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Aging of magnetic properties in MgO films

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In this work we report on the magnetic behavior of MgO thin films prepared by sputtering. A severe aging process of the ferromagnetic properties is detected in magnetic samples exposed to ambient atmosphere. However, ferromagnetism can be successively switched on again by annealing samples in vacuum. We suggest this behavior reflects the key role played by defects in stabilizing ferromagnetism in MgO films and is likely to be closely related to the hydrogen-driven instability of V-type centers in this material. © *2010 American Institute of Physics*. [doi:10.1063/1.3527963]

Combining different functionalities in the same material has become one of the objectives boosting research in materials science in the last decade. The possibility, for instance, of having transparent magnets would drastically simplify the design of magnetic hard disks with laser beam read out. Investigation of new materials has spread out in many directions and in particular in new magnetic materials. In this latter field, attempts to obtain a magnetic semiconductor, which will combine spin and charge degrees of freedom in the same material making possible the development of spintronic devices and their integration in the present microelectronic technology, have been numerous. In pursuit of this paradigm a huge research effort has been concentrated in recent years on the so-called diluted magnetic semiconductors, including wide band-gap nitrides and oxides, such as GaAs and GaN and ZnO.[1] However, so far, the development of industrially attractive prototypes of these materials has been hampered by the inability to achieve the required impurity concentrations, often above thermodynamic solubility limits. For that reason, considerable attention has been devoted lately to the study of magnetism in systems that do not require doping with magnetic ions.[2,3] For instance, Elfimov *et al.*[4] proposed to use cation vacancies to generate magnetic moments in alkaline-earth oxides, such as CaO. In this sense, MgO is in many ways the ideal material for studying the connection between magnetism and native defects since, V-type centers are the most common defects found in MgO.[5] Notably, MgO is of importance for many applications in technology and industry, ranging from ac-type plasma display panels to catalysis, thus scalability and reduced time-to-market could be easily realized.

In a previous work[6] we have shown that hole-doping induced by cation vacancies introduces p states above the valence-band edge in MgO which, in turn, give rise to a spin polarization experimentally confirmed as well by others.[7] The spin polarization of oxygen ions at low-coordinated sites was calculated to increase as site coordination decreases. Figure 1 relates the vacancy concentration to the calculated magnetization values. The smallest concentration for which the density-functional theory calculations suggest the magnetic moment is not vanishingly small is above 2 vacancies per nm^3. We have also shown by using transmission electron microscopy (TEM) and photoluminescence spectroscopy that appropriate annealing treatments can modify the relative concentration of cation vacancies in magnetic MgO films.[6,8] In this work we report on the magnetic behavior of MgO thin films prepared by sputtering that exhibit a severe aging process of the ferromagnetic properties when exposed to ambient atmosphere. However, ferromagnetism can be successively switched on again by annealing samples in vacuum. We suggest that this behavior reflects the key role played by defects in stabilizing ferromagnetism in MgO films and is likely to be closely related to the hydrogen-driven instability of V-type centers in this material.

MgO thin films used in this work have been grown by rf magnetron sputtering in an oxygen atmosphere (0.25 torr) above 800 °C, while magnetic characterization of the samples was performed at 10 K by using a superconducting quantum interference device SQUID magnetometer (Quantum Design), San Diego, CA, USA. It is worth mentioning that deposition at such high substrate temperature increases notably the vaporization of the alkaline element which is

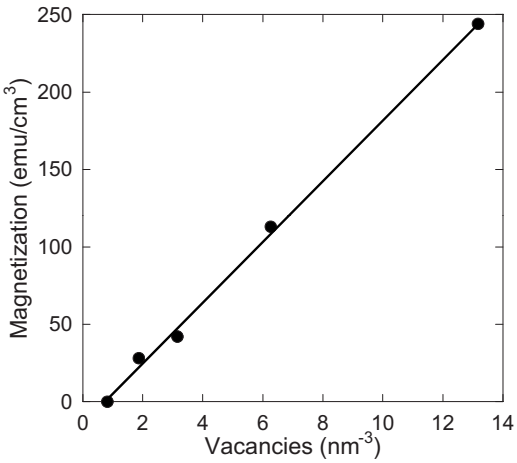

FIG. 1. Dependence of the calculated saturation magnetization, M_S, on the vacancy concentration obtained as indicated in Ref. 6.

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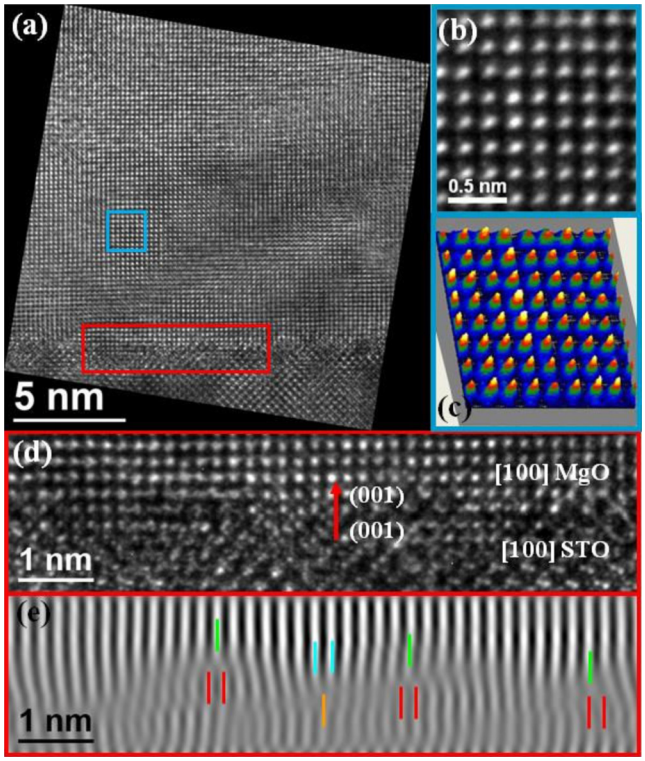

FIG. 2. (Color online) (a) High resolution electron micrograph of a MgO layer grown on a $SrTiO_3$ (STO) (001) substrate. (b) Detail of the MgO layer corresponding to the (blue) squared area in (a). (c) 3D mapping of the intensity for the area shown in (b). (d) Detail of the MgO/STO interface [(red) rectangle area in (a)]. (e) Mismatch dislocation analysis of the same interface. Dislocations are expected to occur every 12.8 $(020)_{STO}$ planes.

expected to promote the development of cation vacancies in the deposited film.[9,10] Under these circumstances, by keeping all the other parameters constant, increasing the sputtering power density would increase the growth rate which would, in turn, reduce the number of cation vacancies. This allows for control on the final number of cation vacancies in the films. We present evidence of the latter in Fig. 2, where we show a TEM picture corresponding to a MgO film prepared at high growth rate. The presence of Mg vacancies in this sample seems to be lower than in samples prepared at a lower growth rate (see Fig. 2 in Ref. 6), as shown in the 3D intensity mapping [Fig. 2(c)], where the intensity in the (100) atomic columns is highly homogeneous. As demonstrated in a recent work,[6] variations in the HRTEM intensity in the $(100)_{MgO}$ atomic columns could evidence the presence of Mg vacancies, variations that are not observed in the present case. Accordingly, this sample exhibits a very low magnetic signal (respective hysteresis cycle shown in Fig. 3). Thus, confirming the relation between the cationic vacancies and the existence of ferromagnetism in MgO films.

We have also investigated the stability of ferromagnetism in MgO films exposed to different ambient conditions and annealing processes. Figure 3 shows magnetization loops of a sample after selected time intervals to follow the evolution of the magnetic properties. A reduction of almost 50% of the saturation magnetization, M_S, is observed after three days exposure to ambient atmosphere, with respect M_S value measured just after preparation (it takes about 15 min to convey the sample from the evaporation chamber to the SQUID measuring chamber). To accelerate the aging process this sample was annealed in air at 500 °C for 2 h observing

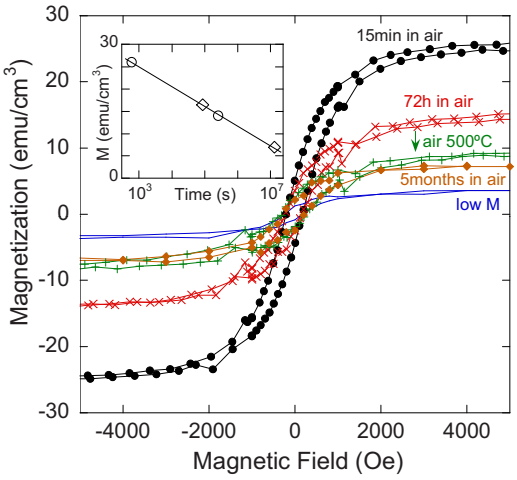

FIG. 3. (Color online) Evolution of the magnetization curve of a MgO film after different aging processes. The hysteresis loop of a film with weak ferromagnetism (depicted as low M) is also shown for comparison. Inset: magnetization decay is linear on a logarithmic scale of time.

a further reduction of the magnetization down to 1/3 of the initial M_S. Similar results were obtained after a long lasting (five months) exposure to ambient atmosphere. These results make evident that aging process proceeds very fast at the early stages and tend to stabilize after a few months (see inset in Fig. 3) resembling a typical exponential decay. We interpret this result as a strong indication that a metastable state has been attained. Indeed, the trapped holes at V-type centers have a half-life of several hours at room temperature, with the tail of the decay persisting for several years.[11]

Noteworthy, very different results were obtained when the annealing process was done in vacuum. A sample after five months of exposure to ambient atmosphere, i.e., with a very low magnetic signal was annealed in vacuum ($\sim 10^{-7}$ torr) at 850 °C for 1 h to ensure complete release of hydrogen.[12] A strong increase of M_S, reaching again the initial values (see Fig. 4), was detected after the annealing process. This is a very interesting result indicating that ferromagnetism in defective MgO films can be switched off and on by annealing processes in air or in vacuum, respectively.

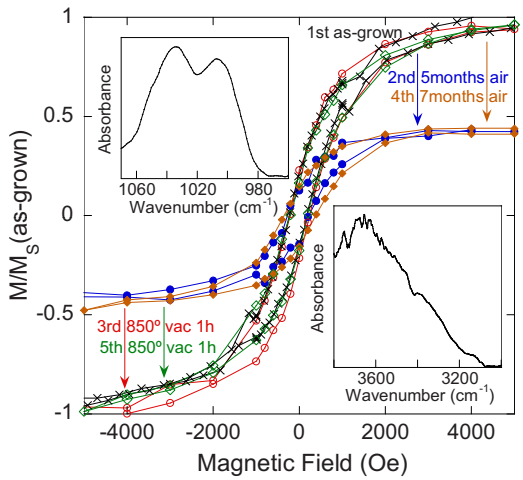

FIG. 4. (Color online) Evidence of the reversible switching of ferromagnetism by aging and successive annealings in vacuum. The inserts reveal selected FTIR spectra from a MgO film in contact with water vapor at room temperature.

To precisely determine the mechanism behind this reversible behavior deserves further investigation. However, we should mention here that H is ubiquitous and can easily be incorporated in the films during growth or annealing processes. In fact, previous reports based on theoretical and experimental studies have shown that the conductivity and magnetic properties of diluted magnetic semiconductors, though traditionally been attributed to oxygen vacancies, depend on the hydrogenation process.[13] MgO absorbs moisture, forming $Mg(OH)_2$ easily.[14] Furthermore, considering protons might reside in the cation vacancies the hydrogenation activity must fall to a low value as the holes are filled,[15] as indeed is shown in Fig. 4.

Fourier transform infrared (FTIR) spectroscopy was used to monitor the states of hydrogen. Apart from a great number of carbonate ion bands spanning the 1000–2200 cm^{-1} range,[16] infrared peaks at 990–1060 cm^{-1} are observed (inset Fig. 4), in good agreement with the calculated frequency for substitutional hydrogen in MgO.[17] Adsorption of H_2 has also been observed to form reversible modes centered about 3450 cm^{-1}, already reported in previous studies at 300 K.[14] The broad low frequency band 3600–3650 cm^{-1} is assigned to hydrogen bond donor OH groups whereas isolated hydroxyl groups are responsible for the narrow high frequency band around 3750 cm^{-1}.[18] Therefore, we suggest that once samples are exposed to air, Mg^{2+} vacancies are charge compensated by OH^-.[19] These sites are gradually eliminated in vacuum as the temperature is increased above 500 °C, and could be reactivated when the MgO sample is exposed to water vapor at room temperature.[20,21] These results are also supported by parallel photoluminescence spectroscopic investigations.[8,22]

In conclusion, our results make evident the existence of a close correlation between ferromagnetism and Mg vacancies. Cation vacancies in MgO create a polarization on the 2p O orbitals; however, with time these centers age, leading to decreasing of the saturation magnetization. We also demonstrate the existence of reversible switching phenomena of ferromagnetism in the samples depending on the annealing conditions. The aging mechanism of vacancies probably relates with the formation of hydrogen-containing complex, a full recovery of the magnetic properties could be expected upon dehydrogenation, though the effect of nitrogen impurity states needs to be further determined.[12,23]

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[1]T. Dietl, H. Ohno, F. Matsukura, J. Cibert, and D. Ferrand, Science **287**, 1019 (2000).
[2]N. H. Hong, J. Sakai, N. Poirot, and V. Brizé, Phys. Rev. B **73**, 132404 (2006).
[3]J. Červenka, M. I. Katsnelson, and C. F. J. Flipse, Nat. Phys. **5**, 840 (2009).
[4]I. S. Elfimov, S. Yunoki, and G. A. Sawatzky, Phys. Rev. Lett. **89**, 216403 (2002).
[5]W. C. Las and T. G. Stoebe, Radiat. Prot. Dosim. **8**, 45 (1984) http://rpd.oxfordjournals.org/content/8/1–2/45.abstract..
[6]C. Martínez-Boubeta, J. I. Beltrán, Ll. Balcells, Z. Konstantinović, S. Valencia, D. Schmitz, J. Arbiol, S. Estrade, J. Cornil, and B. Martínez, Phys. Rev. B **82**, 024405 (2010).
[7]C. Moyses Araujo, M. Kapilashrami, X. Jun, O. D. Jayakumar, S. Nagar, Y. Wu, C. Århammar, B. Johansson, L. Belova, R. Ahuja, G. A. Gehring, and K. V. Rao, Appl. Phys. Lett. **96**, 232505 (2010).
[8]C. Martínez-Boubeta, A. Martínez, S. Hernández, P. Pellegrino, A. Antony, and J. Bertomeu, Ll. Balcells, Z. Konstantinović, and B. Martínez, Blue Luminescence at room temperature from defective MgO films (submitted).
[9]C. Zaldo, D. S. Chill, R. W. Eason, J. Mendiola, and P. J. Chandler, Appl. Phys. Lett. **65**, 502 (1994).
[10]J. L. Vassent, A. Marty, B. Gilles, and C. Chantillon, J. Cryst. Growth **219**, 444 (2000).
[11]M. M. Abraham, Y. Chen, and W. P. Unruh, Phys. Rev. B **9**, 1842 (1974).
[12]S. Higashimoto, G. Costentin, B. Morin, and M. Che, Appl. Catal., B **84**, 58 (2008).
[13]Y. C. Cho, S.-J. Kim, S. Lee, S. J. Kim, C. R. Cho, H.-H. Nahm, C. H. Park, I. K. Jeong, S. Park, T. E. Hong, S. Kuroda, and S.-Y. Jeong, Appl. Phys. Lett. **95**, 172514 (2009).
[14]J. H. Lee, J. H. Eun, S. Y. Park, S. G. Kim, and H. J. Kim, Thin Solid Films **435**, 95 (2003).
[15]D. A. Dowden, J. Chem. Soc. **1–2**, 242 (1950).
[16]G. Spoto, E. N. Gribov, G. Ricchiardi, A. Damin, D. Scarano, S. Bordiga, C. Lamberti, and A. Zecchina, Prog. Surf. Sci. **76**, 71 (2004).
[17]A. Janotti and C. G. Van de Walle, Nature Mater. **6**, 44 (2007).
[18]M.-L. Bailly, G. Costentin, H. Lauron-Pernot, J. M. Krafft, and M. Che, J. Phys. Chem. B **109**, 2404 (2005).
[19]F. Freund, A. Staple, and J. Scovill, Proc. Natl. Acad. Sci. U.S.A. **98**, 2142 (2001).
[20]E. Longo, J. A. Varela, A. N. Senapeschi, and O. J. Whittemore, Langmuir **1**, 456 (1985).
[21]Z. G. Huang, A. P. Guo, A. Calka, D. Wexler, C. Lukey, and H. K. Liu, J. Alloys Compd. **422**, 299 (2006).
[22]S. Coluccia, A. Barton, and A. J. Tench, J. Chem. Soc., Faraday Trans. 1 **77**, 2203 (1981).
[23]M. Pesci, F. Gallino, C. Di Valentin, and G. Pacchioni, J. Phys. Chem. C **114**, 1350 (2010).