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FMR study of strain-induced magnetic anisotropies in CrO_2 thin films

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Epitaxial CrO_2 thin films were grown on TiO_2 (100) single-crystalline substrates by chemical vapour deposition (CVD) process with use of CrO_3 solid precursor. The films with different thickness (27–530 nm) were studied by Ferromagnetic Resonance (FMR) technique. Strong dependence of FMR signal on the film thickness was observed in the series of CrO_2 films deposited onto the pre-etched TiO_2 substrates. It is shown that the magnetic behaviour of the CrO_2 films arises from competition between magnetocrystalline and strain anisotropies that favour the [001] and [010] magnetization directions, respectively. For the thinnest film the strain anisotropy dominates, and the magnetic easy axis switches from [001] to the [010] direction. On the contrary, the CrO_2 film grown on the unetched substrate demonstrates essentially strain-free magnetic anisotropy behaviour.

1 Introduction

Enormous progress of conventional semiconductor electronics, which is based on the manipulation of electrical charge, has realized in modern computer technology. However, further progress in electronics requires utilizing new physical phenomena, which incorporate manipulation not only with charge but spin and optical degrees of freedom of the electron as well. Magnetoelectronic devices, which exploit spin-polarized currents and spin-dependent conduction, have already found well-known commercial applications as spin-valve sensors of magnetic field and magnetic random access memories [1]. Performance of the magnetoelectronic devices depends critically on the conduction band polarization of the ferromagnetic components. In this respect, half-metallic ferromagnets are considered to be a key material due to highly spin-polarized conduction band. One of such half-metallic materials is chromium dioxide (CrO_2), which has the conduction band polarization as high as 100% [2–6]. The single-crystalline CrO_2 films grown epitaxially on TiO_2 substrates have been synthesized recently by chemical vapor deposition (CVD) [7], and there are very few papers on electric and magnetic properties of this material [4–13].

Magnetic anisotropies of single-crystalline CrO_2 films as well as possibilities to tailor them in a desirable way have crucial importance for applications in magnetoelectronic devices. It has been shown [7] that the effect of strain anisotropies becomes dominant in the ultrathin (≤60 nm) CrO_2 films deposited on (100) TiO_2 substrates. However, there is still some controversy in the results received by different methods and on CrO_2 films prepared by various modifications of CVD technique. The origin of this contro-

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versy is apparently related to very fine features of CVD growing technique that determine the morphology of the interface layer between TiO_2 substrate and CrO_2 film producing (or relieving) strains.

In this study we present preliminary results of the ferromagnetic resonance (FMR) studies of magnetic properties of the epitaxial chromium-dioxide films grown with use of the CrO_3 solid precursor. The magnetocrystalline and magnetoelastic anisotropy fields have been studied as a function of the film thickness, and the switching behavior of magnetic easy axis due to the effect of strain anisotropy has been demonstrated, for the first time, by FMR technique.

2 Sample preparation and experimental techniques

Epitaxial (100) thin films of CrO_2 were fabricated by chemical vapour deposition (CVD) onto TiO_2 (100) single-crystal substrates with use of the CrO_3 solid precursor, as described elsewhere [7]. A set of films with thicknesses of 27 nm, 65 nm, and 434 nm was prepared by deposition onto the HF pre-etched TiO_2 substrates (see details in [7]). A film with the thickness of 535 nm was also grown on the un-etched TiO_2 substrate for comparison. The field derivative of FMR spectra were taken on Bruker EMX electron spin resonance spectrometer at X-band frequency (9.8 GHz). The angular dependence of the FMR spectra was studied by varying the direction of the external magnetic field with respect to the crystalline axes in the two standard experimental geometries: in the sample plane (in-plane geometry) and out of the sample plane towards the film normal (out-of-plane geometry).

3 Experimental results

The in-plane and out-of-plane FMR spectra of the pre-etched CrO_2 films with the thickness of 27 nm and 434 nm as well as the spectra of the thick (535 nm) unetched CrO_2 film are presented in Fig. 1. The in-plane and out-of-plane angular dependencies of FMR resonance fields for these samples are shown in Fig. 2. As it is expected for thin films, a dominant contribution of the shape anisotropy is observed in the out-of-plane FMR measurements of all CrO_2 samples. As a result, the easy axis of magnetization is oriented in the plane of the CrO_2 film. Effect of the magnetocrystalline anisotropy is clearly observed in the in-plane measurements, where the easy axis of magnetization corresponds to the minimal in-plane FMR resonance field, and the hard axis corresponds to the maximal in-plane resonance field.

It is seen from Figs. 1 and 2 that for the CrO_2 films *pre-etched* prior to deposition process the minimal FMR resonance field and magnitude of the in-plane anisotropy strongly depend on the film thickness.

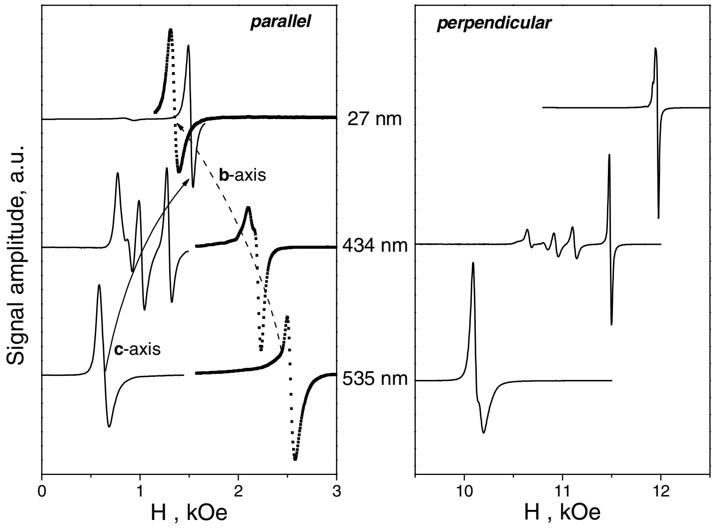

Fig. 1 FMR spectra of CrO_2 samples in parallel (left) and perpendicular (right) orientation of film plane with respect to the applied magnetic field. At the left panel the in-plane spectra with DC magnetic field along (*b*)- and (*c*)-axes of the CrO_2 films are presented by symbols and solid lines, respectively.

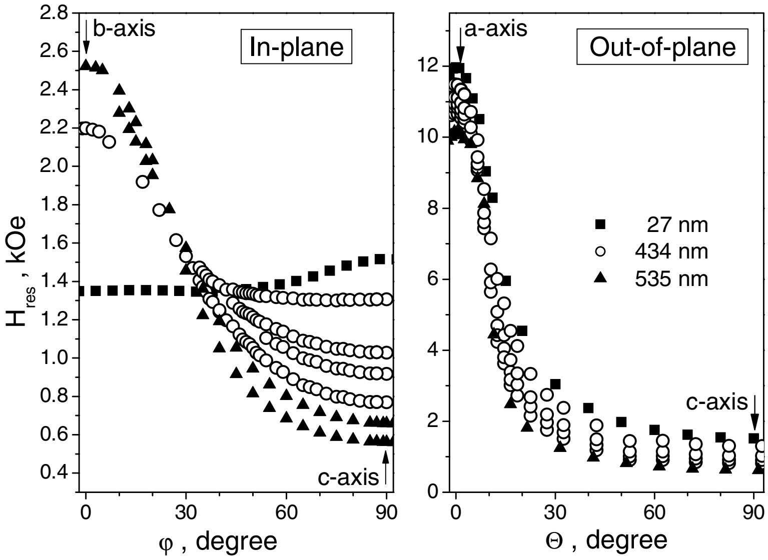

Fig. 2 Experimental in-plane (left) and out-of-plane (right) angular dependences of the resonance field for CrO_2 films.

The magnitude of in-plane anisotropy in general decreases with the film thickness. The most striking result is that, contrary to the thick (434 nm) film, the thinnest (27 nm) film shows the minimal resonance field in the direction of DC magnetic field along the (*b*)-axis of the CrO_2 film. Therefore, the easy axis switching from the (*c*)-direction to the (*b*)-direction expected from literature [7] is in fact observed in this series of the samples even at room temperature. FMR measurements of the pre-etched CrO_2 film of intermediate thickness (65 nm) show very unusual angular dependence (not presented) revealing two main FMR modes with “antiphase” behaviour, that is the minimal resonance field of the first mode corresponds to the maximal field for the second one, and *vice versa*. This may imply an existence in this film of two magnetic phases with mutually perpendicular easy axes along [001] and [010].

It is remarkable that the in-plane FMR spectra of the *unetched* CrO_2 film with thickness of 535 nm reveal not only the easy axis along the (*c*) direction similar to the 434 nm pre-etched CrO_2 film, but also larger magnitude of the in-plane anisotropy.

4 Discussion

It is known [7, 8, 10] that both the CrO_2 epitaxial film and the TiO_2 single-crystalline (100) substrate have the rutile structure (tetragonal symmetry). The unit cell values of the bulk CrO_2 are: $a = b = 4.421$ Å, and $c = 2.916$ Å. The lattice mismatch with (100) TiO_2 substrate, –3.79% along the [010] (*b*)-direction and –1.48% along the [001] (*c*)-direction, results in an anisotropic tensile strain in the plane of the CrO_2 films [7]. The unstrained crystal structure of the film results in the tetragonal magnetocrystalline anisotropy with an easy axis parallel to the c crystalline axis, while the additional perturbation due to the lattice mismatch produces magnetoelastic anisotropy energy. Thus, the anisotropy energy takes a form:

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

where θ is the angle between the magnetization M and the (*c*) axis of the CrO_2 crystal, K_i are the anisotropy constants of crystalline anisotropy, K_σ is the magnetoelastic anisotropy constant, and the stress is applied at the angle δ with respect to the (*c*)-axis [7, 10, 11].

All observed features of the FMR anisotropy indicate that the films deposited onto the pre-etched surface are highly strained due to lattice mismatch of CrO_2 epitaxial film with the TiO_2 single-crystalline substrate (while the film synthesized on the unetched TiO_2 substrate is essentially strain-free). As a result, in the strained films there is a competition between magnetocrystalline and strain anisotropies that favour the [001] and [010] magnetization directions, respectively. Multiple FMR modes observed in Fig. 1 for the films with thicknesses of 65 and 434 nm may be explained by inhomogeneous distribution of strains in the lateral or cross dimension of the strained films.

The preliminary analysis of the in-plane and out-of-plane resonance field angular dependencies showed that effect of strain anisotropy may be correctly taken into account with use of the simplified model:

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

where a single parameter $K_{1\text{eff}}$ absorbs the second order magnetocrystalline anisotropy term and the magnetoelastic term in Eq. (1). This means that for this specific set of the strained CrO_2 films the easy axis of magnetoelastic anisotropy is applied at the angle $\delta = 90$ with respect to the (*c*)-axis, that is along the (*b*)-axis of the rutile structure as it has been observed in Ref. [7]. The parameter $K_{1\text{eff}}$ decreases for thinner films and becomes negative for the strained film with the thickness of 27 nm. The value of effective anisotropy field $K_{1\text{eff}}/M_S = (K_1 - K_\sigma)/M_S$, estimated from our preliminary simulations, is about of –60 G. It is worthy to note that our simulations show that the forth- order anisotropy parameter (K_2) is also has to be taken into account to reproduce theoretically the rather smooth angular dependence of the in-plane FMR for the 27 nm film around the (*b*)-axis direction.

Discussing the out-of-plane FMR results (the right panel in Fig. 2) one can note an increase of the maximal resonance field in the thinner films that is only in part due to decrease of the effective in-plane anisotropy $K_{1\text{eff}}$, but also indicate the effect of perpendicular anisotropy. The later one is observed in FMR modeling as increase of the "effective" magnetization: $M_{\text{eff}} = M_s - K_\perp/2\pi M_s$, where M_s is the saturation magnetization at room temperature, and $K_\perp$ is the perpendicular anisotropy constant. The origin of the perpendicular anisotropy is also related to the in-plane strains. Stretching (compressing) in the film plane causes a consequent compression (stretching) in the direction perpendicular to the film along the (*a*)-axis. Therefore, an additional perpendicular anisotropy with the symmetry axis along the film normal should be expected. In this case, an increase of the effective magnetization for the thinner films point to negative sign of the perpendicular anisotropy constant $K_\perp$, that correspond to the hard axis in the direction perpendicular to the film plane. Computer modeling of the experimental results are currently in progress and more comprehensive information on the anisotropy parameters of the CrO_2 films will be the subject of a forthcoming publication.

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