JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 9, No. 2, February 2007, p. 456 - 459

Magnetron sputtering deposition and characterization of $GdMnO_3$ thin films

E. VLAKHOV[*], B. BLAGOEV [a], E. MATEEV [a], L. NESHKOV [a], T. NURGALIEV [a], L. LAKOV [b], K. TONCHEVA [b], Y. MARINOV, K. NENKOV[c,d], I. RADULOV [d], K. PIOTROWSKI [e], W. PASZKOWICZ [e], A. SZEWCZYK [e], M. BARAN [e], R. SZYMCZAK [e]

Institute of Solid State Physics, Bulgarian Academy of Sciences, 72 Tzarigradsko Chaussee Blvd., 1784 Sofia, Bulgaria

[a] *Institute of Electronics, Bulgarian Academy of Sciences, 72 Tzarigradsko Chaussee Blvd, 1784 Sofia, Bulgaria*

[b] *Institute of Metal Science, Bulgarian Academy of Sciences, 67 Shipchensky prohod Str. 1574 Sofia, Bulgaria*

[c] *Institut für Festkörper- und Werkstofforschung Dresden, P.O.Box 270016, O1171, Dresden, Germany*

[d] *International Laboratory for High Magnetic Fields and Low Temperatures, 95 Gajowicka Str., 53 421 Wroclaw, Poland,*

[e] *Institute of Physics, Polish Academy of Sciences, Al. Lotnikov 32/46, 02-668 Warszawa, Poland*

Thin films of $GdMnO_3$ were deposited by RF magnetron sputtering on $SrTiO_3$ (100) and Si (100) substrates. XRD analysis revealed that $GdMnO_3$ films grown on $SrTiO_3$ (100) substrates are well textured. The out-of-plane *c* axis is elongated by 0.75 % - 1.10 % in comparison to bulk lattice value and depends on film thickness. The minimal elongation was found for the $GdMnO_3$ film deposited on a $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) buffer layer. *M/H* vs. *T* (5<T<100K) as well as *M* vs. *H* (T=5K) dependences obtained for a 100 nm thick sample of $GdMnO_3$ / $SrTiO_3$ (100) point to the absence of magnetic anisotropy unlike the case of a $GdMnO_3$ single crystal. This effect is attributed to the significant structural disorder due to misfit stress. AC resistivity measurements show a measurable influence of the static magnetic field on the impedance parameters, in accordance with the (*H, T*)-phase diagram of the $GdMnO_3$ single crystal.

(Received November 1, 2006; accepted December 21, 2006)

Keywords: $GdMnO_3$, Thin films, Magnetron sputtering, Misfit stress

1. Introduction

Magnetism and ferroelectricity usually exclude each other but they can coexist in a few materials called multiferroics and magnetoelectrics [1]. Multiferroics exhibit magnetic and electric order, providing the possibility to exploit several functionalities in a single material. Recently, magnetoelectric switching has been observed in orthorhombic manganites, $RMnO_3$ (R = Tb, Dy, Gd, Eu) [2, 3] as well as in hexagonal manganites, $HoMnO_3$ [4]. Aside from the fundamental importance, mutual control of the electric and magnetic properties is of significant interest for applications in magnetic storage media and spintronics. Promising new approaches in competition to magnetoelectric switching´approach

have been proposed: 1) magnetic switching driven by light [5] or 2) spin-polarized currents [6]. It is important to emphasize that the implementation of all these concepts in new devices requires the deposition and characterization of nanoscale thin layers, tunnel heterostructures or multilayers. Manganites are promising candidates for integrating into tunnel heterostructures, especially if LSMO half-metallic ferromagnetic material is used as an electrode.

The aim of present work is to investigate the influence of the induced misfit strain on the structural and magnetotransport properties of magnetron sputtered thin films of $GdMnO_3$ on $SrTiO_3$ (100) and Si (100) substrates as well as on a $SrTiO_3$ (100) / $La_{0.7}Sr_{0.3}MnO_3$ buffer layer.

2. Experimental

The RF magnetron sputtering setup has been described previously [7]. The deposition procedure used for $GdMnO_3$ thin films is close to that developed for the epitaxial growth of $La_{0.7}Ca_{0.3}MnO_3$ (LCMO) and $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) thin films [7-9]. The chamber pressure was ~13 Pa. The substrate temperature was changed in the range 500ºC to 720ºC. The $La_{0.7}Sr_{0.3}MnO_3$ buffer layer was also obtained by magnetron sputtering. The deposited $GdMnO_3$ thin films were slowly cooled in situ in an oxygen environment at a pressure of 600 Torr. The magnetic properties of the films were characterized in a wide temperature range T= 2 K to 300 K using a commercial SQUID magnetometer in magnetic fields up to 5 T. AC resistivity measurements were performed in a superconducting solenoid in magnetic fields up to H=14 Tesla, at temperatures of 4 to 300 K and in the frequency range 1 Hz < *f* < 250 kHz.

3. Results

X-ray diffractograms revealed that $GdMnO_3$ thin films grown on Si(100) substrates are polycrystalline, while films obtained on $SrTiO_3$(100) substrates exhibite strong n00 reflections only (see the XRD patterns of samples GMS1, GMS2 and GTS22 shown in Fig. 1 and characterized in Table 1). An exception is a very weak peak at 2Θ=37.6º which can be identified as the 101 reflection of MnO_2 due to some trace of unreacted material in the target. The out-of-plane *c* axis was elongated by 0.75 % ÷ 1.10 % in comparison to the bulk $GdMnO_3$ lattice value [10] and depended on the film thickness (see Table 1).

Table 1. Characterization of $GdMnO_3$ thin films deposited on a STO_3(100) / buffer; c – thin film lattice constant (out - of – plane direction); c_b – bulk lattice constant of $GdMnO_3$, after[10].

Sample	Substrate / Layers	*c* axis (Å)	*Δc / c_b* (%)
Sample GMS1	STO(100) / $GdMnO_3$ (100 nm)	7.512	+ 1.10
Sample GMS2	STO(100) / $GdMnO_3$ (40nm)	7.492	+ 0.83
Sample GTS22	STO(100) / $La_{0.7}Sr_{0.3}MnO_3$ (40nm) / $GdMnO_3$ (40 nm)	7.486	+ 0.75

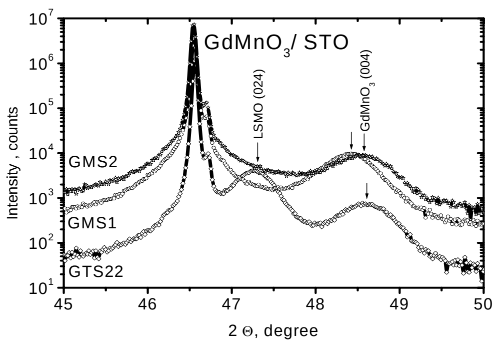

Fig. 1. X-ray diffraction patterns of $GdMnO_3$ thin films on $SrTiO_3$(100) substrates. The arrows indicate the 004 $GdMnO_3$ peak of samples GMS1, GMS2 and GTS22 as well as the *024 peak of the* LSMO *buffer layer.*

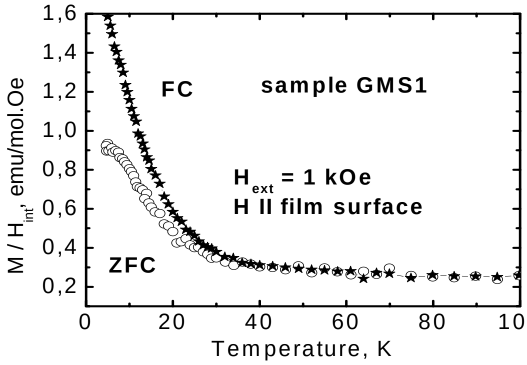

Fig. 2. Temperature dependence of the susceptibility M / H_{int} vs. T of sample GMS1 measured in the ZFC and FC regimes. The external magnetic field H_{ext} = 1 kOe was parallel to the film surface.

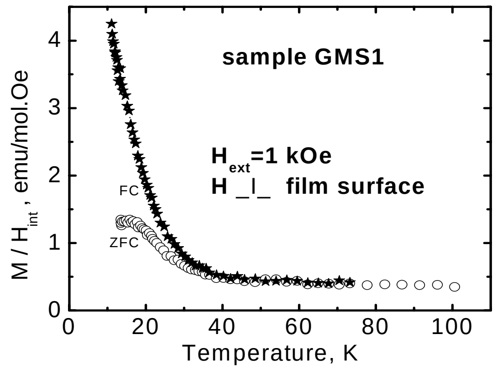

Fig. 3. Temperature dependence of the susceptibility M / H_{int} vs. T of sample GMS1 measured in ZFC and FC regimes. The external magnetic field H_{ext} = 1 kOe was directed perpendicular to the film surface.

Magnetic measurements of $GdMnO_3$ layers of 100 nm thickness (sample GMS1) were carried out. The temperature dependences of the susceptibility *M/H vs. T* of sample GMS1 are presented for in-plane and out-of-plane directions of the magnetic field (Fig. 2 and Fig. 3, respectively). The magnetisation M vs. H dependence at 5 K for three different orientations of the magnetic field is shown in Fig. 4. The magnetic contribution of the substrate was subtracted.

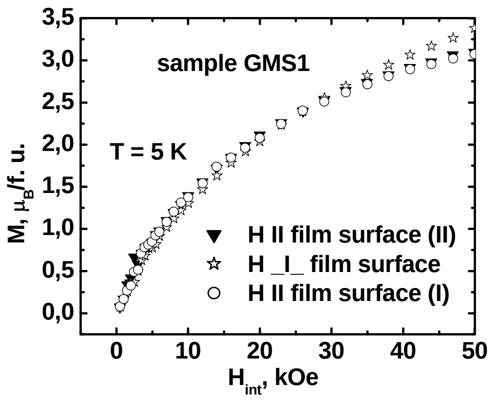

Fig. 4. Magnetisation M as a function of the external magnetic field H_{ext} directed "in- plane" (two "in-plane" directions are perpendicular to each other) and "out-of-plane" direction at 5 K.

AC resistivity measurements of the sample GMS1 were also performed. The impedance dependences *Z* v*s. T* and *Z* vs. *f* were measured in variable magnetic fields up to H=14 Tesla and in the frequency range 1 Hz < *f* < 250 kHz. Fig.5 represents the impedance dependence Z_y vs. Z_x obtained in magnetic fields of 0; 4 and 14 Tesla at 25K.

4. Discussion

It is useful to compare the thin film´ behaviour and characteristics with those of $GdMnO_3$ single crystals investigated systematically by other authors [10-13]. The thin film structural properties in Fig. 1 and Table 1 differ from those of the single crystal [10]. This is attributed to a misfit between the lattices of the substrate and the $GdMnO_3$ layer. One can expect epitaxial growth of the $GdMnO_3$ layer close to the substrate / buffer layer and the biaxially strained "in-plane" thin film. By increasing the layer thickness, a relaxation process usually occurs and the surface layer possesses a nearly bulk structure lattice. Surprisingly, the thicker film sample GMS1 exhibited maximal elongation $\Delta c/c_b$ =1.10 % while a minimal elongation $\Delta c/c_b$ of 0.75 % was found for the $GdMnO_3$ film deposited on a 40 nm thick LSMO buffer layer. Employing the LSMO buffer could be favourable for preparing heterostructures on $SrTiO_3$ (100) substrate.

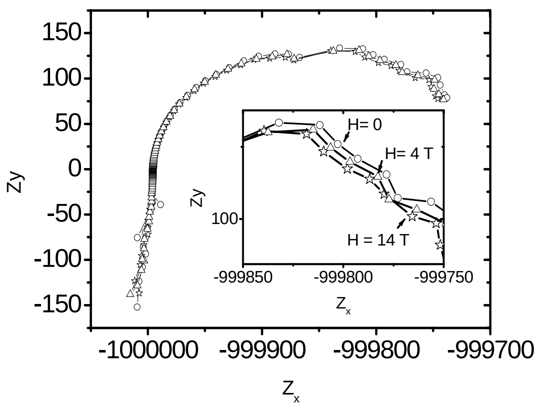

Fig. 5. Imaginary part of the complex impedance $\mathbf{Z_y}$ *vs. Real part of the complex impedance* $\mathbf{Z_x}$ *of the sample GMS1 at T=25 K in different magnetic fields H=0; 4 T and 14 T. The inset shows an enlarged view.*

The magnetic properties of $GdMnO_3$ single crystals reveal great complexity [10]. Magnetisation vs. temperature measurements show pure paramagnetic behaviour above 100K. The magnetisation follows a Curie-Weiss law with a Curie-Weiss temperature Θ = - 35 K. At T< 20K a significant anisotropy has been registered with the easy axis along the *c*-axis.

Let us analyze the magnetic properties of sample GMS1 in relation to $GdMnO_3$ single crystals. One can note (see Fig. 2 and Fig. 3) that the *M/H* vs. *T* dependence for a magnetic field directed "out-of-plane" at temperatures < 20 K increases in a more pronounced way than that "in-plane", but does not possess such an abrupt increase as for the case of the single crystal *H* || *c*-axis. No significant difference in magnetisation (T=5 K) in three perpendicular directions of the magnetic field is found (Fig.4). Thus, the results obtained for the 100 nm $GdMnO_3$ layer on a STO substrate point to the absence of such a significant magnetic anisotropy as in the single crystal. The reason could be the relatively large misfit between the $SrTiO_3$ substrate and $GdMnO_3$ lattices resulting in significant structural disorder. This disorder can be suppressed if a thinner (≤ 30-40 nm) elastically strained epitaxial thin film is employed.

AC resistivity measurements (see Fig. 5) reveal a measurable influence of the static magnetic field on the impedance parameters. They are in good correspondence with the (*H*,*T*)- phase diagram of a $GdMnO_3$ single crystal. Increasing the magnetic field of sample GMS1 from 0 to > 2T at T=25 K has lead to a transition of an incommensurate sinusoidal antiferromagnetic (AFM) phase to a canted AFM phase, as proposed in [10]. Our observations are also in agreement with the data of refs [3, 13] where a dielectric constant′ peak has been registered at ~20 K.

To measure the dielectric constant, a new LSMO/$GdMnO_3$/Ag structure has to be prepared and tested. Further, more detailed AC measurements, are needed to find possible magnetoelectric behaviour in magnetron sputtered $GdMnO_3$ thin films.

There are discrepancies in the literature about the magnetoelectric properties of single crystal $GdMnO_3$ [11, 12]. No trace of spontaneous polarization has been found at T > 2K by Goto *et al.* [11] while Noda *et al*. [12] found a small spontaneous polarization in the *a*-axis direction at T < 13K. Kadomtseva *et al.* [13] have registered the appearance of electric polarization in both the *a*- and *b*-axis directions when *H* is in *b*-axis direction of $GdMnO_3$. Different properties and discrepances could be due to subtle structural differences of $GdMnO_3$ single crystals obtained by different techniques [13]. One can suppose that epitaxial growth of $GdMnO_3$ thin films on an appropriate substrate/buffer could result in elastically strained and well structured ordered thin films, with tailored magnetoelectric properties.

5. Conclusions

Thin films of $GdMnO_3$ were deposited by RF magnetron sputtering on $SrTiO_3$(100) and Si(100) substrates. XRD analysis revealed that $GdMnO_3$ films grown on STO_3 (100) are well textured. The out-of-plane *c* axis was elongated by 0.75 % – 1.10 % in comparison to the bulk lattice value; its value depends on film thickness. Minimal elongation was found for the $GdMnO_3$ film deposited on a 40 nm thick $La_{0.7}Sr_{0.3}MnO_3$ buffer layer. Magnetic measurements of *M/H* vs. *T* dependence (5 K<T<100 K) and M vs. H (5 K) dependence carried out on a 100 nm $GdMnO_3$ thin film indicate the absence of magnetic anisotropy, unlike in the single crystal. This is attributed to the relatively large misfit between the STO substrate and $GdMnO_3$ lattices, resulting in significant structural disorder. AC resistivity measurements reveal a measurable influence of the static magnetic field on the impedance parameters. They are in good agreement with the (*H,T*) phase diagram of $GdMnO_3$ single crystals.

Acknowledgements

This study was supported by Grant No.F-1503 /05 from the Ministry of Education and Science of Bulgaria.

References

[1] W. Eerenstein, N. D. Mathur, J. F. Scott, Nature **442**, 759 (2006).
[2] T. Kimura, G. Lawes, T. Goto, Y. Tokura, A. P. Ramirez, Phys. Rev. B **71**, 224425 (2005).
[3] V. Yu. Ivanov, A. A. Mukhin, V. D. Travkin, A. S. Prokhorov, Yu. F. Popov, A. M. Kadom-tseva, G. P. Vorob´ev, K. I. Kamilov, A. M. Bulbashov, Phys. Stat. Solidi (b) **243,** 107 (2006).
[4] B. Lorenz, F. Yen, M. M. Gospodinov, C. W. Chu, Phys. Rev. B **71**, 014438 (2005);
[5] A. V. Kimel, A. Kirilyuk, P. A. Usachev, R. V. Pisarev, A. M. Balbashov, Th. Rasing, Nature **435**, 655 (2005).
[6] M. Gajek, M. Bibes, A. Barthélémy, K. Bouzehouane, S. Fusil, M. Varela, J. Fontcuberta, A. Fert, Phys. Rev.B **72**, 020406(R) (2005).
[7] E. S. Vlakhov, R. A. Chakalov, R. I. Chakalova, K. A. Nenkov, K. Dörr, A. Handstein, K. - H. Müller, J. of Appl. Phys. **83**, 2152 (1998).
[8] E. S. Vlakhov, T. I. Donchev, A. Y. Spasov, K. Dörr, K. A. Nenkov, A. Handstein, S. Pignard, H. Vincent, Vacuum **69,** 255 (2003).
[9] E. S. Vlakhov, K. Dörr, K. - H. Müller, K. A. Nenkov, A. Handstein, T. I. Donchev, A. Y. Spasov, G. D. Beshkov, Vacuum **58,** 364 (2000).
[10] J. Hemberger, S. Lobina, H. - A. Krug von Nidda, V. Yu. Ivanov, A. A. Mukhin, A. M. Balbashov, A. Loidl, Phys. Rev. B **70,** 024414 (2004).
[11] T. Goto, T. Kimura, G. Lawes, A. P. Ramirez, Y. Tokura, Phys. Rev. Lett. **92,** 257201 (2004).
[12] K. Noda, S. Nakamura, J. Nagayama, H. Kuwahara, J. Appl. Phys. **97,** 10C103 (2005).
[13] A. M. Kadomtseva, Yu. F. Popov, G. P. Vorob´ev, K. I. Kamilov, A. P. Pyatakov, V. Yu. Ivanov, A. A. Mukhin, A. M. Balbashov, JETP Letters **81**, 17 (2005).

*Corresponding author: evlakhov@issp.bas.bg