Thickness dependent magnetic transitions in pristine MgO and ZnO sputtered thin films

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Abstract

We report a systematic study of the thickness dependency of room temperature ferromagnetism in pristine MgO (~100–500 nm) and ZnO (~100–1000 nm) thin films deposited by reactive magnetron sputtering technique under the respective identical controlled optimum oxygen ambience. As far as we know this is the first such report on ferromagnetic pure MgO thin films, a result which should be of significance in understanding the functional aspects of magnetic tunnelling characteristics in devices using MgO dielectrics. From the magnetic characterization we observe a distinct variation in the saturation magnetization (M_S) with increasing film thickness. In the case of MgO thin films M_S values vary in the range 0.04–1.58 emu/g (i.e. 0.0012–0.046 μB/unit cell) with increasing film thickness showing the highest M_S value for the 170 nm thick film. Above this thickness M_S is found to decrease and eventually above 420 nm the films show a paramagnetic behaviour followed by the well known diamagnetic property for the bulk (>500 nm). It is obvious that since initially the M_S values increase with thickness, there has to be a maximum before the films become diamagnetic at some finite thickness. We also note that the M_S values observed for MgO are the highest (more than twice the value observed for ZnO) to be reported for such a defect induced ferromagnetism in a pristine oxide. The origin of ferromagnetic order in both the oxides appears to arise from the respective cat-ion vacancies. The discovery of film thickness dependent ferromagnetic order should be very useful in developing multifunctional devices based on the technologically important materials MgO and ZnO.

Keywords: *d^0-magnetism, oxide thin films, ferromagnetic order, rf/dc sputtering*

I. Introduction

The ultimate success of spintronics technology relies heavily on the development of suitable room-temperature ferromagnetic (RTFM) semiconductors. RTFM has recently been reported for undoped MOs such as HfO_2, TiO_2, MgO and ZnO (nanoparticles, powders, nanorods), the so called *d^0-magnetic materials* to emphasize the fact that the observed magnetism is not coming from any partially filled d-orbitals but from moments induced in the p-orbitals of the oxygen band [1–3]. Experimental studies reported to date on the observation of magnetism in nanoparticles contain little information, if none, on the optimum conditions for obtaining the maximum possible ferromagnetic moment and the appropriate processing parameters. Furthermore results on studies from nanoparticles are subject to particle size, size distribution, morphology and the inevitable complexities of surface magnetic disorder arising from the particle size dependence of the energetics of surface to volume ratio involved. In contrast, thin films, in the size range corresponding to those for the nanoparticles, are more reliably produced and characterized from a structural as well as other physical properties point of view. Moreover it is in the thin film form we need to understand the properties at a nanoscale for applications. In this present work, we report a systematic study of the film thickness dependency of RTFM in pristine MgO (~100–500 nm) and ZnO (~100–1000 nm) thin films deposited by reactive magnetron sputtering technique under the respec-

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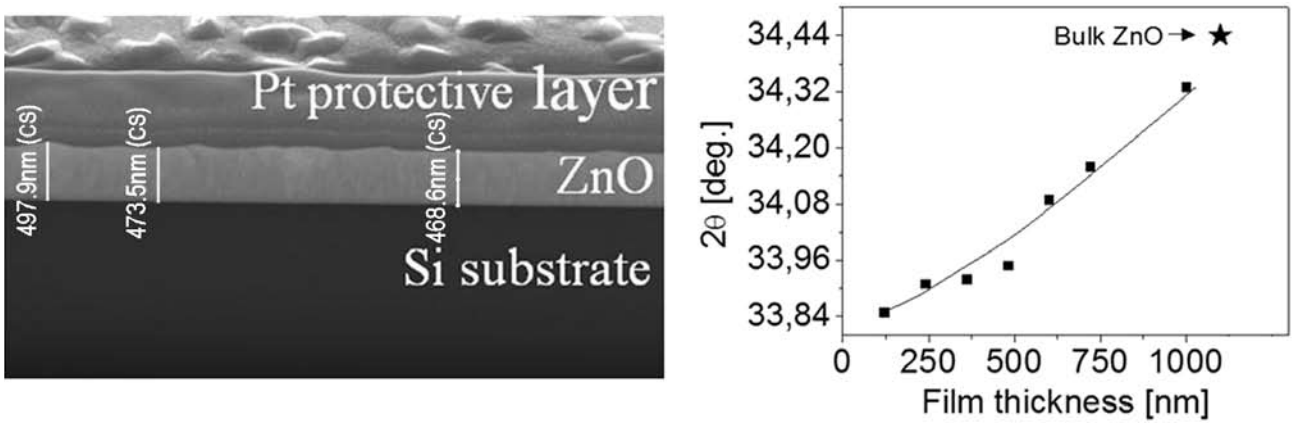


a) b)

Figure 1. (a) Cross-section of the 480 nm thick ZnO film using FIB showing a dense and pin-hole free structure. (b) Variation in (002) peak position with increasing film thickness (all films are deposited on Sapphire), the line is only a guide to the eye [2]

tive controlled optimum oxygen ambience appropriate for these technologically important oxides. As far as we know ours is the first comprehensive study of the thickness dependent transformations of ferromagnetic to diamagnetic order in pure MgO thin films, a result which should be of significance in understanding the functional aspects of tunnelling magneto properties in devices using MgO as dielectrics.

II. Experimental

ZnO thin films (~0.1–1 μm thick) were deposited by DC magnetron sputtering under an oxygen partial pressure of 1.3×10^{-4} mbar (in the mixture of $Ar^{+}O_2$ with a total pressure of 15×10^{-4} mbar) at a substrate (Al_2O_3) temperature of 350°C. Similarly, MgO thin films (~0.1–0.5 μm) were deposited by RF magnetron sputtering under an oxygen partial pressure of 1.3×10^{-4} mbar (in the mixture of $Ar^{+}O_2$ with a total pressure of 40×10^{-4} mbar) at room-temperature on Si substrates. The samples were characterized for their purity by means of X-ray Photoelectron Spectroscopy (XPS) by Scienta® ESCA 200 spectrometer (using monochromatized Al(Kα) X-rays at $h\cdot\upsilon$ = 1486.6 eV) and Energy Dispersive X-ray Spectroscopy (INCA EDXS detector, Oxford Instruments). The resolution of the XPS measurements is 0.65 eV, obtained from the full width half maximum of the Au($4f_{7/2}$) core level peak, and the base pressure of the system is 10^{-10} mbar. The thickness of the thin films was determined by cross-section analysis using a Dual Beam UHR SEM/FIB system (FEI Nova 600 Nanolab). The crystal structure of the films was characterized by XRD (Siemens D5000 powder X-ray diffractometer) and magnetic characterization was carried out using a MPMS2–1 Superconducting Quantum Interference Device Magnetometer (from Quantum Design, USA). Both the MgO and Zn targets as well as the substrates were characterized prior to the film depositions for their purity and their magnetic properties. They were found to be purely diamagnetic with no trace of any contamination of magnetic impurity.

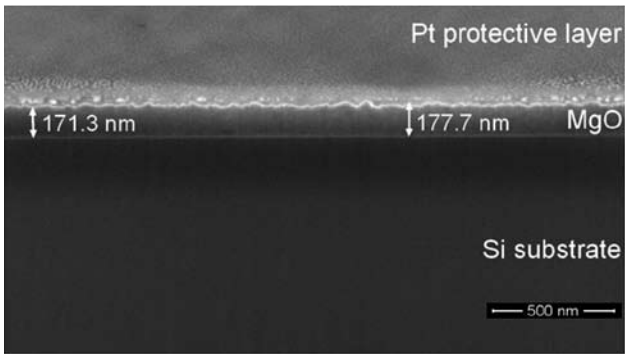
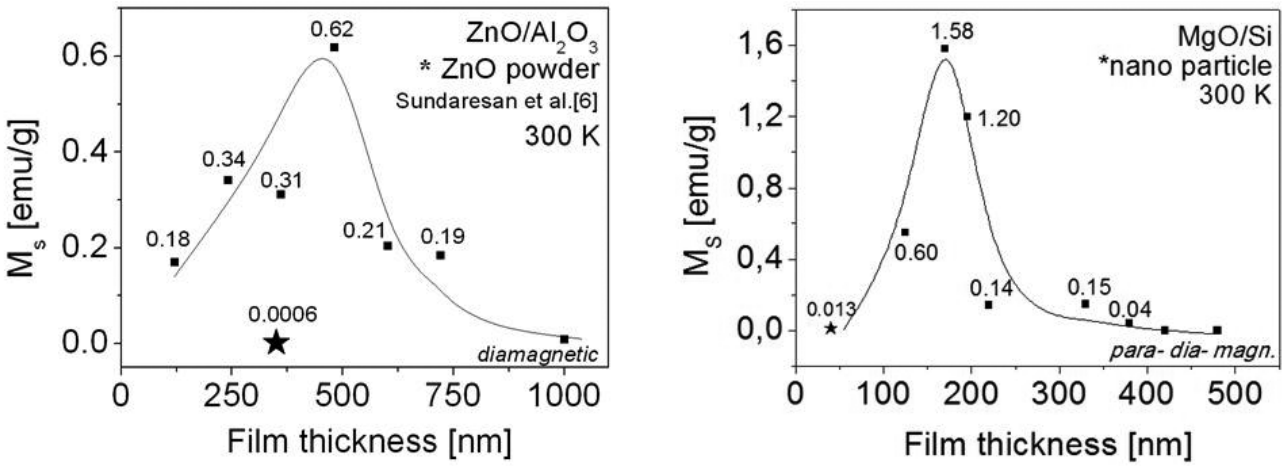


Figure 2. Typical cross-section of the 170 nm thick MgO film (P_{O2}:1.3×10^{-4} mbar) using FIB showing a dense and pore free structure [2]

III. Results and discussion

Figure 1a shows an example for the typical FIB cross-section of the ~480 nm ZnO film deposited on Si substrate. Such thickness determination was carried out at various regions of the film with rather good reproducibility. Clearly, size effects like film thickness in particular are best studied using a FIB facility. X-ray diffraction based structural characterization shows that the ZnO films have grown predominently along the c-axis (002) direction where the angular position of the (002) peak varies from 33.85°–34.33° with increasing film thickness (see Fig. 1b). The shift in the position of the (002) peak to lower angles (2θ) indicates lattice expansion ($2\theta_{ZnO\ bulk}$ ~ 34.44°) due to stress which may be due to a combination of (i) intrinsic defects (e.g. Zn_i and O_i) in the ZnO matrix and/or (ii) the strain at the film/substrate interface because of the lattice mismatch. We do observe a weak time dependent substrate/film related relaxation expected [4,5] on annealing under controlled atmosphere for longer periods.



a) b)

Figure 3. Variation in M_S with increasing film thickness: (a) ZnO [2] and (b) MgO

Similarly, MgO thin films (~0.1–0.5 μm) were deposited under an oxygen partial pressure of 1.3×10^{-4} mbar (in the mixture of $Ar^{+}O_2$ with a total pressure of 40×10^{-4} mbar) at room-temperature on Si substrates. From the XRD study it was revealed that all the MgO thin films deposited at RT had crystallized with a rock-salt structure ((200) oriented), but it should be pointed out that traces of non-crystallinity was also revealed in the XRD characterization. Figure 2 shows a typical cross-section for a 170 nm thick film deposited at RT (P_{O2}: 1.3×10^{-4} mbar). All the deposited films were found to be uniform with no obvious pinholes, and during these analyses we found the films to heavily accumulate charge in the presence of the ion/electron beam indicating that they are highly insulating. The deposited metal layer (Pt) on the film surface (as seen in Figs. 1a and 2) serves as a protective layer which will prohibit the film surface to be affected (damaged) during the sectioning of the film (by ion-beam milling) and hence provides a more accurate measure of the film thickness. It should be pointed out that all the magnetic measurements were carried out on the thin films before they were characterized for their film thickness and thus are free from any ion beam effects.

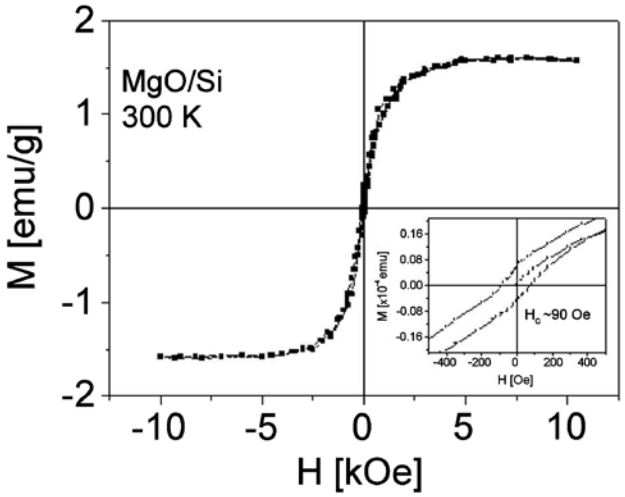


Figure 4. *M*(*H*) loop at RT for the 170 nm thick MgO film, data has been corrected for the diamagnetic background. Inset shows low field hysteresis loop with low value for the coercivity [7]

We have confirmed from the XPS and EDXS measurements that no magnetic impurity elements are present in the deposited thin films, the results from these studies are reported in detail elsewhere [7]. SQUID magnetometer measurements of the deposited ZnO and MgO thin films revealed RTFM in the films with a distinct variation in the saturation magnetization (M_S) with increasing film thickness. In the case of ZnO, M_S is found to vary from 0.18–0.62 emu/g reaching a maximum value for the 480 nm thick film, whereas in the case of MgO the M_S value varied from 0.04–1.58 emu/g showing a maximum value for the 170 nm thick film. Above these maximum the M_S values are found to decrease with increasing film thickness (see Fig. 3). Eventually at larger thicknesses both ZnO and MgO films are diamagnetic as expected for the bulk. It appears the initial characteristics of the magnetization and its dependence on the film thickness is a universal character among oxide thin films.

It has been argued that a cation vacancy surrounded by oxygen atoms is expected to develop a net spin. Further, an active defect is believed to interact with another closely situated active defect (and so on), and will in this way make the path for long range ferromagnetic ordering as they will couple ferromagnetically [1–3,8–12]. In the present case, as the films are grown thicker, two competitive processes are taking place simultaneously: (i) ferromagnetic coupling between active defects and (ii) increase in the intermittent distance between two closely situated defects with increasing film thickness. The initial, almost linear increase in the M_S represents the increase in the number of actively interacting defects increasing with film thickness, thus (i) > (ii). When the intermittent distance between two active defects becomes so large

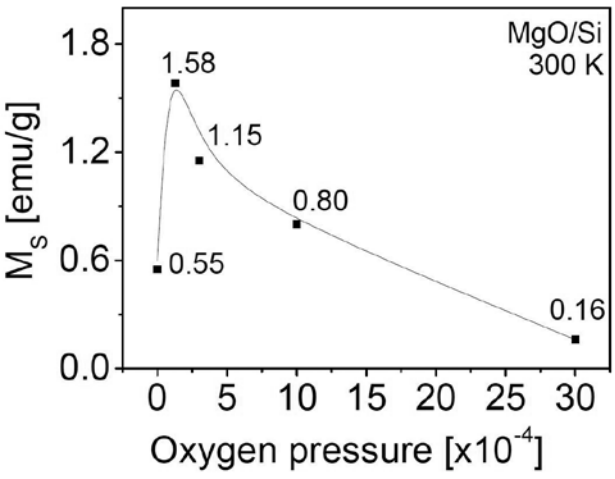


Figure 5. Variation in M_S with increasing oxygen partial pressure of the 170 nm thick MgO film [7]

that (ii) starts dominating over (i) break- up of long range ferromagnetic ordering takes place which lowers the net magnetization of the material. With increasing film thickness, the films are believed to undergo a magnetic transition from ferro- to para- and eventually to the well known diamagnetic property of the bulk [2]. This sequential transition is evident in thicknesses >480 nm (in the ZnO system) and >170 nm (in the MgO system) where (ii) > (i) with increasing film thickness, hence the decrease in the M_S with increasing film thickness. Figure 4 shows a typical RT $M(H)$ loop for the 170 nm thick MgO film. In the data the diamagnetic background from the substrate has been subtracted. The inset shows a low remanence, and coercivity of around 90 Oe, which is a typical soft magnetic behaviour observed for oxide ferromagnetic semiconductors.

After studying how the magnetic properties of ZnO and MgO thin films scale with their increasing film thickness, it was of great interest to investigate the role of the oxygen stoichiometry and the oxygen related defects on magnetic properties for a given film thickness. Hence, MgO thin films (170 nm) have been deposited under controlled oxygen partial pressure ranging from 0 (i.e. base-pressure) to 30×10^{-4} mbar (in the mixture of $Ar^{+}O_2$ with a total pressure of 40×10^{-4} mbar), at RT. Figure 5 shows the observed variation in the M_S as a function of increasing oxygen partial pressure.

The initial increase in M_S (P_{O2}: 0–1.3×10^{-4} mbar) could be due to increasing oxygen content in the films. However, continued increase of the oxygen pressure (P_{O2} >1.3×10^{-4} mbar) also increases the probability of creating oxygen antisites (O_{Mg}) and interstitials (O_i). This in turn would break up the long range ferromagnetic chains (i.e. the coupling between active defects) by extinguishing the active defects and as a result lower the net magnetization [2,13]. The reduced magnetization at lower oxygen pressure excludes the possibility that ferromagnetic ordering in these thin films originates from oxygen vacancy related defects.

IV. Conclusions

In summary, from a systematic study carried out on the thickness dependency of defect induced ferromagnetism in undoped ZnO and MgO thin films in the range 0.1–1.0 μm (for ZnO) and 0.1–0.5 μm (for MgO) we find the M_S value to be as high as 0.62 emu/g and 1.58 emu/g respectively for the two different systems which are at least 2–3 orders higher than that reported in nano-particles and powders. The phenomenon of magnetic transition from ferro to para and then to diamagnetism as a function of film thickness observed in pristine undoped MgO and ZnO appears to be a remarkable common feature for oxides films which merits further exploration. From the study of the oxygen partial pressure dependency of the magnetic property of 170 nm MgO thin film, we find that initially the magnetization is significantly enhanced with increasing oxygen content in the thin film suggesting the importance of an optimum oxygen stoichiometry on the magnetic property. Clearly, understanding the mechanism for the defect induced magnetism in pristine metal oxides is necessary before doping the host metal oxide matrix with transition metal atoms and speculating on commercially applicable devices.

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