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6. AUTHORS

7. PERFORMING ORGANIZATION NAMES AND ADDRESSES
EpoXtal LLC
3401 Market Street
Suite 200
Philadelphia, PA 19104 -

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INVESTIGATOR(S):

Name: James McCambridge
Email: mccambridge@epoxtal.com
Phone Number: 6102990167
Principal: Y

Organization: **EpoXtal LLC**
Address: 3401 Market Street, Philadelphia, PA 19104
Country: USA
DUNS Number: 079864945
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Submitted By: James McCambridge
Email: mccambridge@epoxtal.com
Phone: (610) 299-0167

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Major Goals: 1) Demonstrate the feasibility of a commercial deposition process for a multi-ferroic multilayer film by first demonstrating deposition by scalable processes separately for high quality ferroelectric and ferromagnetic thin films on substrates compatible with CMOS processing. The deposition process and any post-deposition processing must be compatible with CMOS processing. In general, this will require the initial film deposition and subsequent processing steps including any annealing to be at temperatures below 450°C.
2) Determine film quality by scanning electron microscopy, energy dispersive spectroscopy, x-ray diffraction/x-ray reflectivity, atomic force microscopy and Rutherford backscattering.
3) Determine the dielectric loss tangent for the films separate from the substrate. Determine remnant and maximum polarization and coercive field of the ferroelectric film and saturation polarization of the magnetic film.
4) Demonstrate piezomagnetic coefficient of > 5 ppm/Oe and magnetic loss tangent < 5% at 1 GHz for the magnetic film and dielectric loss tangent of < 1% for the ferroelectric film at room temperature.

Accomplishments: 1) We demonstrated the deposition of ferroelectric strontium-doped hafnia (SHO) and ferromagnetic cobalt ferrite (CFO) thin films by atomic layer deposition. Film thickness was varied between 10 and 50 nm. Strontium doping was varied between 2 and 10 at%. CFO readily crystalized at deposition temperatures above 300 C, however we found the crystalization temperature of SHO was increased by higher Sr doping levels and that at 2 at%, SHO crystalized above 500 C.

2) We characterized the quality of our SHO and CFO films by SEM, EDS, XRD/XRR, AFM, and RBS. We grew SHO and CFO on bare (100) Si as well as (111) oriented Pt and polycrystaline TiN buffer layers and other substrates as well.

3) For 2 at% SHO thin films at a measurement frequency of 1 MHz, the relative permittivity was 17-18.5, the dielectric loss tangent was 0.02-0.25, the remnant polarization was 3 uC/cm2, and the coercive field was 1000 kV/cm. We found we could not obtain ferroelectric films that met the Army's requirements for processing temperatures below 450 C.
For CFO films at low frequencies, the remnant magnetization was 85-100 emu/cm3, the saturation magnetization was 275-455 emu/cm3 (depending on the crystalline quality), and the coercive magnetic field was roughly 1 kOe.

4) Other workers have demonstrated that CFO has both high magnetostriction and piezomagnetic coefficients. We measured the piezoelectric coefficients of our SHO films using piezoforce microscopy and found them to be small. We performed ferromagnetic resonance measurements on our CFO films and found magnetic loss tangents below 5% at 1 GHz. We were unable to make microwave measurements of our SHO films during this phase, though we

did not expect them to be promising based on our low frequency measurements.

Training Opportunities: Nothing to Report

Results Dissemination: We are in the process of preparing a paper for submission to a technical journal to describe our results on the deposition and characterization of cobalt ferrite by ALD.

Honors and Awards: Nothing to Report

Protocol Activity Status:

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PARTICIPANTS:

Participant Type: PD/PI
Participant: James Drury McCambridge
Person Months Worked: 2.00 **Funding Support:**
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Participant Type: Co-Investigator
Participant: Matthias Falmbigl
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1 Results of Phase I

In our Phase I program entitled "All-ALD Hafnia and Ferrite-based Multiferroics for CMOS-Compatible Tunable Microwave Applications," epoXtal LLC chose to focus on atomic layer deposition (ALD) for its precise control of composition and potential for low processing temperatures. Our original intent was to use ferrimagnetic cobalt ferrite ($CoFe_2O_4$) and ferroelectric strontium-doped hafnia to form multiferroic bilayers. We found the properties of the doped hafnia lacked promise for this application. We have shown the material properties of $CoFe_2O_4$ meet or exceed the Army's requirements to develop extrinsic multiferroic heterostructures.

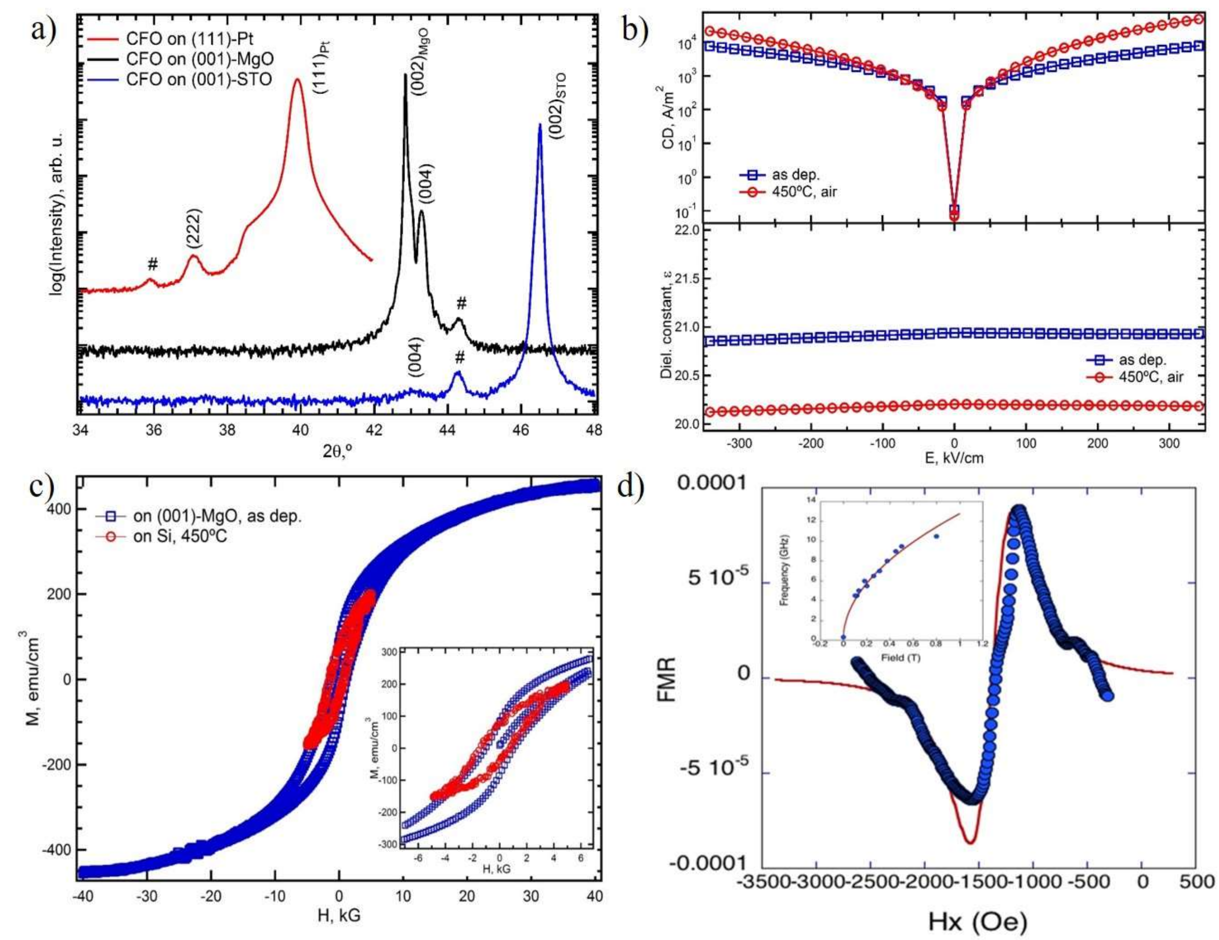

Figure 1. a) XRD of CFO films grown at 300°C on (111) Pt and (001) MgO. b) Leakage current and dielectric constant vs electric field of Pt/CFO/Pt MIM capacitors for as-deposited and 450°C anneal. c) In-plane magnetization loops of CFO on (001) MgO and on Si (450°C anneal). d) Results from FMR measurements of CFO on Si showing the resonance peak at 5 GHz. Inset: resonance frequency of magnetization as a function of the applied field. The solid line is a fit to the Kittel equation.

1.1 Cobalt Ferrite Ferromagnetic Thin Films

In Phase I, we produced high quality piezomagnetic $CoFe_2O_4$ (CFO) thin films. We **chose CFO because it has high magnetostriction** (λ_{111} ≈ 120 ppm, λ_{100} ≈ -590 ppm), **high piezomagnetic coefficient** (q_{33} ≈ -1.5x10^{-7} Oe^{-1}) [1], and a moderate saturation magnetization (M_s ≈ 325 emu/cm^3), which make it attractive for multiferroic bilayers. CFO had also been successfully deposited by ALD previously [2, 3] and widely used in multiferroic composites [4].

In Phase I, we successfully demonstrated growth of CFO films between 250°C and 300°C in a Picosun R200 ALD at Drexel University and showed precise control of the Co/Fe ratio and film thickness as well as high uniformity and reasonable growth rates. We deposited CFO on (001) silicon, (111) Pt- and TiN-buffered silicon substrates, (001) MgO, and (001) $SrTiO_3$. The low growth temperatures during ALD usually result in amorphous films for most complex oxides and a post-deposition anneal is required to crystallize the desired phase. However, our results showed that **$CoFe_2O_4$ readily crystallizes during the deposition at 300°C** on all the above substrates. Moreover, it exhibits a tendency for oriented/epitaxial growth for a range of substrate lattice parameters and crystallographic orientations (see Figure 1a).

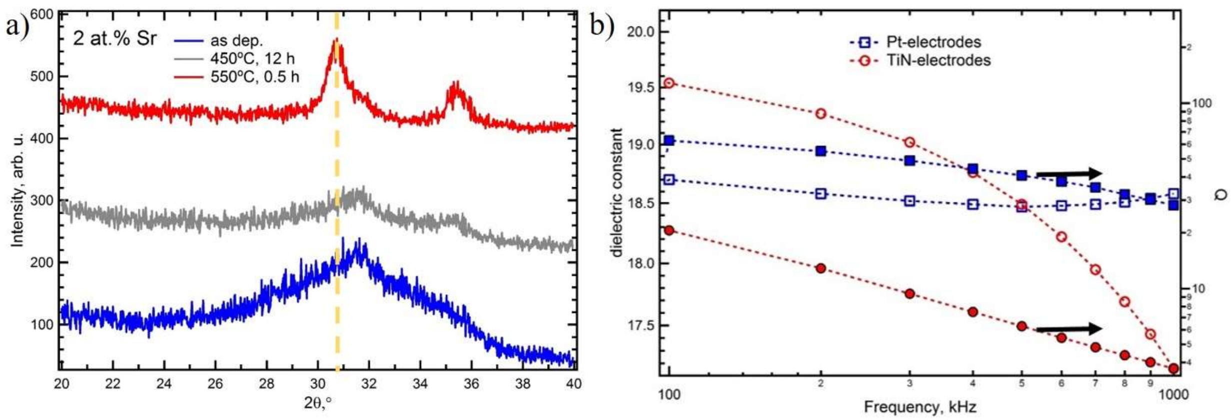

Figure 2. a) XRD of as-deposited $Sr_{0.02}Hf_{0.98}O2$ films (blue) and after annealing at 450°C (gray) and 550°C (red). The films do not crystallize at 450°C. b) Dielectric constant ε_r and quality factor Q vs frequency of $Sr_{0.02}Hf_{0.98}O2$ films grown on TiN and Pt after annealing at 550°C.

CFO grows as a relaxed (111) oriented layer on (111) Pt, a tensile-strained epitaxial layer on (001) MgO (a_{MgO} = 0.422 nm), and a relaxed epitaxial layer on (001) $SrTiO_3$ (a_{STO} = 0.3905 nm). In bulk, $CoFe_2O_4$ is a spinel with a = 0.838 nm. The ability of the $CoFe_2O_4$ films to adopt oriented growth in all cases is promising for its use in multiferroic composites, where control of strain and orientation are two of the key parameters for a functional material by design.

In Figure 1b, we present the electrical properties of an ALD-grown 57 nm thick CFO film sandwiched between Pt electrodes. The measured conductivity is typical for a semiconducting material. CFO is a ferrimagnetic material; its magnetic hysteresis is displayed in Figure 1c. In plane magnetization loops were measured for CFO on (001) MgO as deposited (blue squares) and on (001) Si after a 450°C anneal (red circles). We found the coercive fields H_C ≈ 1 kOe for both. The remnant magnetization for CFO on MgO is 85 emu/cm^3. The saturation magnetization M_s for the epitaxial film on MgO is 455 emu/cm^3, while for the polycrystalline CFO film on Si M_s ~ 275 emu/cm^3, highlighting that the **higher quality of an epitaxial film results in superior material properties**. All these values are consistent with those found in the literature [1, 2, 3, 5]. Ferromagnetic resonance measurements are shown in Figure 1d. The resonance peak at 5 GHz has a small FWHM of 300 Oe and inhomogeneous line broadening of 66 G/GHz, which are encouraging results for microwave applications.

1.2 Strontium-doped Hafnia Ferroelectric Thin Films

We selected the ferroelectric Sr-doped HfO_2 based on the wide use of ALD-deposited HfO_2 in CMOS processes [6]. During Phase I, we established a scalable deposition process for $Sr_zHf_{1-z}O_2$ thin films with high uniformity on various substrates. We demonstrated that the crystallization temperature for the doped films declines with decreasing doping content: decreasing the Sr-content from z = 0.10 to z = 0.02 decreased the crystallization temperature from 800°C to 550°C. Extensive *annealing at the target temperature of 450°C did not appear to initiate crystallization* (see Figure 2a). A careful analysis of the XRD pattern reveals a multi-phase film with fractions of cubic, orthorhombic (the desired ferroelectric phase), and monoclinic structures, which is consistent with literature reports [7].

We performed single frequency piezoforce microscopy (PFM) on $Sr_{0.02}Hf_{0.98}O_2$ films to measure their piezoelectric response. The images are shown in Figure 3. While the average surface roughness of 0.7 nm for a 100 µm^2 area is very small (Figure 3a), the piezoelectric response displayed as amplitude and phase in Figure 3b and Figure 3c reveal that a *significant piezoelectric coefficient d_{33} is only achieved locally*, as would be expected from a multi-phase polycrystalline film of small non-ferroelectric and ferroelectric grains.

Finally, to determine the dielectric and ferroelectric properties, we measured MIM capacitors with a 30 nm thick $Sr_{0.02}Hf_{0.98}O_2$ layer and Pt or TiN electrodes. In both cases, the capacitors were annealed at 550°C under N_2. The frequency dependence of the dielectric constant ε_r and the quality factor $Q = 1/\tan\delta$ up to 1 MHz are depicted in Figure 2b. While the dielectric constant of the Pt-based MIM capacitor is essentially frequency independent, we found a pronounced decline with increasing on TiN electrodes. This highlights the high sensitivity of hafnia-based ferroelectrics to the electrode material, which may limit their application in multilayer heterostructures. For both capacitors, the *quality factor is far below the desired value of 100*.

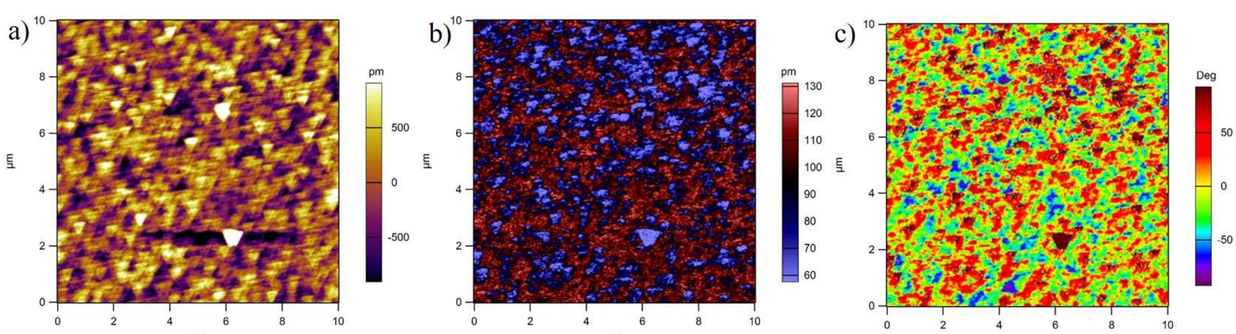

Figure 3. Single frequency PFM image of the surface of a $Sr_{0.02}Hf_{0.98}O_2$ on TiN after annealing at 550°C. a) Surface height. RMS roughness = 0.7 nm. b) The piezoresponse amplitude and (c) phase which do not indicate a large piezoelectric coefficient.

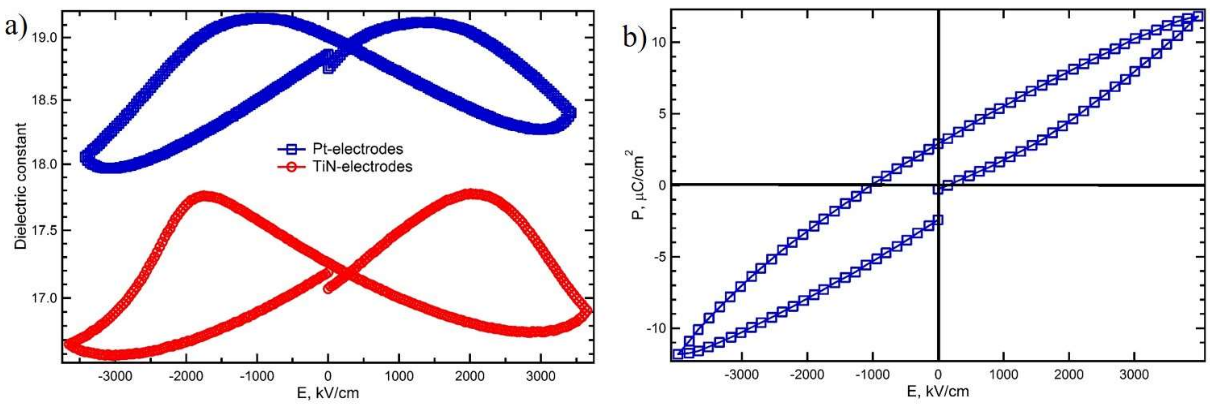

Figure 4. a) Electric field dependence of the dielectric constant for $Sr_{0.02}Hf_{0.98}O_2$ films on Pt and TiN electrodes. b) Polarization loop for the film on TiN. The dielectric tunability is disappointingly small, as is the remnant polarization.

The response of the dielectric constant at 1 MHz to an electrical bias is displayed in Figure 4a and demonstrates ferroelectricity in both capacitors, as evidenced by the "butterfly" shape. The larger hysteresis for the TiN-based structure points towards a higher content of the ferroelectric phase in this film. *However, the tunability is only 1.07*. These properties result in a P-E loop (shown in Figure 4b) with small remnant polarization (≈ 3 $\mu C/cm^2$) which does not saturate below fields of 4000 kV/cm. Although we found some interesting properties, the overall performance of *Sr-doped hafnia falls short in many of the desired benchmarks*.

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