Blue luminescence at room temperature in defective MgO films

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ABSTRACT

Luminescence spectroscopy has been used to characterize MgO films prepared by rf-sputtering. A clear correlation is found between the appearance of an emission peak centered at approximately 460 nm and the detection of ferromagnetic ordering in the samples. We suggest that cationic vacancies are responsible for the blue-light emission by introducing *p* states into the electronic band-gap. In accordance with this, our results strongly indicate that cationic vacancies are at the heart of the appearance of long-range magnetic ordering in MgO films.

1. Introduction

Investigation of new materials in recent years has spread out in many directions and oxide materials, in particular, have been deeply analyzed in the search for new functionalities and applications. One of the objectives hardly pursued is to combine in the same material the properties of semiconductors and ferromagnets that will allow adjoining charge and spin degrees of freedom for the development of new spintronic devices and their integration in microelectronic technology. In this search, much attention has been paid to the so-called dilute magnetic semiconductors and diluted magnetic oxides (DMOs) [1]. Nevertheless, in spite of intense research, the origin and control of ferromagnetism in these materials remain elusive [2]. This is especially true in the case of DMOs where extrinsic causes, such as contamination or segregation of magnetic dopants [3], have been pointed out as the origin of the observed magnetic response. For instance, it has been recently shown that the presence of the anomalous Hall effect itself does not imply intrinsic magnetism in DMOs [4]. As pointed out by Ando [5], an element-specific spectroscopy technique sensitive to magnetism, such as X-ray magnetism circular dichroism, is required to reveal intrinsic ferromagnetism [6]. In this regard, we have recently shown [7,8] that hole doping induced by cation vacancies introduces *p* states above the valence-band edge in MgO, which in turn gives rise to spin polarization experimentally confirmed by others [9] as well.

In this work, we present a photoluminescence spectroscopy (PL) study of MgO films under ambient conditions. Experimental results demonstrate that an emission peak at approximately 460 nm (2.7 eV) appears in samples exhibiting ferromagnetic behavior at room temperature. Previous results in MgO indicate that this new level does not result from impurities, but is associated with the reduced coordination of Mg ions [10], i.e. V-type centers. Both, the threshold nature of emission intensity and the observed fast decay time, suggest that the emission at 2.7 eV could be related to holes trapped at magnesium ion vacancies acting as acceptors. The close correlation between this blue luminescence and the magnetic behavior at room temperature strongly indicates that both have the very same origin i.e. hole doping induced by cation vacancies.

2. Preparation of films and characterization

MgO films used in this work have been prepared by rf-magnetron sputtering on top of different substrates, namely, (001) $SrTi_2O_3$ (STO) and Corning 1737F glass, though similar results have also been found in silicon and sapphire [11]. It is well known that the film growth, and consequently, the anion/cation ratio density, depend on the substrate temperature, the plasma atmosphere and the power density. Thus, magnetic properties of thin films can be modified by using non-equilibrium growth conditions [9]. To analyze the correlation between the magnetic and PL features in defective MgO films, we have prepared several samples under different conditions, thus exhibiting different magnetic properties.

3. Results and discussion

In Table 1, we summarize some typical examples to illustrate the different magnetic behaviors found in our work. For instance, when the deposition of atoms occurs at temperatures well above the Mg melting point (923 K), Mg vacancies can be stabilized in an excess of oxygen atmosphere (0.33 mbar). On the contrary, if the substrate temperature is held below 700 K, a pressure of about 5×10^{-4} mbar is required to optimize the film quality, while the replacement of oxygen with heavier Ar^{+} plasma ion, which increases the growth rate, significantly altered the Mg-to-O ratio [12,13]. This allows for a control on the final number of cation vacancies in films [8].

Magnetic measurements were performed by using a commercial SQUID magnetometer (Quantum Design) (see Ref. [7] for details). Regarding luminescence spectroscopy, the samples were excited by photon energy much smaller than the band-gap energy of the bulk oxide. We measured the light emission after the excitation of the samples using a 325 nm light from a He–Cd laser. For the time-resolved measurements, 5 ns individual pulses from the third harmonic output (355 nm) of a Nd:YAG laser were used. The optical absorption measurements were performed at room temperature using a UV–vis–NIR Perkin Elmer Lambda 950 spectrophotometer. Results for films (about 80 nm thick) deposited onto Corning glass are summarized in Fig. 1. A distinct shoulder is found on the longer-wavelength side for sample D which exhibits ferromagnetism. The broad optical absorption band centered at about 540 nm (approximately 2.3 eV) appears to be a transition from the unpaired electron delocalized over the V-centers [14,15], whereas the absorption at 270 nm is attributed to the excitation of low coordinated anions [16]. Regarding non-magnetic samples, the optical absorption spectrum of sample E shows a band at 330 nm that has been attributed to cluster-type defects [17]. Upon doping with hydrogen (sample C), it is found that this band is actually the convolution of two distinct absorption bands at about 3.6 and 3.8 eV, attributed to dimer centers F_2 by Kotomin and Popov [18].

Fig. 2 shows the luminescence spectra for the aforementioned samples. The shape of the emission peaks is asymmetrical, and attributed to the contribution from the higher-order phonon replicas to the emission, as typically observed in highly polar materials [19]. Based on a broad number of theoretical and experimental studies on defects in MgO crystals, the 420, 440 and 530 nm bands can be assigned to F-type centers [20–22]. The emission feature at about 480 nm is ascribed to recombination processes resulting from the formation of higher-order vacancy complexes, probably associated to hydroxyl groups in a state of low coordination [23]. It is worth noting that, there is a general agreement that hydrogen introduced as an impurity diffuses through the lattice, and is trapped by F-centers (thus called an H^- center) [20]. Consequently, the high hydrogen content sample C exhibits the purest example of F-center luminescence that we have seen in our samples.

The 460 nm emission, assigned to the lowest coordinated oxide ions in earlier works, is scarcely mentioned and discussed in the recent literature, although it is often observable in published spectra [10]. Another distinct characteristic that should be pointed out is that, in samples that do not exhibit ferromagnetic order, this blue PL band is absent. Measurements performed at different probe wavelengths and on films prepared onto different substrates, exhibit a similar behavior, confirming the generality of the results. Fig. 3(a) shows the PL emission spectrum of a 22 nm MgO ferromagnetic film on STO. In the latter case, the PL spectrum is quite similar to that of the substrate together with a broad emission band peaking around 2.7 eV (460 nm) and a full-width-half-maximum of 0.47 eV. Blue and green emissions have been previously observed in the PL spectra from MgO nanostructures [24,25].

We further investigate the physics underlying the blue luminescence of magnetic MgO samples by analyzing the PL spectra and its time dependence as a function of the laser excitation energy. Fig. 3(a) illustrates the increase of the emission peak intensity in the blue region on increasing excitation intensity from 50 to 2.5×10^3 W/cm^2. It is worth noting that, it has been previously reported that intrinsic optical modes of the MgO, in particular, excitons trapped at low coordinated anion sites, are stimulated only at high energies [26]. Regarding the time dependence of PL, assuming a first-order de-excitation process exponential decay is anticipated. The 460 nm peak exhibits a fast decay time (around 26 ns), close to the time response of our detector, but similar to the case reported by Uchino and Okutso [27]. This response is a good indication that the emission comes from a single electronic level strongly interacting with the lattice. Generally, the less-localized states shows a longer lifetime, while the states bounded near defects decay more quickly. Such a behavior related to the 460 nm band is also compatible with the existence of spin polarization already reported in the literature [7–9].

To elucidate the possible magnetic origin of the 460 nm band, magneto-luminescence measurements were performed. Magnetic fields up to 12 kOe were applied in the Faraday geometry by means of a NdFeB permanent magnetic ring. In Fig. 3(b), PL spectra corresponding to a sample grown on glass are shown. It is found that the application of a magnetic field promotes a downward shift of the peak and a slight decrease of the maximum intensity of the PL peak, in agreement with previous reports of magneto-PL in magnetic semiconductors [28]. Worth to mention, the weak peak at about 442 nm, assigned to the Cd^{+} $(5s^{22}\,D_{5/2})$ level emitting from the He–Cd laser, was used to ensure wavelength correction [29]. Thus, the observed magneto-PL likely reflects the interaction of the magnetic field with the spin polarization of the defects [30].

4. Conclusions

In summary, PL response at visible wavelengths was observed from MgO thin films at room temperature. On the one hand, both the V-type absorption and the F luminescence peak at 2.3 eV (530 nm). On the other hand, the threshold nature of emission intensity and the fast observed decay time, suggest that the emission at 2.7 eV could be related to holes trapped at Mg ion vacancies acting as acceptor levels. The appearance of this PL peak emission only in samples showing long-range magnetic ordering strongly suggests that the origin of magnetism in MgO films is the very same that also causes optical emission, providing a further step toward novel applications such as “see-through” spin photonic devices.

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References

[1] See e.g. S.A. Chambers, Y.K. Yoo, MRS Bulletin (October) (2003).

[2] T. Dietl, Nat. Mat. 9 (2010) 965. and references therein.

[3] T. Fukumura, Y. Yamada, H. Toyosaki, T. Hasegawa, H. Koinuma, M. Kawasaki, Appl. Surf. Sci. 223 (2004) 62.

[4] Y.J. Lee, M.P. de Jong, W.G. van der Wiel, Y. Kim, J.D. Brock, Appl. Phys. Lett. 97 (2010) 212506.

[5] K. Ando, Science 312 (2006) 1883.

[6] T.S. Herng, D.-C. Qi, T. Berlijn, J.B. Yi, K.S. Yang, Y. Dai, Y.P. Feng, I. Santoso, Sanchez-Hanke, X.Y. Gao, Andrew, T.S. Wee, W. Ku, J. Ding, A. Rusydi, Phys. Rev. Lett. 105 (2010) 207201.

[7] C. Martinez-Boubeta, J.I. Beltran, Ll. Balcells, Z. Konstantinović, S. Valencia, Schmitz, J. Arbiol, S. Estrade, J. Cornil, B. Martinez, Phys. Rev. B 82 (2010) 024405.

[8] Ll. Balcells, J.I. Beltran, C. Martinez-Boubeta, Z. Konstantinović, J. Arbiol, B. Martinez, Appl. Phys. Lett. 97 (2010) 252503.

[9] C. Moyses Araujo, M. Kapilashrami, X. Jun, O.D. Jayakumar, S. Nagar, Y. Wu, C. Arhammar, B. Johansson, L. Belova, R. Ahuja, G.A. Gehring, K.V. Rao, Appl. Phys. Lett. 96 (2010) 232505.

[10] C. Chizallet, G. Costentin, J.-M. Krafft, H. Lauron-Pernot, M. Che, Chem. Phys. Chem. 7 (2006) 904.

[11] C. Martinez-Boubeta, et al. (in preparation).

[12] H.K. Yu, W.-K. Kim, J.-L. Lee, E.C. Park, J.S. Kim, J.H. Ryu, Jpn. J. Appl. Phys. 48 (2009) 076003.

[13] D.J. Kim, W.S. Choi, F. Schleicher, R.H. Shin, S. Boukari, V. Davesne, C. Kieber, J. Arabski, G. Schmerber, E. Beaurepaire, W. Jo, M. Bowen, Appl. Phys. Lett. 97 (2010) 263502.

[14] Y. Chen, W.A. Sibley, Phys. Rev. 154 (1967) 843.

[15] E.H. Izen, R.M. Mazo, J.C. Kemps, J. Phys. Chem. Solids 34 (1973) 1431.

[16] S. Stankic, M. Muller, O. Diwald, M. Sterrer, E. Knozinger, J. Bernardi, Angew. Chem., Int. Ed. 44 (2005) 4917.

[17] W.C. Las, T.G. Stoebe, Radiat. Prot. Dosim. 8 (1984) 45.

[18] E.A. Kotomin, A.I. Popov, Nucl. Instrum. Methods 141 (1998) 1.

[19] H. Qu, L. Cao, G. Su, W. Liu, Y. Sun, B. Dong, J. Appl. Phys. 106 (2009) 093506.

[20] G.H. Rosenblatt, M.W. Rowe, G.P. Williams Jr., R.T. Williams, Y. Chen, Phys. Rev. B 39 (1989) 10309.

[21] L.A. Kappers, E.B. Henslev, Phys. Rev. B 6 (1972) 2475.

[22] Q.S. Wang, N.A.W. Holzwarth, Phys. Rev. B 41 (1990) 3211.

[23] M.-L. Bailly, G. Costentin, H. Lauron-Pernot, J.M. Krafft, M. Che, J. Phys. Chem. B 109 (2005) 2404.

[24] J. Zhang, L. Zhang, Chem. Phys. Lett. 36 (2002) 293.

[25] N. Kumar, D. Sanyal, A. Sundaresan, Chem. Phys. Lett. 477 (2009) 360.

[26] H.-M. Benia, P. Myrach, N. Nilius, New J. Phys. 10 (2008) 13010.

[27] T. Uchino, D. Okutsu, Phys. Rev. Lett. 101 (2008) 117401.

[28] M. Poggio, R.C. Myers, N.P. Stern, A.C. Gossard, D.D. Awschalom, Phys. Rev. B 72 (2005) 235313.

[29] C. Boulmer-Leborgne, B. Dubreuil, J. Phys. D: Appl. Phys. 23 (1990) 1029.

[30] M. Di Vece, B. Kolaric, K. Baert, G. Schweitzer, M. Obradovic, R.A.L. Vallee, P. Lievens, K. Clays, Nanotechnology 20 (2009) 135203.

Table 1

Details of some preparation parameters and the magnetic behavior (at room temperature) of the samples used in this work.

Sample	Substrate temperature (K)	Atmosphere	Magnetic behavior
A	1000	O_2	Ferromagnetic
B	650	O_2	Diamagnetic
C	650	H_2O	Paramagnetic
D	650	Ar/O_2	Ferromagnetic
E	550	Ar/O_2	Diamagnetic

Fig. 1. Differential transmittance ($\Delta T/T$) of MgO films onto Corning 1737F substrates. The positions of absorption bands discussed within the text are shown by arrows. Inset shows a representative transmission spectrum.

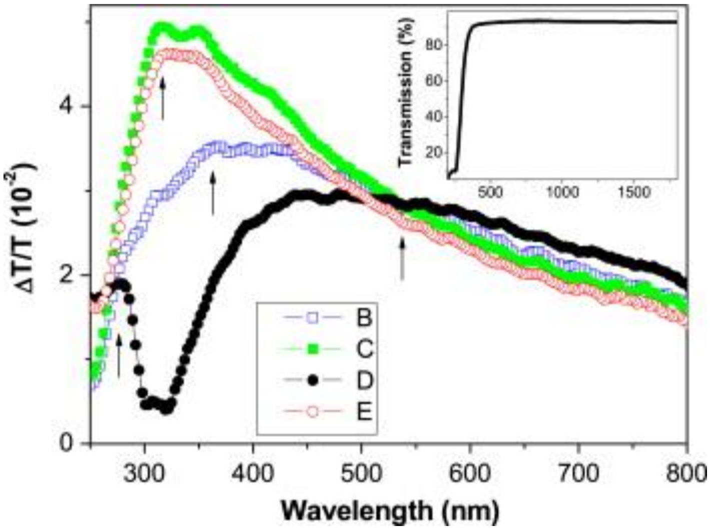

Fig. 2. Photoluminescence spectra at ambient atmosphere with normalized amplitudes from MgO films upon excitation with 325 nm photons. The curves are vertically offset for the sake of clarity. The dashed line is set to indicate the 460 nm spectral position associated to low coordinated oxygen.

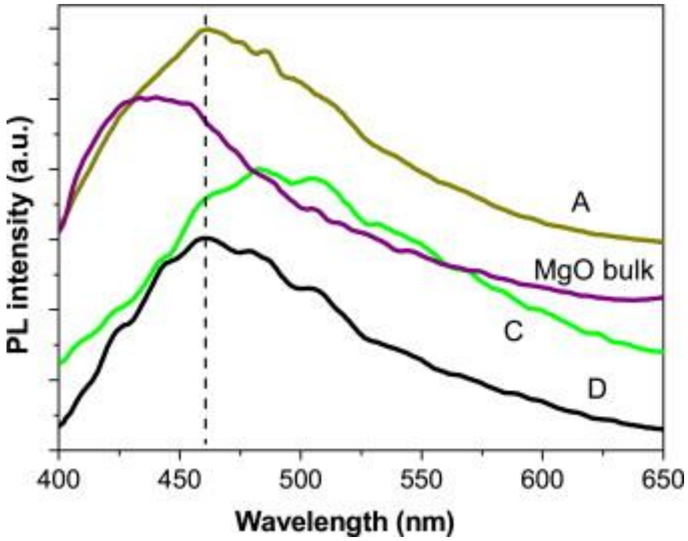

Fig. 3. (a) Room temperature PL intensity of a ferromagnetic MgO film excited at two different intensities at 355 nm. Dots depict data collected under high excitation-power 2.5×10^{3} W/cm^{2}, while the shadowed area accounts for PL at low excitation fluency (50 W/cm^{2}). Inset: Photoluminescence curve at 460 nm detection wavelength as a function of time after the optical pulse. The solid line is a pure exponential fit, yielding a decay time of 26 ns. (b) Luminescence from a magnetic sample excited by continuous irradiation with 325 nm light, with and without a magnetic field, which is applied in the Faraday geometry. The vertical line indicates the 442 nm laser contribution.