Piezoelectric and ferroelectric response enhancement in multiferroic YCrO₃ films by reduction in thickness

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A study of the piezoelectric response and polarization switching of YCrO₃ films as function of thickness, is presented. The films, 20 to 180 nm thick, were deposited on Pt/TiO₂/Si substrates by r.f. sputtering at room temperature, and then annealed at 900 °C for 1 h in air. Better grain coalescence and reduction of charge accumulation at grain boundaries was observed in thinner films, leading to the appearance and enhancement of the piezoresponse. A piezoelectric coefficient of d₃₃≈6.4 pm/V and a coercive voltage of Vₐc~12.5 V were obtained in the 20 nm film, which also showed a magnetic hysteresis loop. Therefore, while maintaining the ferromagnetic behavior, ferroelectricity, hence multiferroicity, is induced in YCrO₃ when film thickness is reduced to 20 nm.

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1. Introduction

Materials that combine ferroelectric and ferromagnetic properties, called multiferroics, have attracted great attention in recent years because of the possibility of novel applications. However, due to the fact that ferroelectricity and ferromagnetism are mutually excluding phenomena, many aspects about the obtainment as well as the explanation of the simultaneous presence of both properties, remain unsolved. As a consequence, even the most studied multiferroic material, BiFeO₃ [1], is still subject of numerous studies. In contrast, other proposed systems, such as YCrO₃, have been shallowly investigated [2–10]. Ceramics of this orthochromite exhibit antiferromagnetism and a weak ferroelectricity below Tₘ=140 K and Tᵢ₁=473 K, respectively [2]. The ferromagnetic response is caused by a canted antiferromagnetic ordering [2]. Ferroelectricity, on the other hand, is a consequence of the local non-centrosymmetry originated by the chromium displacements along the z-direction [3]. However, high dielectric losses have impeded the acquisition of clear experimental evidence of the ferroelectric behavior, particularly when the sample is in thin film form [2,4–5]. Nonetheless, properties in films are strongly related to thickness. In BiFeO₃ for example, ferroelectricity is difficult to measure in ceramics because of the dielectric loss. In contrast, a 100 nm thick film of BiFeO₃ shows excellent ferroelectric and piezoelectric properties brought about for the more ordered crystal growth, free from porus and grain boundaries, and a strained structure caused by the film-substrate lattice mismatch [1]. In YCrO₃, however, films reported by other authors were around 70 nm [4] and 300 nm in thickness [5], thick enough to achieve relaxation and too thick to reduce the accumulation charge. In other works film thickness was not even mentioned [2]. Consequently, as seen in the case of BiFeO₃, it is reasonable to propose the growth of very thin films of YCrO₃ as a means to improve their piezoelectric and ferroelectric properties, which is the aim of this work.

2. Experimental procedure

YCrO₃ films 20 to 550 nm thick were grown by rf magnetron sputtering at room temperature, 13.0 mT of a mixture of argon (70%) plus oxygen (30%), 200 W of power supplied and a target-substrate distance of 6.3 cm. Pt(1500 Å)/TiO₂(300 Å)/SiO₂/Si(1 0 0) substrates from Radiant Tech. Inc. were used. The YCrO₃ target was prepared by the solid state reaction of Y₂O₃ and Cr₂O₃ powders (99.99% and 99.97% purity, respectively), from Alfa Aesar, sintered at 1450 °C. After deposition, films were heat treated in air at 900 °C for 1 h. X-ray diffraction (XRD) patterns were collected in a Phillips X'pert powder diffractometer with the Cu-Kα radiation. A JEOL JMS-5300 scanning electron microscope (SEM) was used for the
morbidity. In the same microscope, electron beam induced current (EBIC) images were taken with a Keithley-428 amplifier while the beam was kept at 15 keV and 1 nA. A Veeco Dimension 3100 Nanoscope IV atomic force microscope (AFM), with Cr/Pt cantilevers (Multi75E-G from BudgetSensors), was employed in the piezoresponse force microscopy (PFM) and switching-PFM (S-PFM) analysis. Magnetic measurements were carried out in a Quantum Design 6000 physical properties measurement system (PPMS) with a vibrating (40 Hz) sample magnetometer (VSM).

3. Results and discussion

X-ray diffraction patterns of 550 nm thick films grown at room temperature, post-annealed in air at 800 and 900 °C for 1 h, are presented in Fig. 1. The as-deposited amorphous films acquire the polycrystalline YCrO$_3$ phase after the heat treatment at 800 °C, a result in agreement with that obtained by Durán et al. [6] in powders synthesized by the combustion method. Crystallinity is improved further by increasing the annealing temperature to 900 °C, as evidenced by the sharpness of the (2 0 0) and (0 0 2) reflections.

Hence 900 °C was the annealing temperature used for the subsequent series of studied samples.

A granular morphology is observed in the 180 nm and thicker films. Island-like grains are formed in the 90 and 45 nm samples and, as a result of the higher influence of the substrate surface energy, graininess gives way to a smoother surface in the 20 nm film (see Fig. 2).

The electron beam induced current (EBIC) images (not shown here) coincide exactly with those in Fig. 2 but grain boundaries appear as lighter zones which, according to Maestre et al. [11], are associated to charge accumulation. This result is in agreement with the literature where it has been reported that grain boundaries in ceramics are regions of enhanced charge carrier recombination due to the presence of electric charge [7]. Movement of the charge carries gives rise to dielectric losses at low frequencies [7]. In particular in YCrO$_3$ ceramics, dielectric loss is so high [8–10] that rounded hysteresis loops are obtained [2]. However, Bahadur et al. [7] found that in YCrO$_3$ nanoceramics, dielectric loss at low frequencies decreases with total porosity. In the same manner, the improvement of homogeneity by thickness reduction in YCrO$_3$ films, shown in Fig. 2, leads to the reduction of the charge carrier accumulation. Moreover, such carrier accumulation at the grain boundaries of the 180 nm thick film could be creating depolarizing electric fields that reduce to the point of disappearing, the net polarization in grains [7]. This would be the reason for the homogeneous “neutral” contrast of the corresponding phase-PFM image on Fig. 3, associated to the absence of a piezoresponse [12]. When thickness is reduced, a piezoresponse comes into sight getting stronger, as made evident by the well defined contrast for the 45 and 20 nm samples (see Fig. 3).

Polarization reversal was achieved in the 20 nm sample by applying $+12$ V in a $2 \times 2 \, \mu$m$^2$ area, and then $-12$ V in a $1 \times 1 \, \mu$m$^2$ square inside, as can be determined by the change in contrast of the phase-PFM image on Fig. 4a. Such ferroelectric behavior was further confirmed by the phase and amplitude PFM-signals vs. voltage curves in Fig. 4b, from which a coercive voltage, $V_c \sim 12.5$ V, similar to that used to switch the polarization on Fig. 4a, and a piezoelectric coefficient $d_{33} \sim 6.4$ pm/V, were calculated using the method described by Hong et al. [13].

![Fig. 1. XRD of 550 nm films as deposited and after annealing in air at 800 and 900 °C.](image1)

![Fig. 2. SEM micrographs of YCrO$_3$ films of different thickness (same scale in all images).](image2)
Fig. 3. Phase-PFM images of \( \text{YCrO}_3 \) films of different thickness (same scale in all images).

Fig. 4. (a) Phase-PFM image after applying \( \pm 12 \, \text{V} \), (b) phase and amplitude PFM-signals vs. voltage and (c) magnetization vs. magnetic field curves of a 20 nm thick \( \text{YCrO}_3 \) film.
In addition, and despite the low thickness of the sample, a hysteresis loop is appreciable in the magnetization vs. magnetic field measurements, after the substrate signal subtraction, performed at a temperature of 50 K (see Fig. 4c).

In conclusion, a clear piezoelectric response and polarization reversal was achieved in polycrystalline YCrO$_3$ films when film thickness is reduced to 20 nm. The improved performance is associated to the reduction of charge accumulation at grain boundaries, a result of the more homogenous growth. Besides being piezoelectric ($d_{33} \sim 6.4$ pm/V) and ferroelectric ($V_c \sim 12.5$ V), the film is ferromagnetic, therefore multiferroicity is attained in YCrO$_3$ when film thickness reaches 20 nm. These are promising results that encourage further investigation of YCO$_3$ films as a magnetoelectric multiferroic option.

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