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Bismuth iron oxide thin films using atomic layer deposition of alternating bismuth oxide and iron oxide layers

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ABSTRACT

Bismuth iron oxide films with varying contributions from Fe_2O_3 or Bi_2O_3 were prepared using atomic layer deposition. Bismuth (III) 2,3-dimethyl-2-butoxide, was used as the bismuth source, iron(III) tert-butoxide as the iron source and water vapor as the oxygen source. The films were deposited as stacks of alternate Bi_2O_3 and Fe_2O_3 layers. Films grown at 140 °C to the thickness of 200–220 nm were amorphous, but crystallized upon post-deposition annealing at 500 °C in nitrogen. Annealing of films with intermittent bismuth and iron oxide layers grown to different thicknesses influenced their surface morphology, crystal structure, composition, electrical and magnetic properties. Implications of multiferroic performance were recognized in the films with the remanent charge polarization varying from 1 to 5 μC/cm^2 and magnetic coercivity varying from a few up to 8000 A/m.

1. Introduction

Atomic layer deposition (ALD) is a low-temperature chemical growth method particularly suited to the build-up of very thin solid conformal films of arbitrary composition for a variety of applications, including those in electronics [1–7]. For nanoelectronics, spintronics and sensing applications, multiferroic materials are promising and have gained significant interest over the past few years due to their simultaneous ferromagnetic and ferroelectric ordering. Among the multiferroic compounds, bismuth ferrite, $BiFeO_3$, has been one of the most widely studied materials due to its high Curie and Néel temperatures [8], and recently in THz spectroscopy [9] observed optical diode effect at spin-wave excitations [10].

$BiFeO_3$ films have earlier been produced by pulsed laser deposition (PLD), sputtering and sol–gel techniques. At the early stages, $BiFeO_3$ films produced by PLD technique directly on $Pt/TiO_2/SiO_2/Si$ substrates yielded a polarization saturation, P_s, and remanent polarization, P_r, of 2.2 and 0.83 μC/cm^2, respectively [11] which are at levels comparable to those achieved in the films produced by sol–gel technique [12], as well as in bulk $BiFeO_3$ [13]. The polarized domains in the bulk $BiFeO_3$ have naturally been larger than those achievable in thin films [14]. Wang et al. [15] have later demonstrated high P_s, P_r, and noticeable magnetic coercivity, H_c, in epitaxial $BiFeO_3$ films deposited by the PLD technique on single crystal $SrTiO_3$ substrates. However, the use of single crystal $SrTiO_3$ substrates inevitably leads to high cost, which would hamper the commercialization process. Regarding the optimization of the process directly on Pt-coated silicon substrate electrodes, $BiFeO_3$ films recently produced by PLD and sputtering technique showed appreciably high P_r [16,17], with also magnetization apparent in the same films [17]. A nanocomposite of $BiFeO_3/Fe_2O_3$ produced using PLD, possessing better electrical properties than $BiFeO_3$ alone, has been reported [18]. However, in the case of PLD and sputtering techniques, when $BiFeO_3$ thin films of different Bi/Fe ratio or heterostructures (multilayers) of $BiFeO_3/Fe_2O_3$ are to be produced, high purity ablation and sputtering targets of different compositions are required [19].

Often films, powders and crystals of bismuth iron oxides consist of mixed crystallographic phases instead of being phase-pure $BiFeO_3$. Herewith, phases with stoichiometry different from that of $BiFeO_3$ may also exhibit useful physical and physicochemical properties. Studies on the effects of nonstoichiometry on $BiFeO_3$ base material have revealed that excess of iron leads to the separation of pyrochlore $Bi_2Fe_4O_9$ and γ-Fe_2O_3 phases, causing an increase in conductivity in macroscopic scale [20]. However, such films with stoichiometry deviating from that of $BiFeO_3$ can still exhibit both magnetic and electric polarization loops [20]. Dominantly rhombohedral crystalline phase was formed in sol–gel $BiFeO_3$ films after annealing at 50 °C, but with $Bi_2Fe_4O_9$ and

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$Bi_{24}Fe_2O_{39}$ as impurity phases [21]. $Bi_2Fe_4O_9$ and $Bi_{25}FeO_{40}$ secondary phases have also been recognized in $BiFeO_3$ films chemical vapor deposited from metal *tert*-butoxide precursors [22]. $Bi_2Fe_4O_9$ [22,23,24,25] and $Bi_{25}FeO_{40}$ [26,27] have been of interest as photocatalytic films and powders. Dielectric behavior and conduction mechanisms in $Bi_2Fe_4O_9$ have been studied as well [28], and $Bi_2Fe_4O_9$ has also exhibited multiferroic performance [29]. Furthermore, sputtered high-permittivity tetragonal $Bi_{24}Fe_2O_{39}$ thin films have shown appreciable insulating and dielectric properties [30].

ALD has shown certain potential to overcome the limitations related to thickness non-uniformity, poor step coverage and pinholes often faced during thin film processing, allowing, in addition, uniform coating over large substrates. Hence, ALD appears to be a commercially viable technique and the corresponding process chemistry offers an attractive field of research. Regarding possible ALD routes to $BiFeO_3$, 5 nm thick continuous films have been grown at 250 °C on Nb-doped $SrTiO_3$ (STO:Nb) using equal amounts of alternate Bi_2O_3 and Fe_2O_3 ALD cycles from β-diketonates $Bi(thd)_3$ and $Fe(thd)_3$ with H_2O, where thd denotes 2,2,6,6-tetramethyl-3,5-heptanedionato ligands [31]. These films were crystallized upon annealing at 650 °C. In another ALD process, also carried out at 250 °C on STO:Nb the $BiFeO_3$ films were grown from ferrocene ($FeCp_2$, $Cp = C_5H_5$), tris(1-methoxy-2-methyl-2-propoxy)bismuth, $Bi(mmp)_3$, and ozone, O_3 [32]. In the latter two studies, ferroelectric polarization domains in $BiFeO_3$ were observed using piezoresponse force microscopy (PFM). More recently, ferroelectric characterization by PFM has also been carried out on films grown again at 250 °C on STO:Nb substrates by alternate pulsing of $Bi(thd)_3$ and $FeCp_2$ combined with O_3 [33]. Furthermore, bismuth ferrite films with Bi/Fe ratio of 1.00 ± 0.02 were grown by ALD to the thickness of 60 nm from tris(2,3-dimethyl-2-butoxy)bismuth(III), $Bi(dmb)_3$, iron(III) tert-butoxide, $Fe(O^tBu)_3$, and H_2O on $Pt/SiO_2/Si$ substrates at a temperature as low as 150 °C [34]. The latter films were crystallized at 500 °C and characterized by superconducting quantum interference device (SQUID) magnetometry.

In this work, $BiFeO_3$ films with varying contributions from secondary phases ($Bi_2Fe_4O_9$, Bi_2O_3 or Fe_2O_3) were grown by ALD on $Pt/SiO_2/Si$ substrates from $Bi(dmb)_3$, $Fe(O^tBu)_3$, and H_2O. The structure and bismuth to iron atomic ratio in the films was modified and studied after changing the relative amounts of Bi_2O_3 or Fe_2O_3. The films were initially grown as sequentially stacked layers of binary iron and bismuth oxides, with variable numbers of deposition cycles for either constituent oxide. For some samples regarded as uniform heterostructures or even-layered stacks, the period of the stacks, i.e. the thickness of the Bi_2O_3 or Fe_2O_3 double layers, was kept constant. These films will further be denoted as uniform stacks. For the rest of the samples with intentionally more nonuniformly distributed composition, the thickness of the double layers was changed during the growth, creating films consisting of two halves with different periods. These stacks will further be denoted as nonuniform ones. The crystallization and formation of different phases became evident after annealing of the films upon solid state reactions between constituent oxides and intermixing of the layers. Thicknesses and periods of stacked layers were changed in order to get possible implications of structural and magnetoelectric behavior to the variations in the eventual stoichiometry of the films. The double layers were deposited to somewhat higher thicknesses closer to the substrate to better complete the formation of chemically defined component oxides, starting with the deposition of Fe_2O_3 layer due to its higher chemical stability on the substrate. The ferroelectric and ferromagnetic characteristics of the films were examined.

2. Experimental details

The metal precursors exploited were synthesized in house. The synthesis and handling of the compounds were performed under inert gas atmosphere or vacuum in standard glove box and using Schlenk techniques. The bismuth precursor, bismuth(III) 2,3-dimethyl-2-butoxide, $Bi(dmb)_3$ was synthesized according to a recipe published earlier [35]. The iron precursor, bis(μ_2-*tert*-butoxo)-tetrakis(*tert*-butoxy)-di-iron(III), $[Fe(O^tBu)_3]_2$, i.e. iron(III) *tert*-butoxide, was synthesized using a metathesis reaction between anhydrous $FeCl_3$ and $K(O^tBu)_3$ in tetrahydrofurane. The reaction mixture was stirred overnight after which the solvent was evaporated under vacuum. The product was then sublimed out of the resulting solid residue at 140 °C and 0.05 mbar. The product was a dark brown solid. The yield of the synthesis process was 74.9%.

For the film deposition, a flow type F-120 reactor (ASM Microchemistry Ltd.) [1] was used with a pressure of approximately 10 mbar. N_2 (99.999%) was used as the carrier and purging gas prepared using Labgas N2L nitrogen generator. The deposition temperature was 140 °C. The $Bi(dmb)_3$ and $Fe(O^tBu)_3$ were evaporated from open boats inside the reactor at 85 and 105 °C, respectively. The pulse lengths of $Bi(dmb)_3$ and $Fe(O^tBu)_3$ precursors were 0.4 and 0.5 s, respectively. The H_2O pulse length was 0.5 s. The purge length after the metal precursor pulse was 1.5 s, whereas the purge length after H_2O pulse was 3 s.

After the deposition the films were annealed at 500 °C for 60 min in nitrogen atmosphere using a sealed tube furnace.

PANalytical X'pert Pro MPD diffractometer was used to measure the grazing incidence X-ray diffraction patterns, while the incident beam angle was 1°. A Hitachi S-4800 field emission scanning electron microscope was used for studying the surface morphology. To evaluate the film composition, energy dispersive X-ray spectra (EDS) were measured using an Oxford INCA 350 X-ray spectrometer connected to a Hitachi S-4800 microscope. The Bi/Fe ratios in the films were calculated from the EDS data using a GMRFILM program [36]. Cross-sections of Pt/oxide samples were prepared and monitored with a Quanta 3D 200i focused ion beam — scanning electron microscope (FIB-SEM). Transmission electron microscopy (TEM) images were taken using a Tecnai F-20 200 kV FEG-TEM. EDS line scans of the heterostructure specimen were extracted from an EDS map collected from the TEM specimen with the FIB-SEM system with a 30 kV electron beam. Thin specimen enhanced the EDS spatial resolution to 50–100 nm at 30 kV. Content of residual light elements in selected representative samples was determined by time-of-flight elastic recoil detection analysis (TOF-ERDA) [37]. The TOF-ERDA was performed with 5 MV tandem accelerator using 50 MeV ^{127}I ion beam.

$Pt/BiFeO_3/Pt/SiO_2/Si$ capacitor stacks were prepared by depositing approximately 40 nm platinum (Pt) film on thermally oxidized silicon wafer using electron beam evaporator. The platinum film was then annealed to improve adhesion to the SiO_2 surface. This was followed by $BiFeO_3$ film deposition using the ALD technique. For reference, all the films were also grown directly on silicon substrates in the same runs. Finally, Pt top dot electrodes of the area 2.04×10^{-7} m^2 were electron beam evaporated on the $BiFeO_3$ films through a shadow mask. The electrical measurements were made after contacting the platinum bottom and top electrodes to the measurement circuitry. The post-deposition annealing of the $BiFeO_3$ layers was performed after the top electrode deposition. Capacitance was measured using an HP 4284A LCR Meter at 10 KHz frequency. The leakage current was measured using a Keithley 2400 Source meter, with the applied voltage ramped in 0.1 V steps followed by a 3 s delay before measuring the current. Modified Sawyer-Tower circuit [38] was employed to measure polarization curves using 1 KHz sinusoidal signal source, supplied by an Agilent 33220 20 MHz arbitrary waveform generator and using National Instruments NI 5102 high-speed digitizer for recording the voltage signals. The magnetic measurements were performed using vibrating sample magnetometer (VSM) option of the Physical Property Measurement System (PPMS) 14 T (Quantum Design), with the magnetic field parallel to the film surface. Hysteresis measurements were performed by scanning the magnetic fields from −477.6 to +477.6 kA/m at 300 K.

3. Results and discussion

The growth rates of the binary compounds Bi_2O_3 and Fe_2O_3 were approximately 0.04 and 0.02 nm/cycle, respectively, as reported earlier