Use of magnetoplumbite and spinel ferrite seed layers for the growth of oriented Y ferrite thin films

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ABSTRACT

Thin films of $Ba_2Zn_2Fe_{12}O_{22}(Y)$ ferrite were prepared on $SrTiO_3(111)$ single crystal substrates using chemical solution deposition method and two-step crystallization process. A polycrystalline film of seeding phase was deposited first and then heated to break it up into isolated grains that acted as nucleation seeds for crystallization of Y phase. These seed grains modify the high lattice and chemical mismatch of the $SrTiO_3(111)/Y$ hetero-interface by creating two interfaces with reduced mismatch. Two epitaxially grown structures with hexagonal symmetry of the O^{2-} ion layers were used for seeding, namely the cubic (111)-oriented $CoFe_2O_4$ and the hexagonal (001)-oriented $(BaSr)(GaAl)_{12}O_{19}$. Atomic force microscopy and X-ray diffraction measurements show that the Y films grow with the c-axis perpendicular to the surface, matching the orientation of the seed layer. The Y film with the best orientation was obtained for $(BaSr)(GaAl)_{12}O_{19}$ seed layer despite its large misfit with respect to the Y phase. The mechanisms leading to the experimentally observed structures and morphologies are discussed with respect to the influence of lattice mismatch between the relevant structures, and surface coverage and surface topography of the seed layers.

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1. Introduction

Hexagonal ferrites were discovered in the 1950s and since then they have received much attention owing to their important properties providing a large variety of applications as e.g. permanent magnets, magnetic data storage materials, materials for stealth technology, as well as components for mobile and wireless communications [1]. Recently, there has been renewed interest in hexagonal ferrites due to two phenomena that promise development of unexpected applications. Firstly, of particular interest is the magnetoelectric (ME) effect demonstrating ferroelectricity induced by the complex internal alignment of magnetic moments, discovered recently in the hexagonal ferrites with general formula $Ae_2Me_2Fe_{12}O_{22}$ (Ae = alkali earth ion, Me = transition metal ion; hereinafter referred to as Y only) such as $(Ba_{1-x}Sr_x)_2Zn_2Fe_{12}O_{22}$ [2,3], $(Ba_{1-x}Sr_x)_2Zn_2(Fe_{1-x}Al_x)_{12}O_{22}$ [4], $BaSrCoZnAlFe_{11}O_{22}$ [5], and $Ba_2Mg_{2-x}Zn_xFe_{12}O_{22}$ [6]. Secondly, spin Seebeck effect (SSE) [7] was observed in thin film samples consisting of ferrimagnetic hexagonal ferrites [8]. The SSE is a phenomenon enabling the conversion of heat currents into spin voltage as a result of a temperature gradient in magnetic materials including insulators and also provides an essential contribution for the development of the booming field of spintronics.

Considering the demand for downsizing the current microprocessor technologies, production of thin films is vital for components enabling integration of functional elements with standard semiconductor platforms and thus allowing for system-on-a-wafer architectures. There have been considerable reports on growth of epitaxial magnetic films with hexagonal magnetoplumbite type structure with general formula $AeFe_{12}O_{19}$ (Ae = alkali earth ion), hereinafter referred to as M only. Perhaps, due to their chemical and structural complexity, and high temperature needed for their crystallization the literature on preparation of oriented Y films remains scarce [9–13].

In order to prepare $Ba_2Zn_2Fe_{12}O_{22}$ thin films by pulsed laser deposition (PLD) on α-$Al_2O_3(001)$ substrate [9], it was necessary to compensate losses of Ba and Zn. For this purpose targets with strongly nonstoichiometric composition and relatively thick ZnO buffer layer were used. Y thin films on polycrystalline Ag, Au and Pt substrates were prepared by a soft chemistry method using water solution of inorganic salts and citric acid [10]. The films exhibited oriented growth with c-axis perpendicular to the substrate but contained spinel $ZnFe_2O_4$ as an impurity. Authors of [11] prepared Y thin films by PLD using three different target compositions and complex sequential deposition to invoke formation of Y structure. The films showed preferential out-of-plane orientation (with c-axis perpendicular to the substrate) but diffraction

measurements proved presence of noticeable amount of M ferrite impurity. Preparation of thick (80–500 μm) Y films has been reported in [12] employing a rather complex procedure using separately synthesized ferrite nanoparticles filled in column on α-Al₂O₃ substrate covered with stack of three buffer layers (GaN, MgO and M ferrite). The films showed only moderate out-of-plane orientation with 001 planes parallel to the substrate, presence of hkl reflections with h ≠ 0, h ≠ 0 in diffraction pattern indicates that substantial part of the Y phase was randomly oriented.

It is known that if the film and substrate have different structures or large mismatches, fabrication of epitaxial films is still possible as it is reported in [14]. In this case, epitaxy is achieved through control of nucleation at the interface using two-step process. A continuous polycrystalline film of particular thickness is first deposited and then heated to break it up into isolated grains (seeds). Subsequently, a thicker layer is deposited onto this surface and the isolated islands act as nucleation sites (seeds) for the growth of a highly oriented film. Using this strategy, the authors of [13] prepared oriented Y ferrite films on SrTiO₃(111) single crystal substrate covered with thin seeding layer of M ferrite. The authors proved epitaxial nature of films and described orientation relation between the structures of the film, seed layer and substrate using XRD 3D texture analysis.

Fig. 1 shows scheme of the crystal structures of the M, Y hexagonal and cubic spinel ferrites. As it is illustrated in the figure and discussed in Results and Discussion in more detail, the unit cells of both types of hexagonal ferrites contain spinel blocks four O²⁻ layers thick, forming a close-packed cubic structure (S4 block). The crystal structure of the S4 block viewed along the [111] direction is the hexagonal primitive (oblique) while the O²⁻ sublattice in S4 viewed along [111] direction has the face-centered cubic close-packed (fcc) stacking sequence ABCA. In M phase these S4 blocks are joined together by a single intermediate hexagonal close-packed layer B1 forming the mirror plane (Fig. 1a), in Y phase they are joined together by a hexagonal double close-packed layer B2 (Fig. 1b). In both of these interleaved layers one

of the four oxygen atoms in each layer is replaced by an AE ion, giving one AE and two AE ions in the B1 and B2 layer, respectively.

As it can be seen in Fig. 1c, the layers of O²⁻ in both structural motifs S4 and B1 of M structure possess hexagonal symmetry. Accordingly, both these layers could provide structural template for the nucleation and overgrowth of other phases with similar symmetry and lattice parameters, for example Y phase. If spatially resolved regions formed by individual spinel and hexagonal structural motifs can be grown, the following problems could be investigated: Can Y films be grown on substrate seeded both by spinel and hexagonal structures? Are there differences (e.g. in growth mode, in orientation degree) between Y films grown on these two template structures?

It was found that (111)-oriented spinels can be epitaxially grown on various single crystal substrates through the transformation of (001)-oriented layered cobaltates Na(CoFe)O₂ [15,16], and that (001)-oriented M ferrites can be epitaxially grown on SrTiO₃(111) using crystallization stimulated by nucleation seeds [17]. In order to exploit both of these materials as templates for the growth of oriented Y-type ferrite, it is necessary to grow them in a form of effective seed layer. This layer should have epitaxial relation to the substrate. Moreover, it should be sufficiently thin to restrict the initial nucleation events to the substrate interface, and discontinuous in nature to allow for the elimination of high-energy misoriented grains [14].

The objective of the present work is to examine the growth of oriented Y ferrite thin films prepared by chemical solution deposition (CSD) on SrTiO₃(111) (STO) single crystal substrates through a two-step process described above. Two types of materials were employed as a seed layer: the hexagonal M structure with composition (BaSr)(GaAl)₁₂O₁₉ and the cubic spinel structure with composition CoFe₂O₄ formed via transformation of layered cobaltates Na(CoFe)O₂. Instead of more complex stoichiometries for which occurrence of ME effect in Y ferrites has been proved [2–6], films with Ba₂Zn₂Fe₁₂O₂₂ composition were used as a model composition.

2. Experimental

Thin films of Na(CoFe)O₂, (BaSr)(GaAl)₁₂O₁₉ and Ba₂Zn₂Fe₁₂O₂₂ were prepared by spin-coating on (111)-oriented, epitaxially polished SrTiO₃ (STO) single crystals with metalorganic precursor solutions. Aluminium isobutoxide Al(OCH₂CH(CH₃)₂)₃, gallium isobutoxide Ga(OCH₂CH(CH₃)₂)₃, sodium isobutoxide Na(OCH₂CH(CH₃)₂) (all in-house synthetized) and commercial metal 2-ethylhexanoates Me(CH₃(CH₂)₃CH(C₂H₅)COO)ₙ (ABCR Germany, n = 2 for Me=Ba, Sr, Co, Zn; n = 3 for Me=Fe) were used as metal precursors. Isobutanol ((CH₃)₂CHCH₂OH) and 2,2-diethanolamine (NH(CH₂CH₂OH)₂, DEA) were used as solvent and modifier, respectively. Two types of precursor solutions were synthetized. In the first case, calculated amount of Na, Co and Fe precursors were separately dissolved in isobutanol, mixed together and heated for several hours to accomplish homogenization. These solutions were used for the preparation of spinel layers via the transformation of layered cobaltates Na(CoFe)O₂ (details in [15]). In the second case, precursor solutions previously analyzed for their metal content were mixed to achieve the appropriate composition of M phase, heated for several hours at 80 °C to accomplish homogenization. Subsequently, a suitable amount of 2,2-diethanolamine (DEA) used as a modifier was added to both solutions. The modifier to alkali earth metal molar ratio was n(DEA)/n(alkali earth metal) = 2. All reactions and handling were carried out in dry nitrogen atmosphere to prevent reaction with air humidity and formation of alkali earth carbonates in solutions. In order to obtain films of desired thickness the precursor solutions were diluted with isobutanol prior to deposition.

The substrates were cleaned by ultrasound treatment in acetone and then annealed at 1300 °C in air for 24 h to remove surface damages produced by polishing. Prior to the deposition they were cleaned by plasma (Zepto Plasma cleaner, Diener Electronic).
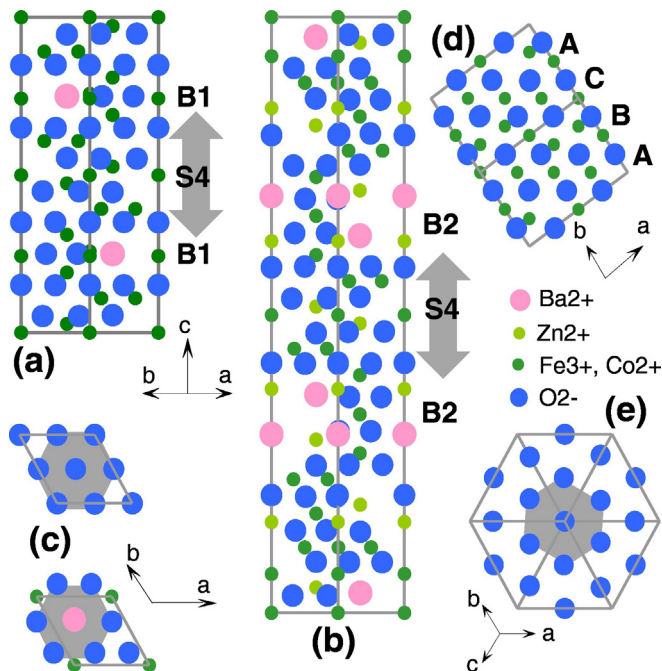

Fig. 1. Schematic diagrams of the crystal structures: (a) cross section view of the M ferrite BaFe₁₂O₁₉ with marked S4 and B1 units, (b) cross section view of the Y ferrite Ba₂Zn₂Fe₁₂O₂₂ with marked S4 and B2 units, (c) plan view of O²⁻ layers in S4 and B1 (B2) in M (Y) viewed along [001] direction, (d) cross section view of the spinel structure with marked sequence of O²⁻ layers, (e) plan view of O²⁻ layer in spinel structure viewed along [111] direction; hexagonal symmetry of O²⁻ layers in (c) and (e) is indicated by gray hexagons.