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ORIENTED BARIUM, STRONTIUM FERRITE FILMS PULSED LASER DEPOSITED ON YSZ(100) AND Si (100) SUBSTRATES

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Abstract- Ba and Sr hexaferrite films with perpendicular magnetic anisotropy were deposited on YSZ (100) and Si (100) substrates. Films on YSZ were highly oriented and grew by a spiral mechanism similar to that observed for growth on sapphire (0001).
An obstacle to oriented growth on Si was its amorphous surface oxide. Substantial improvement in the texturing of the films was achieved by removing the Si oxide prior to deposition and carrying out the initial stage of growth in a reduced oxygen atmosphere.
KEYWORDS: PULSED LASER DEPOSITION, LASER ABLATION, BARIUM FERRITE, STRONTIUM FERRITE, HEXAFERRITES

INTRODUCTION

Magnetoplumbites (M type Ba, Sr, Pb hexaferrites) are expected to play a vital role in a number of important technological areas including ultrahigh density recording and millimeter wave devices. The technological interest in these materials is driven from their intrinsic low optical absorption, high resistivity, strong uniaxial magnetocrystalline anisotropy along the c-axis, as well as the ability to tune the magnetic and MO properties by chemical substitutions in the crystal lattice. Owing to the fact that the magnetic anisotropy of hexaferrites results from their anisotropic structure, the orientation control of the grains during film growth is of paramount importance for achieving improved magnetic properties. The preferred c-axis orientation i.e. vertical or parallel to the films surface, should be selected according to the application.

In an earlier investigation [1] we have shown that growth of perpendicularly oriented, pulsed laser deposited (PLD) SrM films on (0001) sapphire ($\alpha-Al_2O_3$) requires high substrates temperatures (~840 °C) and oxygen pressures in the neighbourhood of 0.1 mbar. Although Al_2O_3 and M-hexaferrites have different crystal lattices, both structures are based on hexagonal close packing arrangements of oxygen ions. Rotation of the hexaferrite lattice around the surface normal by 30 degrees, with respect to the substrate lattice, mates the oxygen layers [2]. As a consequence SrM can be grown heteroepitaxially on Al_2O_3 in spite of the large direct lattice mismatch.

The present study is a continuation of previous efforts and is specifically directed at the elucidation of substrate properties such as structural matching (lattice matching, thermal matching, coincidence sites), chemical compatibility at the growth temperature and substrate surface preparation, in producing oriented films. The study focuses on the in-situ PLD of oriented SrM on YSZ(100) (Yttria Stabilised Zirconia; $(ZrO_2)_{1-x}(Y_2O_2)_x$ with x=0.09) and the deposition of randomly oriented BaM onto oxidised silicon. Substantial improvement in the texturing of the films was achieved by performing appropriate processing of the semiconductor surface and executing the initial stage of growth in a reduced oxygen atmosphere. The work indicates that the substrate type material is a key factor in the control of the orientation and magnetic properties of the hexaferrite layers.

EXPERIMENTAL PROCEDURES

The targets were ceramic discs with compositions $Sr_{0.97}Ba_{0.07}Fe_{12}O_{19}$ and $BaFe_{12}O_{19}$. The excimer laser beam (KrF λ=248 nm, 30 ns pulse width, 10 Hz repetition rate) was focused onto the rotating target to an energy density of ~2J/cm^2, at an angle of incidence of 45 deg, and scanned circularly to improve the uniformity of the deposited material. The ablated material, ejected normal to the target surface, was collected on a heated substrate stage located 3 cm from the target. The substrate was bonded using conductive silver paste to a stainless steel holder which encapsulated a pair of silicon nitride heaters. The oxygen background pressure during deposition was maintained at 0.1 mbar and the substrate temperature at ~840 °C. Each deposition consisted of 10000 pulses which resulted in films approximately 350 nm thick.

Prior to deposition, the YSZ (100) substrates were degreased and immersed in H_2SO_4:H_2O_2:H_2O=10:1:1 solution for several minutes to remove defective surface layers. Following this, they were rinsed in de-ionised water and dried in flowing N_2. After washing with organic solvents the Si wafers were dipped in dilute hydrofluoric acid for 2 minutes and then rinsed in de-ionised water.

The orientation and phases present, were characterised by X-ray diffraction. Preferred orientation was quantified by the FWHM of the rocking curve through a particular reflection. The magnetic characteristics of the films were investigated by using an alternating gradient force magnetometer and a polar Kerr hysteresis looper. Spectroscopic Kerr polarimetry was used to measure the complex Kerr rotation of the magnetically saturated films in the wavelength range 300-900 nm.

SrM FILMS ON YSZ (100)

Zirconia stabilised with 9 mole-% yttria (YSZ) has an oxygen deficient cubic fluorite structure and has been extensively investigated as an epitaxial buffer layer for YBCO growth on silicon substrate. A representative XRD pattern, of SrM films, ~300 nm in thickness, grown on YSZ(100) is shown in figure 1. The pattern is plotted on semi-log scale to enhance the sensitivity for other phases and orientations. Strong (00l) reflections of the magnetoplumbite phase indicate that the film is highly aligned with the c-axis perpendicular to the substrate plane i.e. $[001]_{SrM} \parallel [001]_{YSZ}$.

The relative orientation of the in-plane crystallographic directions cannot be determined from this data. The x-ray rocking curve of the (008) reflection was found to have a FWHM of 0.23 deg. Magnetic easy axis (c-axis) normal to the film plane was confirmed by the magnetic characteristics shown in figure 2. However, both in plane and perpendicular magnetisation curves were broader compared with those measured for SrM films grown on Al_2O_3 under the same deposition conditions.

Explanations for the high values of coercivities observed, require a large number of pinning centres to hinder the domain wall motion. A higher density of structural defects including second phases, stacking faults, screw dislocations, low angle grain boundaries, and oxygen vacancies could be the cause for the wider hysteresis loops measured for SrM films grown on YSZ.

Structural matching in the SrM/YSZ system is bound to be difficult due to the large lattice mismatch and different crystal structures. On the other hand, the structure of magnetoplumbites is closely related to the rhombohedral structure of sapphire giving a large number of coincidence sites. An additional complication in the SrM/YSZ system could be the existence of an interfacial layer as a result of chemical reaction between the materials. It is worth noting that the presence of a thin $BaZrO_3$ layer at the film substrate interface has been reported in many cases for YBCO growth on YSZ.

YSZ has a smaller lattice parameter (a=5.14 °A) than

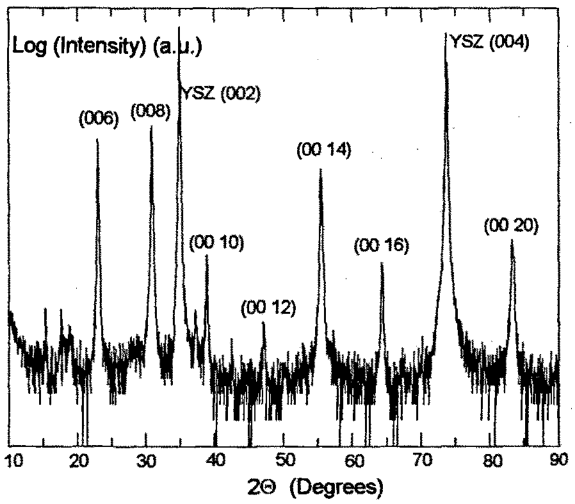

Fig.1. XRD pattern for a SrM film grown on YSZ(100).

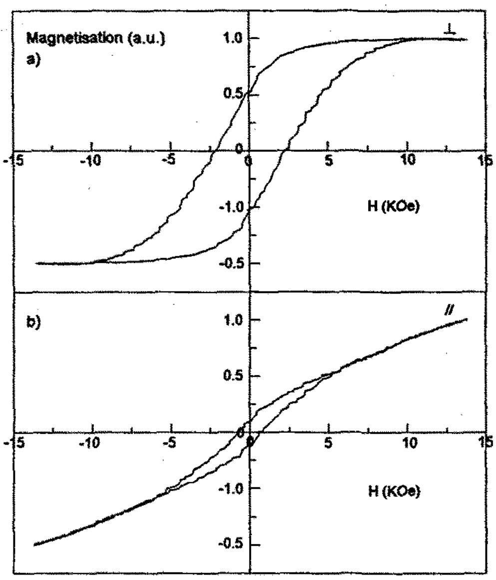

Fig.2. Magnetisation curves with field normal and parallel to the film plane for a SrM film grown on YSZ(100).

SrM (a=5.78 °A). Therefore if the SrM is grown epitaxially on YSZ, an in plane compressive stress is expected, with the c-axis in a state of tension. Moreover the different thermal expansion coefficients of SrM (~7 10^{-6} /K) and YSZ (~ 9.8 10^{-6} /K) are such as to exacerbate the extension of the c-axis. This was observed in the XRD experiment. Analysis of the XRD diffraction pattern gave a lattice parameter 23.14 °A which was derived from the position of the (008) reflection. This was indicative of normal tensile stress relative to the bulk value (c=22.98 °A) of 0.74%. The larger percentage in plane mismatch, between the SrM and YSZ (~12%; smaller misfit is possible by rotation of the SrM lattice relative to the substrate) compared to SrM and Al_2O_3 (7%) may produce a larger strain which introduces lattice defects resulting in broadening.

AFM micrographs revealed a granular microstructure with characteristic pyramidal growth pattern for each hexagonal grain, similar to that observed for SrM on (0001) Al_2O_3 [1]. Because of the SrM layered structure, the rapid growth direction of the film is in directions perpendicular to the c-axis, that is, material is most easily added at an edge. The implication of these observations is that each island grows by incorporation of material to the edge of a spirally rising step, emanating from the screw dislocation [4]. Screw dislocations are believed to run at the centres of the pyramidal grains along the c-direction. It should be noted that the presence of dislocations is a common feature for films grown on mismatched substrates.

A characteristic matrix approach was used to calculate the MO response of the thin films using the optical and MO constants of the bulk BaM single crystal [3]. The general trends in the measured Kerr rotation and ellipticity spectra were as expected from the theory.

We conclude that normal (00l) texture can easily

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be achieved on the YSZ/SrM system however, the structural matching between film and substrate is poor making the growth of films with many grain boundaries more likely.

SrM FILMS ON Si (100)

The growth of BaM on Si has being carried out for reasons related to its low cost along with exploiting issues pertaining to magnetic oxide/ semiconductor integration.

Synthesis of BaM films on oxidised silicon, Si/SiO_2 resulted in randomly oriented crystallites of magnetoplumbite phase along with other phases. MH loops taken with the field perpendicular and parallel to the film plane were only slightly different indicating that the film is magnetically isotropic. The amorphous oxide, SiO_2 seems to suppress the c-axis orientation of the crystallites. Understanding this, was an important part of our effort to obtain oriented BaM films on Si. Such observations are in agreement with recent PLD studies, performed by various groups [5], including ours [6], which demonstrated the difficulty in achieving oriented hexaferrites on amorphous substrates.

Recognising the negative role of amorphous oxide in promoting the nucleation of oriented BaM structure, and that texture control is most easily exercised using single crystal substrates, efforts were made to remove it and avoid its subsequent regrowth. It is known [7] that the immersion of the Si surface in an HF reagent strips away all the oxide and replaces it with a monolayer of hydrogen covalently

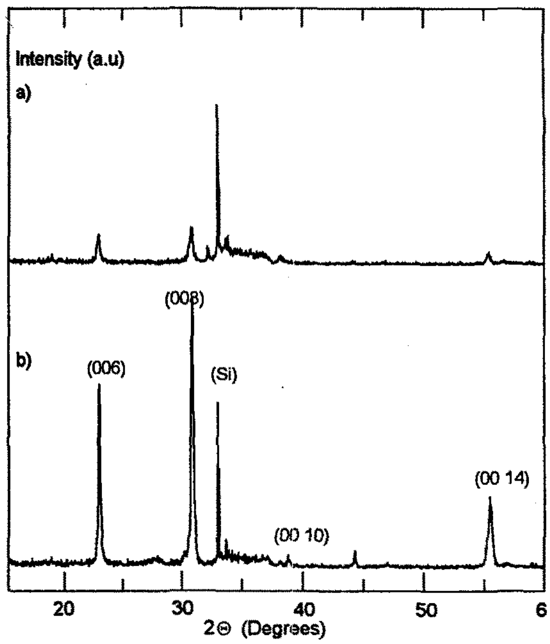

Fig.3. XRD patterns of BaM films grown on Si using a) 0.1 mbar background oxygen pressure and b) base pressure at the initial stages of growth.

bonded (Si-H) to the otherwise clean Si surface. This layer is desorbed by heating the semiconductor above 550 °C in vacuum. This treatment is especially useful with the laser ablation process since the surface remains protected by H-termination, against oxidation until moments prior to growth. Furthermore, of particular concern was the avoidance of amorphising the Si surface during the first stages of growth in the oxygen ambient which was required to oxygenate the magnetic material. In order to circumvent the problems of regrowth of SiO_2 at the Si interface during the critical period of initial film deposition, we attempted to develop a two step process. Initially, the first few hundred pulses were made at the base pressure. These initial (oxygen deficient) layers limited the amorphisation of the Si surface. Upon subsequent deposition the oxygen pressure was raised to 0.1 mbar at which was kept constant for the remainder of thin film synthesis.

To further demonstrate the deleterious effects of too much oxygen during the initial stages of BaM growth, a film was purposely grown performing the whole deposition at 0.1 mbar to compare the results against the BaM grown initially in vacuum. It should be pointed out that as soon as the oxygen pressure was adjusted to 0.1 mbar the growth started immediately.

The two step process prominently improved the XRD (001) spectrum intensities, as well as the magnetic characteristics, shown in figure 3, 4 and 5. However, it is clear that the structural perfection of the BaM grown on Si is still poor in comparison to the best hexaferrite films grown on oxidic single crystal substrates. There are several reasons for this. SiO_2 regrowth is one of them. The wafers used in this study were rinsed in water following the HF treatment, a procedure which left the silicon only partially hydrogen terminated, nevertheless oxidation in air occurs extremely slowly with logarithmic time dependence. Therefore, considerable improvements are likely to come by eliminating the water rinsing step or employing more dedicated cleaning procedures such as spin etching in flowing nitrogen [8]. Interdiffusion and chemical reactions between Ba ferrite and Si or SiO_2 occurring at the deposition temperature is another important factor contributing to the poor quality, especially for the portion of the film nearest to the substrate. In addition, the coefficients of thermal expansion are badly matched, being 2 times less in Si than in hexaferrite compounds. This induces considerable tensile stress in the film upon cooling from the growth temperature. Thermal mismatch is a serious problem that limits the ultimate BaM thickness that can be grown without the film cracking.

Substantial improvements in the BaM growth are expected by the growth of an appropriate buffer layer on Si which acts both as interdiffusion and chemical barrier as well as structural layer for providing oriented or epitaxial BaM growth. The present work on YSZ provides important ground work towards this direction.

In the blue wavelength region where the material is

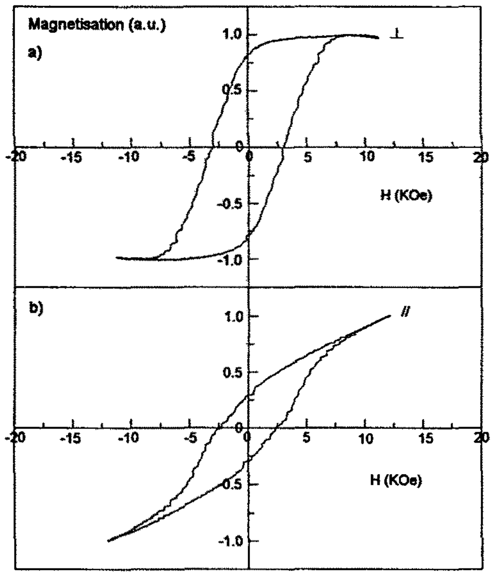

Fig.4. Magnetisation with field a) normal and b) parallel to the film surface for the BaM of fig. 3a.

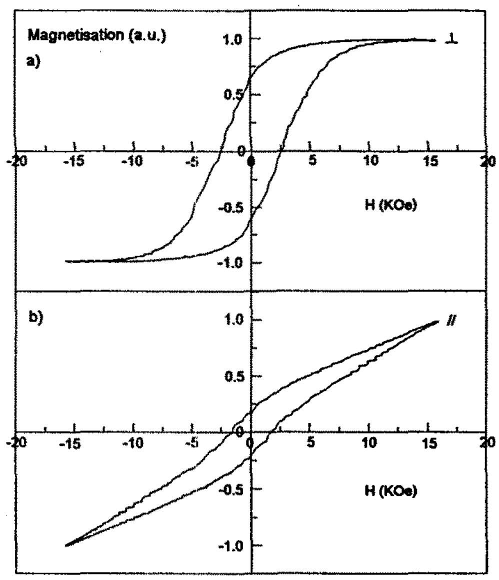

Fig.5. Magnetisation with field a) normal and b) parallel to the film surface for the BaM of fig. 3b.

absorbing, the Kerr rotation was consistently lower than the bulk values of the BaM single crystal. At longer wavelengths the MO performance could not be predicted using the matrix approach. However, implicit in the theory that we used, was the assumption that there was no interdiffusion at the film substrate interface i.e. the interfaces are sharp and the composition of the material does not vary across the interface.

CONCLUSIONS

M type Ba, Sr hexaferrites have been grown on YSZ and Si by laser ablation. These films did not have their deposition process optimised but were made by repeating the recipe for c-axis oriented SrM growth on sapphire reported earlier [1].

SrM films grown on YSZ were perpendicularly oriented with a spread around the surface normal about 0.2 deg and were grown by a spiral mechanism similar to that observed for growth on sapphire substrates. However, the films were characterised by wider hysteresis loops compared to those grown on sapphire, which is related to the poorer structural matching of the SrM/YSZ system.

The structure of the semiconductor surface can play a critical role in controlling the orientation of the magnetic oxide film. In particular, it was found that the amorphous native oxide which forms upon exposure to air defeats the possibility of subsequent oriented growth.

Elimination of the oxide proved to be effective in promoting oriented growth. This was achieved by performing hydrogen termination of the Si surface prior to growth and carrying out the initial stages of the deposition in vacuum. In any case, it is worth pointing out that, in spite of the optimised procedure the films contained other phases. This stems from the high reactivity of the two materials at the deposition temperature, and their difference in thermal and lattice constants.

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