Magnetoelectric Hexaferrite Thin Film Growth on Oxide Conductive Layer for Applications at Low Voltages

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Magnetoelectric (ME) M-type hexaferrite thin films were deposited on conductive oxide layer of Indium-Tin Oxide (ITO) in order to lower applied voltages to observe ME effects at room temperature. The thin film of ME hexaferrites, $\text{SrCo}_2\text{Ti}_2\text{Fe}_8\text{O}_{19}$ / ITO buffer layer, were deposited on sapphire substrate using Pulsed Laser Deposition (PLD) technique. The film exhibited ME effects as confirmed by vibrating sample magnetometer (VSM) in voltages as low as 0.5 volts. Without the oxide conductive layer the required voltages to observe ME effects were typically 500 volts and higher. The thin films were characterized by X-ray diffractometer, scanning electron microscope, energy-dispersive spectroscopy, vibrating sample magnetometer, and ferromagnetic resonance. We measured saturation magnetization of 1064 G, and coercive field of 20 Oe for these thin films. The change rate in remanence magnetization was measured with the application of DC voltage at room temperature and it gave rise to changes in remanence in the order of 15% with the application of only 0.5V (DC voltage). We deduced a ME coupling, α , of $5 \times 10^{-10} \text{ s m}^{-1}$ in $\text{SrCo}_2\text{Ti}_2\text{Fe}_8\text{O}_{19}$ thin films.

I- Introduction

Single-phase magnetoelectric (ME) hexaferrites have exhibited high ME coupling, α , at room temperature comparable or better than composites ME multi-layers [1-12]. In previous work most of the research has been concerned with the electric and magnetic properties of bulk properties of ME hexaferrite materials [1-10]. However, recently M-type hexaferrite films have been deposited successfully in the Microwave laboratory [13] by pulsed laser deposition, PLD, technique. The deposited films exhibited ME effects at room temperature whereby a vibrating sample magnetometer (VSM) was utilized to measure ME coupling, $\alpha = 6.07 \times 10^{-9} \text{ s/m}$. In this experiment the voltage applied to the film ranged from 500 to 1000 volts. Clearly, voltages of that amplitude are simply not compatible with planar technologies of IC circuits on CMOS devices. Thus, we have embarked on a methodology or technique to reduce required voltages to induce a ME effect at room temperature, preferably voltages as low as 1 volt.

Recently, we have explored new techniques for H-field and E-field sensing as well as tunability applications in RF devices [14, 15] using Single-phase hexaferrite films of $\text{SrCo}_2\text{Ti}_2\text{Fe}_8\text{O}_{19}$, on sapphire substrate. In order to reduce the applied voltage required to generate practical E fields to induce measurable ME effects at room temperature we applied E fields in the film plane in a multi capacitive structure [14-16] whereby parallel metallic strips were deposited on the ME film. In order to reduce the required voltage for the case of the E field applied perpendicular to the film, we have introduced a conductive oxide buffer layer between the ME film and sapphire substrate.

To date ME films have not been deposited on a metallic conductive layer, since buffer metallic layers inhibit growth of ME films. Hence, we have introduced an oxide conductive buffer layer to induce growth of ME films. We expect that the lattice constant mismatch between a metallic buffer layer and a ME film is too great to overcome in depositing ME films. However, conductive

oxide buffer layers of ITO (In_2O_3 : SnO_2) and AZO (Al_2O_3 : ZnO) have a better match to the lattice constant of the ME film (5.9°A° for hexaferrites, $5.25^\circ \text{A}^\circ$ for ZnO , and $10.12^\circ \text{A}^\circ$ for ITO).

We have carried out successful deposition of ME films on buffer layer of ITO which proving that conductive oxide buffer layers are essential in depositing ME hexaferrite films. This deposition feasibility allows for the possibility of reducing required voltages to observe ME effects in device applications, such as sensors, filters, IC chips, magnetic recording control valves and tunable inductors. These types of devices require that the ME films to be part of the integrated circuitry.

II- Thin Film Deposition

Targets of $\text{SrCo}_2\text{Ti}_2\text{Fe}_8\text{O}_{19}$ were prepared by conventional ceramics processing [13, 17]. The chemical compositions of the target were verified by x-ray diffraction (XRD), using a $\text{CuK}\alpha$ source, and energy dispersive x-ray spectroscopy (EDXS) and it was determined to be single-phase material. Indium Tin Oxide, $\text{In}_2\text{O}_3/\text{SnO}_2$ (ITO) target was purchased from Sigma Aldrich. Both ITO and $\text{SrCo}_2\text{Ti}_2\text{Fe}_8\text{O}_{19}$ films were deposited on sapphire (0001) by PLD technique, which is an effective epitaxial growth technique for the production of hexaferrite thin films [18].

The base pressure in the deposition chamber was maintained at 9×10^{-6} Torr and for ITO deposition the substrates were heated to 400°C . The films were deposited in a high purity oxygen environment of 10 mTorr. A KrF excimer laser with a wavelength of 248 nm and energy of 400 mJ/pulse was focused on the target surface. The distance between the target and the substrate was set to 5.5 cm and the repetition rate of the laser was set to 10 Hz during deposition and it lasted for 20 min. After deposition, the films were cooled to room temperature at the same oxygen pressure. The vacuum was broken to mask part of the sample in order to have access to ITO later after the ME film deposition. For ME film deposition substrate was heated to 600°C , in a high purity oxygen environment of 200 mTorr. The repetition rate of the laser gradually increased from 1 Hz to 10 Hz during deposition to improve the growth. The deposition run was timed for 90 min and resulted in an amorphous film structure. The film thickness was measured to be $1.2 \mu\text{m}$ using a scanning surface profilometer. Leaving the films in the furnace during temperature ramping appeared to affect crystal structure due to diffusion at the film-substrate interface. To prevent this problem, the films were rapidly inserted into the preheated furnace of 1050°C , annealed for 40 min, and rapidly removed from the furnace. The thin films were evaluated by XRD and EDXS to determine the crystal structure and composition of the film and buffer layer.

III- Experimental Results

1. Magnetic characterization of The Films

The composition and structure of these films were determined by X-ray diffractometer, energy dispersive x-ray spectroscopy, and SEM image. Fig. 1a is the SEM data of a film tilted at 15° . Fig. 1b is the magnified image of the same part by two times and Fig. 1c shows the image from another part of the sample. The XRD patterns are illustrated in Fig. 2. It shows that the film has a polycrystalline structure but has strong and sharp diffraction peaks at $(0\ 0\ 2n)$ [$n\ 3, 4, \dots$]. Other peaks correspond to other crystal phases, sapphire substrate and the buffer conductive layer of ITO deposited in between the sapphire substrate and the ME film, for example the peak at 32° , 51° , 66° have been observed on any film and any substrate but with the ITO buffer layer, and the peak at 42° corresponds to sapphire substrate. However, in addition to these aforementioned

background phases the interfacial region between ME film and ITO layer may consist of extraneous weak XRD peaks associated with other magnetic phases, not consistent with the M-type crystal structure. Since the film was deposited at relatively low temperatures (600 °C), we estimate this interfacial region to be in the order of 50-80 nm [19] which is much smaller than the ME film thickness of 1000-1300 nm.

Fig. 1 SEM image of the $\text{SrCo}_2\text{Ti}_2\text{Fe}_8\text{O}_{19}$ thin film on ITO/Sapphire substrate.

Fig. 2. XRD pattern of $\text{SrCo}_2\text{Ti}_2\text{Fe}_8\text{O}_{19}$ thin film on ITO/ Sapphire.

Fig.3. VSM hysteresis loop of $\text{SrCo}_2\text{Ti}_2\text{Fe}_8\text{O}_{19}$ /ITO thin film.

The static magnetic properties of the films were studied by VSM with the magnetic field applied perpendicular and parallel to the film plane. In Fig. 3, typical hysteresis loops of the films are shown. The coercive field for the cases that the external field applied parallel or perpendicular to the film plane was measured to be 20 Oe. We measured saturation magnetization of 1064 G.

In addition to above experiments, we performed FMR measurements at high frequency of 9.5 GHz. Fig. 4 shows the FMR derivative absorption is shown for two cases of interest: (a) the magnetic field H was applied in the plane ($\parallel$) of the film and (b) perpendicular ($\perp$) to the film plane. We measured a FMR linewidth of ~ 1000 Oe which is typical of cobalt-based ferrites. The FMR line- width in other hexaferrites ranges from 100 Oe to 2000 Oe [20].

The FMR for the magnetic field H applied in the film plane ($\parallel$) occurred at $H_{\parallel} \sim 2700$ Oe, whereas for H applied perpendicular ($\perp$) to the film plane $H_{\perp} \sim 3000$ Oe. The FMR condition for H , DC magnetic field, applied perpendicular to the film plane is $\frac{\omega_{\perp}}{\gamma} = H_{\perp} - 4\pi M - H_A$. $\omega_{\perp}$ is the resonance radial frequency, $4\pi M$ is the saturation magnetization, H_A is the magnetic anisotropy field, and $\gamma = g \frac{e}{2m_e}$ where e and m_e are electron charge, and mass. H_A may be cumulative due to an intrinsic component [21] and due to lattice constant mismatch. Assuming a g value in the order of 2 [22] we estimate $H_A \sim 1500$ Oe.

Fig.4. Magnetolectric test set-up for the film on a conductive ITO layer.

2. Magnetolectric measurements

We performed ME measurements by measuring the changes in remanence magnetization with the application of a DC voltage, see fig. 5. The ME effect at room temperature was observed at much smaller DC voltages in films of $\text{SrCo}_2\text{Ti}_2\text{Fe}_8\text{O}_{19}/\text{ITO}$.

Fig.5. Magnetolectric test set-up for the film on a conductive ITO layer.

In Fig. 6, the magnetization is plotted as a function of applied voltage across only the film. The $\mathbf{M}$ and $\mathbf{E}$ fields are normal to the ME film plane. This measurement has been performed by VSM measurement and applying different voltages. Changes in remanence magnetization were measured to be 15% by applying 1 Vdc only. The ME coupling coefficient was deduced from the experiment using the formula

$$\alpha = d \times \frac{\mu_0 \Delta M}{\Delta V}$$

where ΔM is the change in magnetization (a/m), ΔV is the change in applied voltage across the film and d is the thickness of the film = 1.2 μm . We have deduced a α value of 5×10^{-10} s/m. For only 0.5 volts M changes significantly, see Fig. 6. The applied electric field, E , is in the order of 0.5×10^6 V/m. However, it would require 500 V to generate the same E without the ITO buffer layer, see ref. [13, 22]. In that case the voltage was applied across both the film and substrate.

Fig. 6 change in magnetization by applying DC electric field perpendicular to the film plane while $\mathbf{H}$ is the same direction

At Fig. 6 we used linear trend to extract magnetoelectric coefficient. Landau and Lifshitz [23] proposed the possibility of linear coupling between the electric field $\mathbf{E}$ and magnetic field $\mathbf{H}$ in special ferrite materials. Dzyaloshinski [24] showed that such coupling might be possible in spin configurations whereby spins may be non-collinear. A general thermodynamic argument was recently proposed by Vittoria et al. [25] to model magnetoelectricity in hexaferrites and it predicted that the magnetoelectric (ME) coupling α is proportional to the product of the magnetostriction and piezoelectric strain coefficients. According to ref [17] Sr substitutions in films of M-type hexaferrite $\text{SrFe}_8\text{Ti}_2\text{Co}_2\text{O}_{19}$ induce local distortions near the 2d site (Wyckoff positions) giving rise to large uniaxial magnetic anisotropy fields. However, substitutions of Fe ions in 2a, 2b, 12k and 4f₁ sites and Co ions in 4f₂ and 12k sites alter the magnetic anisotropy to the extent inducing non-collinearity of spins. In addition, Ti ions substitute in 12k sites diminishing super-exchange interactions between spins in R and R* blocks of the M-type hexaferrite structure, since Ti^{+4} ions are non-magnetic ions. The cumulative effect of these substitutions provide the spin spiral arrangement to facilitate the ME effect at room temperature.

IV- Discussions and Conclusion

It appears that it is feasible to deposit thin films of ME hexaferrites, $\text{SrCo}_2\text{Ti}_2\text{Fe}_8\text{O}_{19}$, on ITO buffer layers. The film exhibited ME effects in VSM measurement technique in voltages as low

as 0.5 Volts. This means that required voltages needed to induce ME effects in ME films are enormously reduced compared to voltages in ME thin films without the buffer layer. A change of 15% in magnetization was observed by applying 1 V DC voltage. We believe that ME films with oxide conductive buffer layers appear to be very promising in future IC circuitry.

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