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Key-features in processing and microstructure for achieving giant electrostriction in gadolinium doped ceria thin films

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ABSTRACT

Gadolinium doped ceria is a well-known oxygen ion conduction material for solid fuel cell electrolytes. With its centrosymmetric average lattice and relatively low bulk dielectric constant it does not look interesting for electromechanical applications. However, a giant electrostriction (ES) effect was recently found in $Ce_{0.8}Gd_{0.2}O_{2-x}$ thin films. It was explained by the dynamic response of oxygen vacancies to an external electric field. In this work, the giant ES response has been reproduced in sputter deposited thin films. The proper transverse bulk ES coefficient has been derived from the measured clamped value. For this purpose, the Young's modulus was measured by nanoindentation. The highest ES coefficient was found as 9.0×10^{-19} $(m/V)^2$ for the strain coefficient, and 2.3×10^{-7} N/V^2 for the effective stress coefficient. Specific growth conditions must be chosen in order to obtain a microstructure exhibiting the giant ES effect. There is evidence for a higher oxygen deficiency than needed to compensate the gadolinium dopants (Gd'). It was observed that the nature of the bottom electrode impacts on the size of the effect. The highest response was obtained at films grown on Al bottom electrodes. To learn more on the mechanisms of the giant ES effect, a bipolar cycling was performed to test the delay time for the ionic reorientation in changing the sign of polarization, as observed in the stress loop. The maximal response was observed below 100 Hz in this bipolar mode, showing that the time for 180° reorientation amounts to several milliseconds.

1. Introduction

Recently, very intriguing properties were discovered in thin films of doped fluorite structures such as HfO_2, ZrO_2, and CeO_2. Intriguing, because one would expect only from more complex materials to display ferroelectricity or incipient ferroelectricity, but not from simple dielectrics. It was found that Si doped HfO_2 exhibits remarkable ferroelectric properties [1], which are so attractive that such films are investigated for non-volatile memories [2]. Another astonishing effect was discovered by Korobko and coworkers at Gd-doped ceria (CGO) thin films [3], normally investigated as solid electrolyte membrane in micro solid oxide fuel cells [4]. They found that the electrostrictive response of CGO was very much larger than that expected for a compound with a relatively low dielectric constant. A huge electrostrictive stress was created upon application of an electric field. Their experiment yielded a generated compressive stress of −30 MPa at an electric field of 78 kV/cm (Fig. 2-f in Ref. [3]), or a stress coefficient of 5.0×10^{-7} N/V^2. The same authors reported even higher values. The size, and also the fact that a compressive stress is generated – in contrast to the piezoelectric effect in thin films that produces a tensile stress at equal geometry – makes this finding extremely interesting for actuators in micro electro-mechanical systems (MEMS). Since in addition, it is a lead free material, there are excellent prospects for such applications.

While ferroelectricity in the hafnia films is ascribed to the occurrence of a non-centro-symmetrical phase due to the impact of mechanical constraints of the sandwiched film, and the local epitaxy to the TiN electrodes [5,6], the high electrostriction in the ceria films is ascribed to a high density of oxygen vacancies $V_{\ddot{O}}$ that are introduced by the choice of dopant atoms and concentrations. Indeed the used $Ce_{1-x}Gd_xO_{2-x/2}(V_{\ddot{O}})_{x/2}$ compound with x = 0.20 leads to a large oxygen vacancy concentration of 5 at%. Electrostriction (ES) was explained by the lability of Ce-$V_{\ddot{O}}$ pairs leading to the possibility to reorient them with an electric field. Korobko et al. [3] could also make plausible that bond reorientation and length

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change in an electric field would lead to a compressive stress. Verifying this hypothesis is somehow challenging and one has to study the defect density and more particularly the content of oxygen vacancies on the final response. In addition, one has also to take into the account that the electrostrictive coefficients of thin films cannot be directly compared to ones of bulk materials as the films are part of a layered composite structure.

In this paper, the electrostriction coefficients in thin film configuration is explained both in the clamped and free body case. It is shown that the giant ES effect in CGO thin films is related to defects, which are produced during rather specific deposition parameters such as a low deposition temperature, an optimal ion bombardment and high deposition rate. The ES effect in ordinary CGO thin films was determined as well. It was found at our optimized films that the giant ES effect means an amplification by a factor 30 to 70 as compared to the ES effect in ordinary CGO thin films. Furthermore, it was discovered that the giant effect depends on the electrode type on which the CGO film is grown, and that the giant ES properties are increasing with lower stiffness. Finally, our work suggests a defect reorientation when changing the sign of the electric field. This reorientation needs several milliseconds time, and could be attributed to a 180° defect polarization change.

2. Electrostriction coefficients in thin films

In general, all materials undergo a change in dimensions when they are subjected to an electric field. In non-piezoelectric materials this is due to the electrostrictive effect generating a strain that is proportional to the square of electric field [7]. The electrostrictive coefficients in bulk materials are usually derived for two special situations. Either the body is free to elongate or shrink in all directions at zero stresses (constant stress (T) condition), or the body is kept at zero strain in all directions (constant strain (S) condition). However, thin films are part of a composite structure with the substrate, meaning that the film is clamped in the plane to the substrate (strain S_1 and S_2 must be continuous across the interface), but free to move out of plane ($T_3 = 0$). This leads to the definition of coefficients at mixed border conditions: constant strain in the plane, and constant stress out of plane, as in the case of piezoelectric thin films [8]. The searched thin film coefficient is obtained from the constitutive equations (equations (1)–(3)) by setting $T_3 = 0$, and $S_1 = S_2 = 0$:

$$S_1 = s_{11}T_1 + s_{12}T_2 + M_{31}^{(T)}E_3^2 = 0 \tag{1}$$

$$S_2 = s_{12}T_1 + s_{11}T_2 + M_{31}^{(T)}E_3^2 = 0 \tag{2}$$

$$= > T_1 + T_2 = -\frac{2M_{31}^{(T)}E_3^2}{s_{11} + s_{12}} \tag{3}$$

The coefficients s_{ik} denote the components of the elastic compliance tensor, $M_{31}^{(T)}$ the electrostriction coefficient at constant stress, following the same notation as for the piezoelectric tensors (first index refers to electric field, and the second index represents the strain component represented in the reduced index notation). Since the film is isotropic in the plane, the two stress components must be equal in magnitude. This leads to the definition of an effective, electrostrictive thin film coefficient, as shown in equation (4) ((S) and (T) stand for constant strain, and stress, respectively):

$$T_1 = -\frac{M_{31}^{(T)}}{s_{11} + s_{12}}E_3^2 = -M_{31,f}^{(S)}E_3^2 \tag{4}$$

where T_1 is the in-plane stress, and E_3 the electrical field perpendicular to the plane of the film. $M_{31,f}^{(S)}$ is a practical coefficient that is directly measured in beam bending experiments. In order to compare this coefficient with the standard strain coefficient $M_{31}^{(T)}$, one needs to know elastic properties, i.e $s_{11} + s_{12}$. In cubic or isotropic materials, the latter are expressed in terms of Young's modulus Y and the Poisson's ratio ν, giving the relation as shown in equation (5):

$$M_{31}^{(T)} = (s_{11} + s_{12})M_{31,f}^{(S)} = M_{31,f}^{(S)}\frac{(1-\nu)}{Y} \tag{5}$$

The M_{31} coefficients were found to be positive [3]. The effect thus produces compressive stress in the clamped case, and a positive strain in the free body case.

3. Experimental

3.1. Thin film synthesis and sample fabrication

$Ce_{0.8}Gd_{0.2}O_{2-x}$ thin films were grown by RF magnetron sputtering on polycrystalline metal electrodes of Pt, Al, and Cr. Passivated silicon wafers served as substrates. All electrodes were deposited at 320 °C. CGO was deposited after a vacuum break. Details of the CGO process are given in Table 1. The electromechanical properties were assessed by beam deflection techniques. The beams had full wafer thickness (525 μm) and were obtained by dicing. The dicing marks were formed together with the top electrodes by sputter deposition of Pt/Cr through a shadow mask (Fig. 1).

3.2. Structural characterization

The texture of the films was determined by Bruker D8 advanced X-ray diffractometer. The Al and Pt electrodes had (111) texture as is expected for FCC sputtered metals, while Cr electrodes texture had (110) texture, also, expected for a BCC metal. The film microstructure was investigated in cross-section by using a FEI Tecnai Osiris Transmission Electron Microscope (TEM) at 200 kV. A chemical mapping by EDX (energy-dispersive X-ray spectroscopy) measurement was done. Chemical composition was measured using Merlin scanning electron microscopy (SEM) at 3 kV.

3.3. Measurement setup

The cantilever beams were mounted on X-Y-Z stage controlled by micro screw drives. The top and bottom electrodes were accessed via micromanipulators. The films had been subjected to sinusoidal bipolar excitation (zero DC offset). The displacement at the tip was tracked using a MTI 2000 “fotonic” sensor (see Fig. 2). From the cantilever deflection, the curvature and thus the film stress is derived. Division by the square of the electric field yields the effective stress ES coefficient $M_{31,f}^{(S)}$. If not stated differently, the values given in this paper correspond to a the maximal effect obtained with a sweeping frequency of 66 Hz. A detailed description of our setup and procedure (derivation of large-signal response)

Table 1
Sputter process conditions for CGO thin film deposition.

Target (100 mm dia)	$Ce_{0.8}Gd_{0.2}O_{1.9}$
Base pressure	$<5 \times 10^{-4}$ mTorr
Sputter pressure (Ar)	10–20 mTorr
Growth temperature	RT –400 °C (HT)
Ar gas flow	15 sccm
RF magnetron power	200 W
Film thickness	2 μm (±10%)