Technical Physics Letters, Vol. 31, No. 9, 2005, pp. 802–805. Translated from Pis'ma v Zhurnal Tekhnicheskoĭ Fiziki, Vol. 31, No. 18, 2005, pp. 78–86.

The Magnetic Anisotropy of Thin Epitaxial CrO_2 Films Studied by Ferromagnetic Resonance

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Received April 5, 2005

Abstract—The magnetic anisotropy of thin epitaxial films of chromium dioxide (CrO_2) has been studied as a function of the film thickness by the ferromagnetic resonance (FMR) technique. CrO_2 films with various thicknesses in the range from 27 to 535 nm have been grown on (100)-oriented TiO_2 substrates by chemical vapor deposition using CrO_3 as a solid precursor. In a series of CrO_2 films grown on the substrates cleaned by etching in a hydrofluoric acid solution, the FMR signal exhibits anisotropy and is strongly dependent on the film thickness. The magnetic properties of CrO_2 films are determined by a competition between the magnetocrystalline and magnetoelastic anisotropy energies, the latter being related to elastic tensile stresses caused by the lattice mismatch between the film and the substrate. In the films of minimum thickness (27 nm), this strain-induced anisotropy is predominant and the easy magnetization axis switches from the [001] crystallographic direction (characteristic of the bulk magnet) to the [010] direction. © *2005 Pleiades Publishing, Inc.*

The development of modern electronics toward the further miniaturization of devices, increasing operation speed, and functional variability implies the use of magnetoelectronic elements whose operation is based on the use of both the charge and spin of conduction electrons. The most important parameter determining the efficiency of such magnetoelectronic elements is the spin polarization of conduction electrons. The ideal materials in this respect are the so-called semimetal ferromagnets, whose unique feature is the completely spin-polarized conduction band. One of these materials is chromium dioxide (CrO_2), in which an extremely high (almost 100%) spin polarization of conduction electrons has been experimentally confirmed [see, e.g., [1, 2]). For this reason, the successful synthesis of thin epitaxial CrO_2 films [3] stabilized by the substrate structure has drawn the attention of researchers to this compound [4–7].

Previously, we studied thin CrO_2 films grown by chemical vapor deposition (CVD) on TiO_2 substrates [8–11]. Based on the results of ferromagnetic resonance (FMR) measurements, we optimized the CVD regimes for chromium dioxide epitaxy (preparation of rutile substrates, substrate temperature during film growth, deposition velocity, etc.). This study was devoted to the FMR measurements in CrO_2 films with reproducible magnetic and structural characteristics obtained using the optimum growth regimes. We have studied the magnetocrystalline and magnetoelastic anisotropy as dependent on the film thickness in a series of samples grown by CVD using CrO_3 as a solid precursor. Using the FMR technique, we have established for the first time that the easy axis in films of minimum thickness (27 nm) exhibits "switching" from *c* to *b* crystallographic direction under the action of the strain-induced anisotropy.

Sample preparation and FMR measurements. Thin epitaxial CrO_2 films were grown by CVD using CrO_3 solid precursor on (100)-oriented TiO_2 single crystal substrates with a rutile structure. The process was essentially the same as that described elsewhere [4]. A series of films with thicknesses of 27, 65, and 434 nm were grown on TiO_2 substrates cleaned by etching in an aqueous hydrofluoric acid (HF) solution. For comparison, we have also grown and studied a film with a thickness of 535 nm grown on the same substrate without preliminary etching.

The orientation of film samples was checked by X-ray diffraction on a Rigaku RINT 2000 diffractometer. The FMR spectra were recorded using an EPR spectrometer of the Bruker EMX type with a working frequency of 9.8 GHz. The FMR investigation was performed according to the standard procedure involving measurements in two geometries: (i) in-plane (whereby

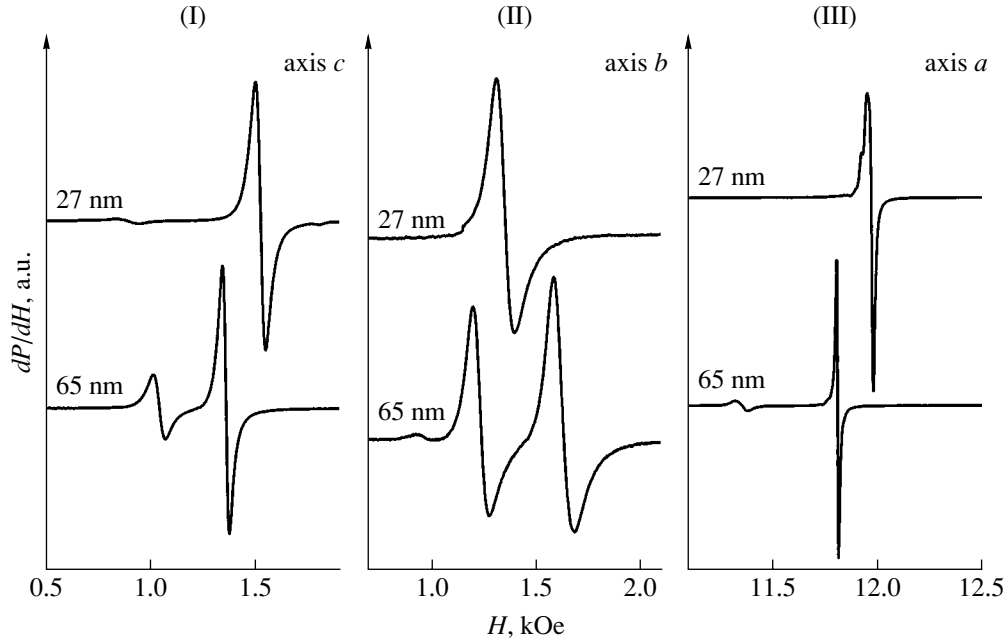

Fig. 1. FMR spectra of 27- and 65-nm-thick CrO_2 films measured with the magnetic field applied (I, II) parallel to the *c* and *b* axes, respectively (in the film plane) and (III) along the *a* axis perpendicular to the film plane.

the external magnetic field is rotated in the sample plane), and (ii) out-of-plane (the magnetic field is rotated in a plane containing the easy axis and the normal to the sample surface).

Experimental results. Figure 1 shows the FMR spectra of thin epitaxial CrO_2 films (27 and 65 nm thick) grown on etched Ti_2 substrates and measured in the in-plane and out-of-plane geometry. The spectrum of a film from the same series with a thickness of 434 nm exhibits splitting into several components, whereas the spectrum of a film grown on the unetched substrate exhibits a single FMR mode signal. Figure 2 shows the angular variation of the resonance field amplitude for all samples (except for the 434-nm-thick film on the etched substrate) measured in both the in-plane and out-of-plane geometry.

As can be seen from Figs. 1 and 2, the results of FMR measurements in the out-of-plane geometry reveal the typical angular dependence with the predominating effect of the demagnetizing field (shape anisotropy), whereby the easy axis occurs in the plane of the CrO_2 film. At the same time, the spectra measured in the in-plane geometry revealed a strong influence of the magnetocrystalline anisotropy. The maximum and minimum values of the resonance field correspond to the hard and easy magnetization axes, respectively.

The FMR spectrum measured in the in-plane geometry for a 535-nm-thick film grown on the unetched substrate exhibits the maximum (among the series of samples studied) anisotropy in the film plane. Apparently, the easy magnetization direction in this film corresponds to the *c* axis ([001] direction) of the crystal structure. A similar behavior was observed for the thickest (434 nm) film in the series of samples grown on the etched substrates, but the degree of anisotropy was somewhat lower. As for the 65- and 27-nm-thick films, their magnetic anisotropy was much less pronounced (Fig. 2), and the film of minimum thickness (27 nm) was characterized by a minimum resonance field for the *b* axis ([010] direction) of the crystal structure. Thus, the easy axis exhibits switching from *c* to *b* direction, in agreement with the results of static magnetic measurements [12]. The FMR measurements performed for a film of the intermediate thickness (65 nm) grown on the

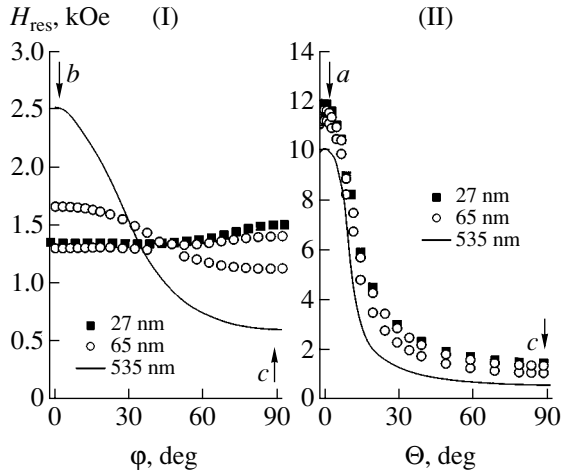

Fig. 2. Experimental angular dependences of the resonance field for CrO_2 films of various thicknesses measured in the (I) in-plane and (II) out-of-plane geometry.

unetched substrate (Fig. 2) showed an unusual angular dependence with the antiphase behavior of the main FMR modes: the minimum resonance field of the first mode corresponds to the maximum field for the second mode and vice versa. This behavior implies the existence of two magnetic phases with mutually perpendicular easy axes oriented in the [001] and [010] crystallographic directions.

Discussion. As is known, both the epitaxial CrO_2 film and the single crystal TiO_2(100) substrate possess a tetragonal rutile structure [3, 4, 6]. The lattice mismatch between the CrO_2 film and the TiO_2 substrate amounts to –3.79% in the [010] direction (*b* axis) and –1.48% in the [001] direction (*c* axis). This lattice mismatch results in the appearance of an anisotropic strain in the CrO_2 film plane [3]. The undistorted structure of chromium dioxide is characterized by a tetragonal magnetocrystalline anisotropy with an easy axis parallel to the *c* axis. The stress related to the lattice mismatch between the film and the substrate leads to the appearance of an additional, magnetoelastic contribution to the anisotropy. Thus, the magnetic anisotropy energy can be expressed as

$$E_{\text{ani}} = K_1 \sin^2\theta + K_2 \sin^4\theta + K_\sigma \sin^2(\theta - \delta), \quad (1)$$

where θ is the angle between the magnetization **M** and the *c* axis of the CrO_2 crystal, K_i is the crystal anisotropy parameter, K_σ is the magnetoelastic anisotropy, and δ is the angle between the *c* axis and the strain direction in the film plane [3, 6, 7].

The FMR spectrum of a CrO_2 film on the unetched substrate is the most simple for interpretation because the X-ray diffraction data [13] show that such films are virtually free from deformations and, hence, the last term in Eq. (1) can be ignored. The results of computer simulations of the resonance fields in both standard geometries gave the anisotropy fields $K_1/M_s = 510$ Oe and $K_2/M_s \sim 0$ Oe at a saturation magnetization of $M_s = 470$ Oe. These values are in very good agreement with the published data for bulk CrO_2 crystals [14] and single crystal CrO_2 films [3, 6].

The FMR spectra of the films grown on etched substrates show that these films are strained to a considerable extent because of a lattice mismatch between the CrO_2 epitaxial film and the single crystal substrate. As a result, the strained film features a competition between the energies of magnetocrystalline and magnetoelastic anisotropy, whose easy axes coincide with the [001] and [010] directions, respectively. As for the different FMR modes observed in the 65- and 434-nm-thick films, this behavior probably reflects inhomogeneity in the distribution of strain in the film plane.

An analysis of the angular dependences of the resonance field in the in-plane and out-of plane geometries shows that the contribution of the magnetoelastic anisotropy can be correctly described in terms of a simplified model,

$$E_{\text{ani}} = K_{1\text{eff}} \sin^2\theta + K_2 \sin^4\theta, \quad (2)$$

where a single parameter $K_{1\text{eff}}$ is used to take into account the quadratic terms of the magnetocrystalline and magnetoelastic anisotropy (the first and third terms in Eq. (1), respectively). In this model, the easy axis of the magnetoelastic anisotropy is oriented at an angle of $\delta = 90°$ relative to the *c* axis, that is, parallel to the *b* axis of the rutile structure as it was observed in [3]. The coefficient $K_{1\text{eff}}$ decreases with the film thickness and even becomes negative for the thinnest (27-nm-thick) film in a series with the strain-induced anisotropy. Numerical simulation yields –60 Oe for the effective anisotropy field $K_{1\text{eff}}/M_s = (K_1 - K_\sigma)/M_s$. It should be noted that the experimental angular dependence of the resonance field observed for the 27-nm-thick film can be reproduced by modeling only with allowance for the parameter K_2 at the fourth-order term of magnetocrystalline anisotropy. The best agreement was obtained for $K_2/M_s = 25$ Oe.

In considering the results of the FMR measurements performed in the out-of-plane geometry (Fig. 2(II)), it is necessary to point out an increase in the maximum resonance field in the thinnest films, which reflects a contribution of the out-of-plane anisotropy. This influence is manifested in the results of numerical modeling by an increase in the effective magnetization, which can be expressed as $M_{\text{eff}} = M_s - K_\perp/2\pi M_s$, where M_s is the room-temperature saturation magnetization and $K_\perp$, the strain-induced out-of-plane anisotropy. The appearance of an additional out-of-plane anisotropy with the asymmetry axis oriented in the normal direction is related to the fact that the tensile stress in the film plane produces a compensating compressive stress in the transverse direction perpendicular to the film plane. The negative sign of the out-of-plane anisotropy $K_\perp$ (which implies an increase in M_{eff}) indicates that the hard magnetization axis is also perpendicular to the CrO_2 film plane.

Conclusions. The results of our FMR investigation of the magnetic properties of thin epitaxial CrO_2 films by the FMT techniques showed that

(i) a lattice mismatch between the CrO_2 films and TiO_2 substrates gives rise to anisotropic elastic tensile stresses, which strongly influence the magnetic anisotropy parameters and even lead to switching of the easy axis from the *c* to the *b* direction in the thinnest (27-nm-thick) film;

(ii) the inhomogeneous character of the magnetoelastic anisotropy in CrO_2 films of an intermediate thickness (~65 nm) is manifested by the coexistence of two magnetic phases with mutually perpendicular easy axes in the [001] and [010] crystal directions;

(iii) by changing the conditions of synthesis, it is possible to control the magnetic anisotropy within

broad limits and to obtain thin CrO_2 films with desired magnetic parameters, which is of considerable importance for the possible applications of such films in magnetoelectronics.

Acknowledgments. This study was supported in part by the Gebze Institute of Technology (grant no. 2003-A-15). One of the authors (L.R.T.) also gratefully acknowledges the support from BRHE (grant REC-007).

REFERENCES

1. Y. Ji, G. J. Strijkers, F. Y. Yang, *et al.*, Phys. Rev. Lett. **86**, 5585 (2001).
2. A. Anguelouch, A. Gupta, G. Xiao, *et al.*, Phys. Rev. B **64**, 180408 (2001).
3. X. W. Li, A. Gupta, and G. Xiao, Appl. Phys. Lett. **75**, 713 (1999).
4. X. W. Li, A. Gupta, T. R. McGuire, *et al.*, J. Appl. Phys. **85**, 5585 (1999).
5. A. Gupta and J. Z. Sun, J. Magn. Magn. Mater. **200**, 24 (1999).
6. F. Y. Yang, C. L. Chien, E. F. Ferrari, *et al.*, Appl. Phys. Lett. **77**, 286 (2000).
7. L. Spinu, H. Srikanth, A. Gupta, *et al.*, Phys. Rev. B **62**, 8931 (2000).
8. B. Z. Rameev, R. Yilgin, B. Aktaş, *et al.*, Microelectron. Eng. **69**, 336 (2003).
9. B. Z. Rameev, B. Aktaş, A. Gupta, *et al.*, in *NATO Science Series II: Mathematics, Physics and Chemistry*, Ed. by B. Aktaş, L. R. Tagirov, and F. Mikailov (Kluwer, Boston, 2004), Vol. 143, pp. 273–282.
10. B. Z. Rameev, A. Gupta, A. Anguelouch, *et al.*, J. Magn. Magn. Mater. **272**, 1167 (2004).
11. B. Z. Rameev, A. Gupta, G. X. Miao, *et al.*, Phys. Status Solidi A **201**, 3350 (2004).
12. G. Miao, G. Xiao, and A. Gupta, Phys. Rev. B **71**, 064407 (2005).
13. A. Gupta, private communication.
14. D. S. Rodbell, J. Phys. Soc. Jpn. **21**, 1224 (1966).

Translated by P. Pozdeev