by r.f. diode and d.c. triode sputtering, respectively. These thin films are interesting because of their possible use as soft magnetic core in recording heads. We observed some well defined differences in the structural and magnetic properties of these films obtained by the two techniques, and which are pointed out clearly in the presentation of the experimental results. We will explain these results by considering the deposition parameters inherent to each of the preparation processes.

2. Experimental procedure

Films prepared by r.f. diode sputtering (hereafter called D films) were obtained in a Perkin–Elmer 2400-6J apparatus. The sputtering conditions used were an Argon pressure P_{Ar} of 10 mtorr and an r.f. input power of 200 W. The films obtained by d.c. triode sputtering (hereafter called T films) were deposited in a Balzers Sputron II system. The deposition parameters were $P_{Ar} = 5$ mtorr, a d.c. voltage of 1000 V and a sputter current of 0.5 A. For more details see de Wit *et al.* [2].

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In both systems, a target having the composition $Co_{86.1}Nb_{8.6}Zr_{5.3}$ was used. For this composition the magnetostriction is zero in samples which are amorphous. The compositions of the deposits were slightly different being $Co_{86.9}Nb_{9.3}Zr_{3.8}$ for D films and $Co_{83.5}Nb_{10}Zr_{6.5}$ for T films, respectively.

The morphological and structural investigations were performed on 0.05 to 0.08 μm thick films deposited on to TEM windows in a JEOL 200CX electron microscope. These windows are Si substrates with a hole at their centre which is covered by a Si_3N_4 layer on to which the magnetic film is deposited. The microstructure was investigated by transmission electron microscopy (TEM) in bright (BF) and dark (DF) field. The structural state was studied on transmission electron diffraction pattern (TEDP) profiles which were traced from photographic films and resolved up to $s = 2\sin\theta/\lambda = 12\ \mathrm{nm}^{-1}$ where s is the scattering vector. The magnetic properties were measured by VSM, a B–H loop tracer at 50 Hz, and ferromagnetic resonance performed at $f = 9.8$ GHz on films of thickness in the range of 0.05 to 1 μm.

3. Structural properties: Results and discussion

The structural properties were studied on as-deposited films and as a function of the annealing treatment using the heating stage of the electron microscope.

3.1. As-deposited state

The TEDP profiles obtained on both D and T films show characteristics typical of an amorphous structure. A detailed study of these diffraction patterns, however, revealed a number of well defined and reproducible differences.

The diffraction profile of D films shows structural modulation as generally detected on amorphous metallic films [3] (Fig. 1). It presents three broad and diffuse halos with a well defined shoulder on the high s side of the second peak. The diffraction profile of the T films has the same properties (Fig. 2) but with some modifications concerning the first halo (Fig. 3) and the shoulder on the second one (Figs 2 and 3). In the spectrum of the T films one detects a supplementary shoulder which is located at the low s side of the second peak (Fig. 2). Simultaneously, a broadening of the half width of the first halo occurs for the low s side of the first peak, while the profile obtained for the high s side remains similar for the two types of film (Fig. 3). This asymmetrical increase of the width of the first halo and the supplementary shoulder on the second one are believed to be related to the same mechanism, as both effects appear on the low s side of the peaks. Finally, the position of the centroid of the first amorphous halo is also slightly different with $s = 4.89\ \mathrm{nm}^{-1}$ from D films and $s = 4.82\ \mathrm{nm}^{-1}$ from T films.

The diffraction pattern of T films can be interpreted by a concentration fluctuation with rich and poor zones in non-magnetic transition metals M. The average nearest-neighbour atomic distance in the M-

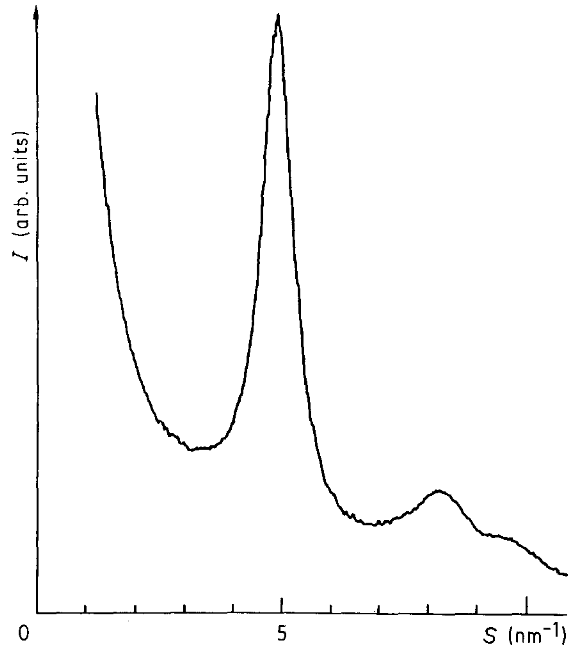

Figure 1 TEDP profile of CoZrNb films deposited by r.f. sputtering (D films).

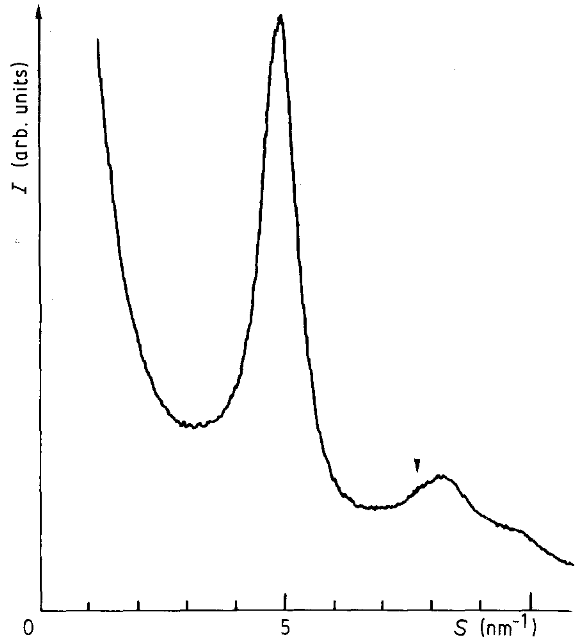

Figure 2 TEDP profile of CoZrNb films deposited by triode sputtering (T films). (▼): location of the supplementary shoulder.

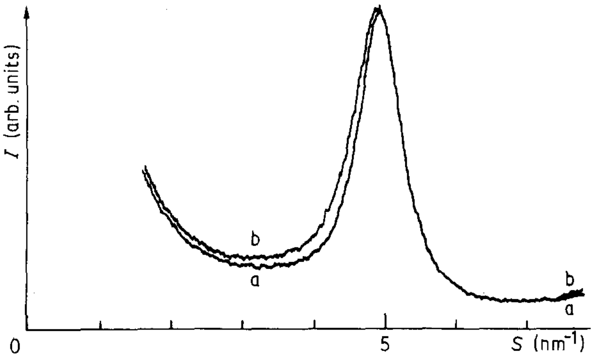

Figure 3 Direct comparison of the first diffraction peak corresponding to D and T films, respectively. (a) D films; (b) T films.

enriched and M-depleted regions is larger and smaller, respectively. The diffraction pattern of such alloys is the superposition of the two spectra, where the profile which corresponds to the M-enriched zones shift toward lower values of s. The compositions of the two amorphous phases are fairly close to each other so it is not possible to differentiate experimentally the position of the first maxima. The shift between the two diffraction profiles increases, however, with increasing values of s. This effect explains the fact that a supplementary shoulder is resolved on the second maximum. We estimated the minimum short range interatomic distance d_m from the position of the first peak using $d_m = 1.23/s$. One obtains $d_m = 0.251$ nm for D films and $d_m = 0.255$ nm for T films, respectively. The higher value of d_m in T films can be attributed either to the higher average transition metal content M or to the concentration fluctuation which induces a larger chemical and/or topological disorder. As will be shown later by the structural relaxation process, a significant part of this difference is related to the concentration fluctuation.

Finally, it can be pointed out that, in D films, d_m satisfies the relation $d_m = 2r_{Co}$ where $r_{Co} = 0.125$ nm is the atomic radius of Co. This result agrees with the main hypothesis of a structural model established by Laridjani *et al.* [4] from a study performed on amorphous Fe-rich Fe–Zr alloys: "The structure of an amorphous TM–M alloy (here Co–ZrNb) rich in transition metal (TM), can be considered as a dilute

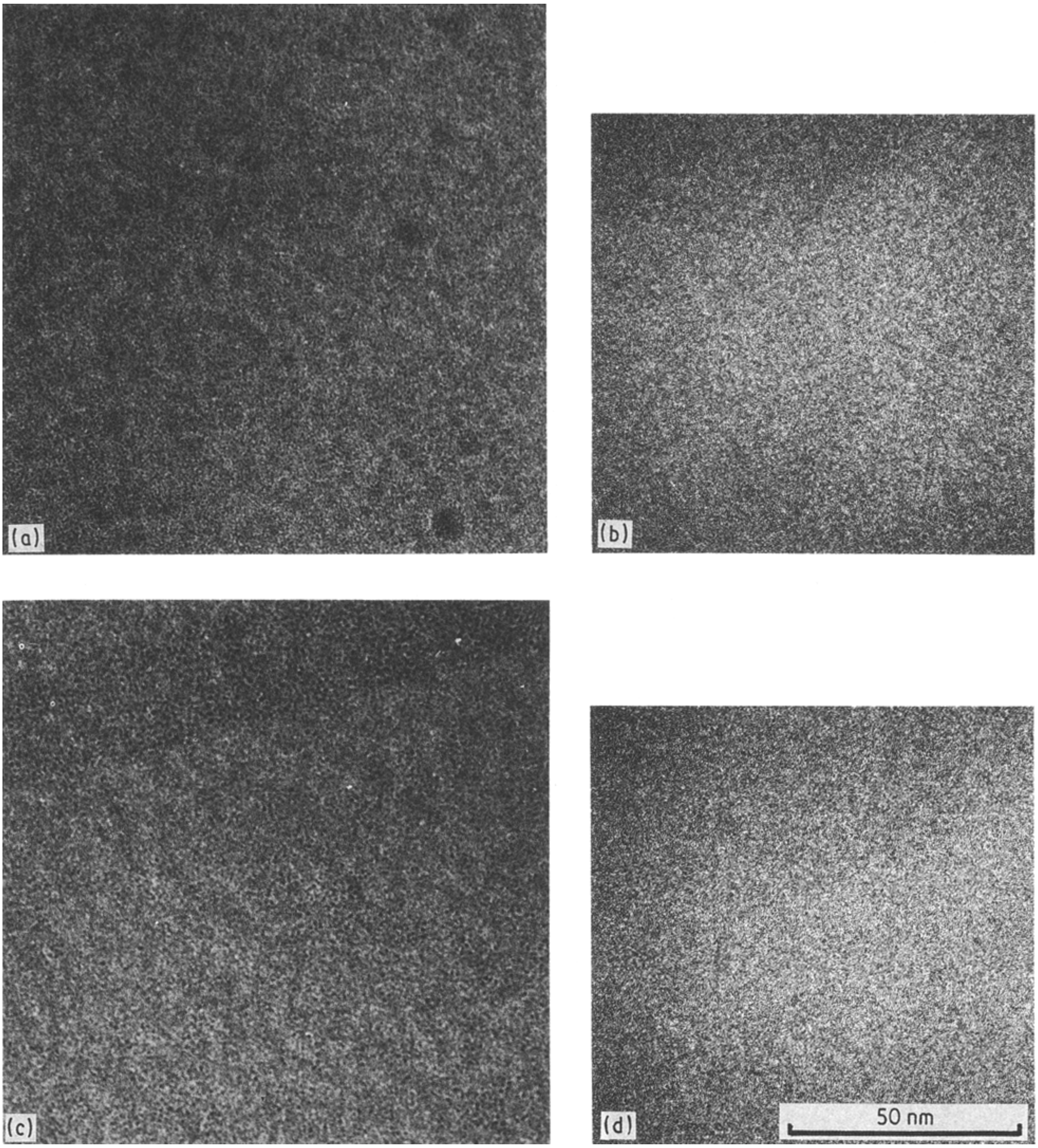

Figure 4 Transmission electron micrographs of CoZrNb films in bright (BF) and dark (DF) field. (a), (b) film deposited by r.f. sputtering (D films); (c), (d) film deposited by triode sputtering (T films).

solution of M(M = Zr, Nb) in a pure amorphous TM (TM =Co) structure".

The amorphous structures of the D and T films were confirmed by the TEM images obtained in DF (Fig. 4b and c), but for the magnification used ($\times 10^5$) these electrons micrographs exhibit practically the same characteristics. BF images of T films present, however, a stronger contrast than those of D films (Fig. 4a and c). These results are probably related to the local fluctuations of density and composition in T films. The regions of lower density are those which possess a larger topological disorder.

3.2. Annealed films: structural relaxation, stability and crystallization process

The difference between the crystallization temperature of D and T films could be shown clearly by annealing the samples at 400 °C. After annealing, the diffraction pattern of D films consists of broad halos corresponding to an amorphous matrix and superimposed weak Bragg reflections corresponding to a microcrystalline phase. The as-detected reflections can be identified as (111), (220), and (311) peaks of fcc Co, the as-computed lattice constant is 0.3542 nm, a value which is fairly close to 0.35446 nm of pure fcc Co [5]. These results show that the first step of crystallization occurs by primary crystallization.

The diffraction profile of T films annealed at 400 °C is still characteristic of an amorphous material (Fig. 5) and in contrast to D films, no reflections corresponding to a microcrystalline phase have been detected, but some well defined modifications are observed. As a result of the annealing, the supplementary shoulder located at the low s side of the second halo and the asymmetrical broadening of the first peak have disappeared (Figs 5 and 6). Simultaneously, the location and the half width of the first peak changed too, now being $s = 4.89\ \text{nm}^{-1}$, and $\Delta s_{1/2} = 0.72\ \text{nm}^{-1}$, respectively. These values are the same as those obtained on D films in the as-deposited state.

The bright and dark field TEM images clearly confirm the results obtained by means of TEDP. The TEM images of as-annealed D films present a partially crystalline structure with small crystals in an amorphous matrix (Fig. 7a and b). On the contrary, no microcrystals can be detected in the TEM image of T films (Fig. 7c and d), but as a result of annealing some changes were observed in the characteristics of the micrograph (compare Fig. 4c and d). The contrast has diminished and the spotty character of the bright field image has disappeared, effects which are due to the suppression of density and concentration fluctuations. These results show that the annealing modifies the local structure of T films, which evolves toward the local structure of D films in the as-deposited state.

In T films, the microcrystals begin to form at about 430 °C. They also have an fcc structure, but their average number per unit area appears smaller than in D films (Fig. 8a and b). When the films were heated from 400 to 530 °C, in both D and T films the remaining amorphous matrix crystallized and a phase transformation occurred. Films heated to 530 °C contain predominantly an hcp (Co, Zr) phase. The average grain size is larger in T films than in D ones (Fig. 8c and d). This result can be understood by considering the activation energy for crystallization which is a combination of the activation energies for nucleation and growth [6]. At 530 °C the crystallized volume fraction in the two types of film is the same. Consequently, the crystal growth velocity is higher in T films, which is in agreement with the better thermal stability of this type of film [6].

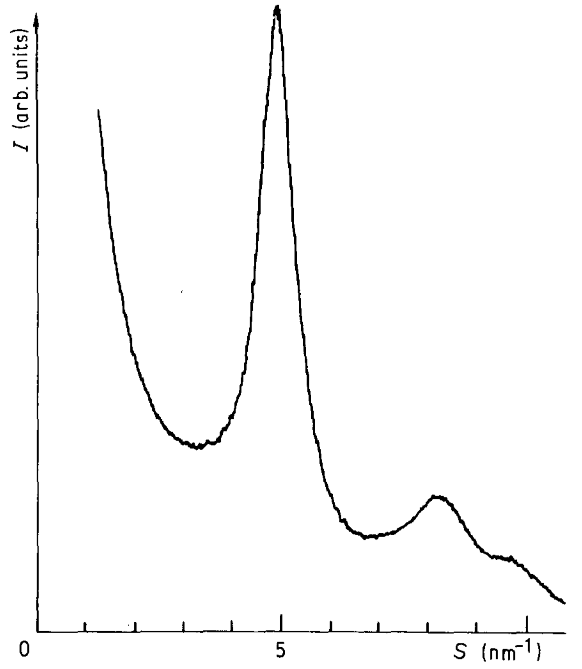

Figure 5 TEDP profile of T film annealed at 400 °C.

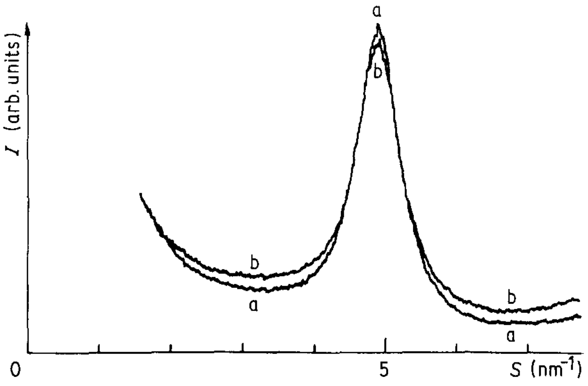

Figure 6 Direct comparison of the first diffraction peak corresponding respectively to (a) D film as-deposited state; (b) T film annealed at 400 °C.

From the structural study, we can conclude that, in the as-deposited state, films prepared by d.c. triode sputtering exhibit a larger topological and chemical disorder than those obtained by r.f. diode sputtering. This effect is related to the composition fluctuations which exist in triode deposited samples and which also affect the structural relaxation and the crystallization process. Annealing experiments showed that the triode sputtered films have a larger thermal stability. This result is related to the higher average M content of T films and/or to the difference in the structural relaxation of the two types of film. Experiments

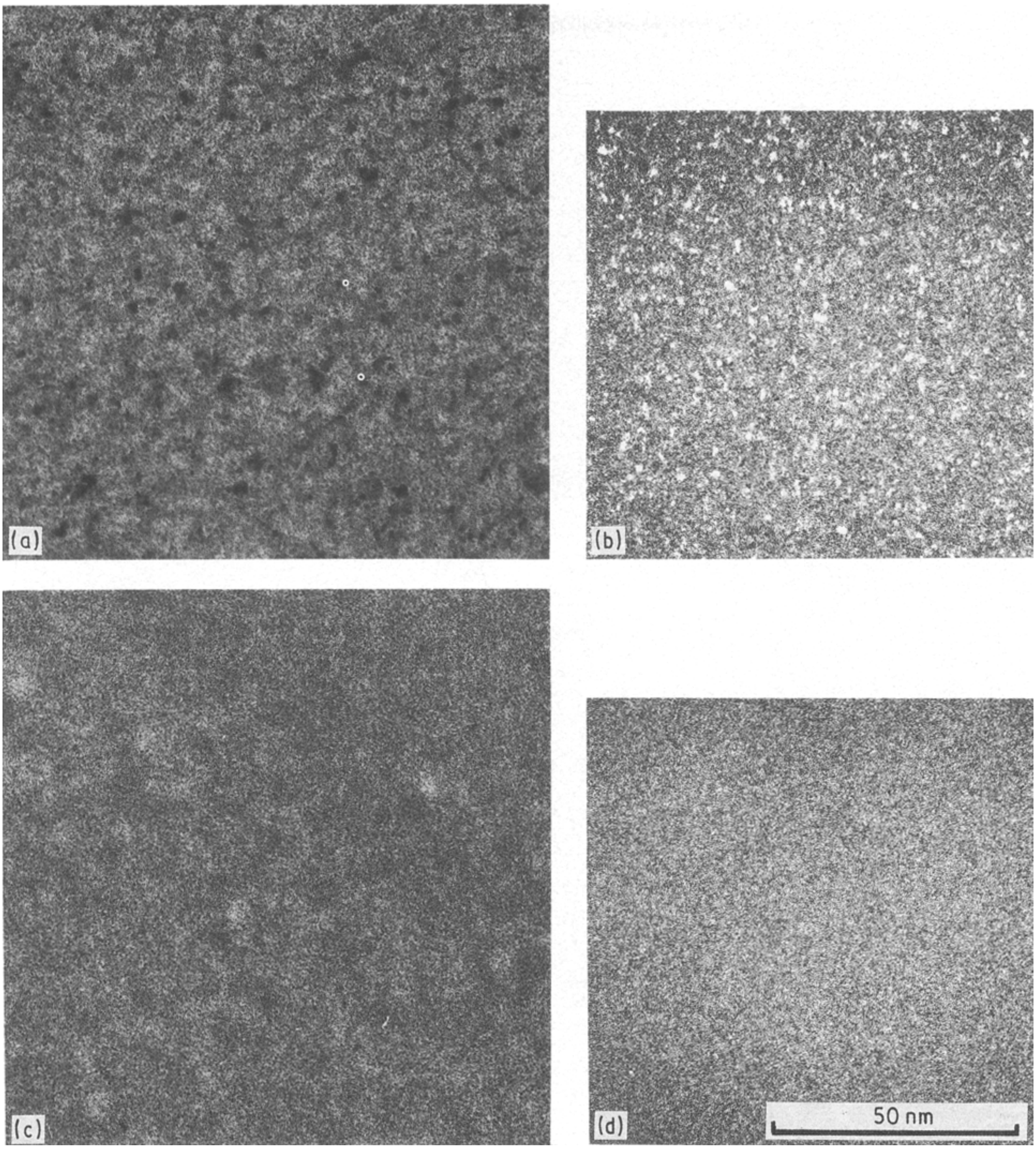

Figure 7 Transmission electron micrographs in BF and DF of CoZrNb film annealed at 400 °C. (a) and (b) D films. (c) and (d) T films.

showed that the crystallization temperature of Co–M amorphous thin films is higher for higher metal M (M = Nb, Zr) concentration [7]. The crystallization process could also be delayed by the structural relaxation specific to T films, which leads first to a higher chemical order by the exchange of chemically different neighbours. This mechanism could be significant, because the annealing temperature is sufficiently high so that the randomizing effect of entropy governs the relaxation process.

It is believed that the difference in the local chemical and topological homogeneity of the two kinds of film is related to the respective deposition parameters.

In d.c. triode sputtering, the energy of the as-sputtered particles is much smaller and the effective deposition temperatures are significantly lower because the substrate remains outside the glow discharge as compared to the r.f. diode process [6]. Both parameters can favour the formation of some chemical inhomogeneities, which result in the concentration fluctuations of the thin film deposited by triode sputtering.

4. Magnetic properties

The characteristic of the hysteresis loop corresponding to the two sets of films did not show any systematic difference. The as-sputtered layers present an in-plane uniaxial anisotropy of the order of 3 to $8 \times 10^{-4}\,\mathrm{J\,cm^{-3}}$. In general, the coercive field H_c decreased with increasing film thickness and for the best samples was smaller than $(1/4\pi)\ \mathrm{kA\,m^{-2}}$.

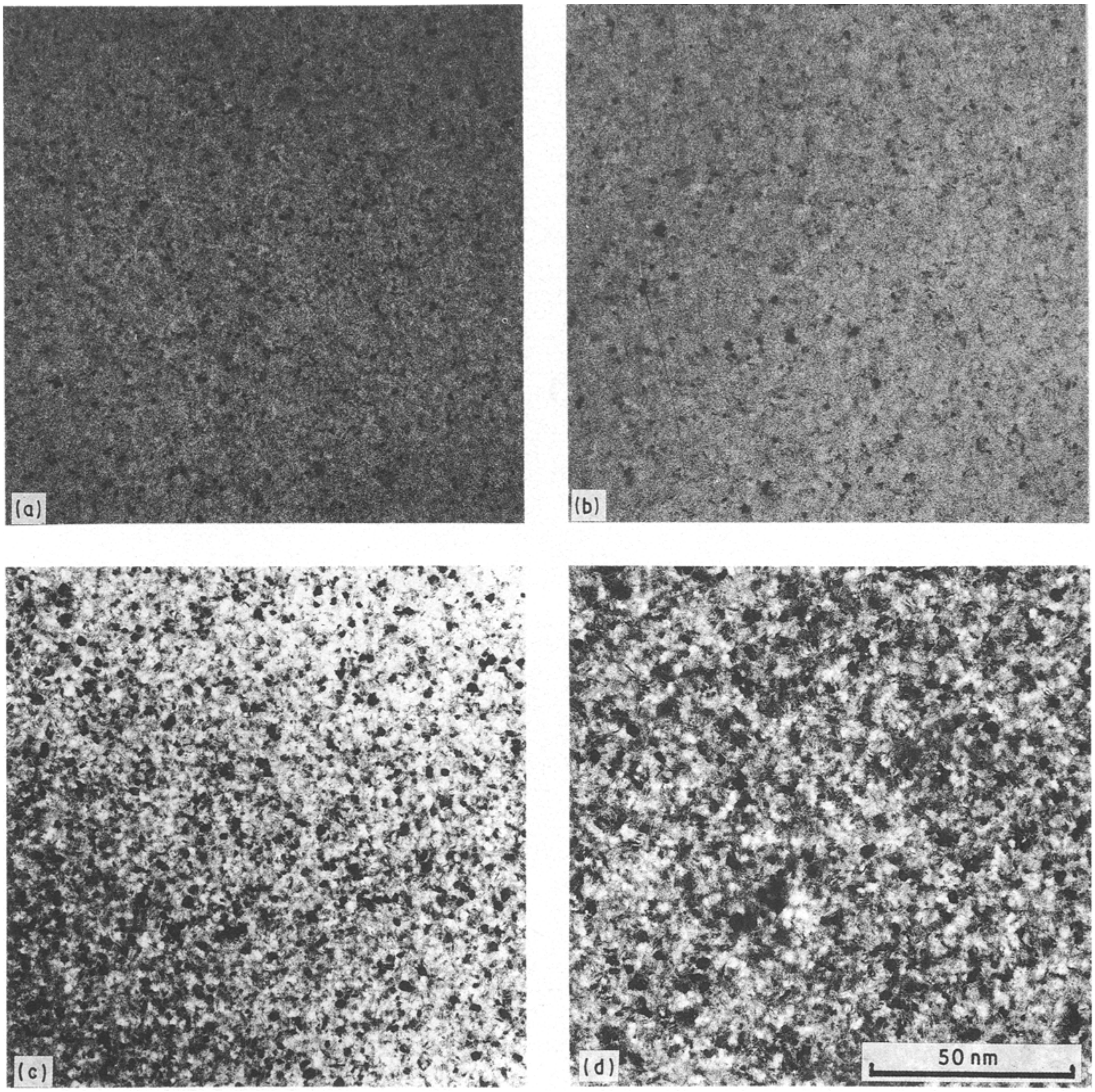

Figure 8 Transmission electron micrographs in bright field of D and T films annealed at various temperatures. (a) D film annealed at 400 °C; (b) T film annealed at 430 °C; (c) D film annealed at 530 °C; (d) T film annealed at 530 °C.

The FMR spectra were studied as a function of film thickness. Typical results are reported in Table I. The 0.06 µm thick layers were deposited simultaneously with those used for structural investigations. $4\pi M_s^{eff}$ deduced from the main mode in perpendicular and parallel resonance using the Kittel formula, is independent of film thickness and varies as expected with the average Co concentration of the layer. The higher value of the resonance linewidth of T film as compared to that of D film is probably related to the composition fluctuation. After annealing at 400 °C, changes are observed in the spectra. On D films, two peaks are detected which could correspond to the crystalline and the amorphous phase, respectively. T films exhibit a single resonance line but with $4\pi M_s^{eff}$ shifted to

TABLE I

Deposition process	Composition	t (µm)		$4\pi M_s^{eff}$ (1/4π kA m^{-2})	$\Delta H_\perp$
r.f. diode (D)	$Co_{86.9}Nb_{9.3}Zr_{3.8}$	0.06	AD	10300	43
			AN	10180	42
				11405	85
		0.5	AD	10150	
d.c. triode (T)	$Co_{83.4}Nb_{10.1}Zr_{6.5}$	0.06	AD	8640	84
			AN	10200	94
		0.5	AD	8600	

Magnetic properties as determined by FMR measurements.
AD as-deposited state, AN annealed sample, t full thickness
$\Delta H_\perp$: resonance linewidth for the applied field perpendicular to the film plane.

higher values. This effect could be due to a preferential oxidation of M = Zr, Nb after annealing [8]. It can be concluded that the results of the magnetic study are coherent with the structural investigations.

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