Research Article

A Low-Field Temperature Dependent EPR Signal in Terraced $\text{MgO}:\text{Mn}^{2+}$ Nanoparticles: An Enhanced Zeeman Splitting in the Wide-Bandgap Oxide

Peter V. Pikhitsa, Sukbyung Chae, Seungha Shin, and Mansoo Choi

Global Frontier Center for Multiscale Energy Systems, Division of WCU Multiscale Mechanical Design, School of Mechanical and Aerospace Engineering, Seoul National University, Seoul 151-742, Republic of Korea

Correspondence should be addressed to Peter V. Pikhitsa; peter@snu.ac.kr

Received 15 November 2016; Accepted 9 January 2017; Published 19 January 2017

Academic Editor: Javier Garcia-Guinea

Copyright © 2017 Peter V. Pikhitsa et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Mn^{2+} ion doping is used as an electron paramagnetic resonance (EPR) probe to investigate the influence of low-coordination structural defects such as step edges at the surface of terraced (001) MgO nanoparticles on the electronic properties. Beside the well-known hyperfine sextet of Mn^{2+} ions in the cubic crystal field of MgO , an additional EPR feature with a striking nonmonotonous temperature dependent shift of the g -factor is observed in terraced nanoparticles in the temperature range from 4 K to room temperature. By linking the difference in the temperature dependence of the Mn^{2+} sextet intensity in cubic and terraced nanoparticles with the possible s-d exchange shift and enhanced Zeeman splitting we conclude that the novel EPR feature originates from the loosely trapped charge-compensating carriers at the abundant structural defects at the surface of terraced nanoparticles due to their exchange interaction with neighboring Mn^{2+} ions.

1. Introduction

Iconic wide-gap oxide MgO has been used for many applications connected with the spin states of electrons, such as spintronics and superconductivity, mostly for buffer tunneling layers in nanoscale. On the other hand, magnetic Mn^{2+} ions, which play a decisive role in spintronics of diluted magnetic semiconductors (DMS), can be easily doped into MgO and its nanostructures. Pure MgO forms an ionic crystal with cubic NaCl structure consisting of Mg^{2+} and O^{2-} . In contrast, the chemical bond in a free MgO molecule is much more covalent than in the bulk of the crystal and the effective charges on the ions are Mg^{1+} and O^{1-} . Thus, in the bulk of MgO crystal the electron affinity is practically eliminated by the Madelung potential. Meanwhile, (001) MgO surface can have structural defects such as step edges, kinks, and corners that can possess various electronic properties interesting for applications such as sensors and catalysts. Having the bandgap of 7.7 eV, completely filled valence bands, and empty conduction bands, MgO would transfer electrons/holes only along the low-coordination structural surface defects, mostly step edges.

It could happen because the Madelung potential decreases rapidly as the Mg and O coordination decreases, and for the Mg ion at the edge, corner, and other low coordinated (LC) sites the electron affinity becomes comparable with the electron affinity for a free ion. The calculated relaxed electron affinities of 3-coordinated Mg sites of 1-2 eV demonstrate that they can serve as electron traps [1, 2]. A trapped electron is almost entirely localized at the terminating Mg ion, which thus becomes similar to Mg^{1+} . The same is true for trapped holes and for O^{1-} ions. One would expect that foreign ions like Mn^{2+} if close enough to the LC sites would also need charge compensation like $\text{Mn}^{2+} + e^-$ to produce an electron- Mn^{2+} complex.

For MgO nanoparticles the surface structural defects depend on the method of synthesis [3] that may also produce bulk defects. Recently we reported that terraced MgO nanoparticles are distinguished by peculiar bulk electronic defect states leading to luminescence with a double-band light emission at 260 nm and 490 nm [3]. A further attempt to investigate electronic states in terraced MgO nanoparticles with the electron paramagnetic resonance (EPR) technique

FIGURE 1: TEM images of type II (a) and type I (b) MgO nanoparticles. In (b) the pronounced LC structural defects are clearly seen.

at the X-band by comparing them with cubic MgO nanoparticles led us to unexpected results. In fact, as far as the Inductively Coupled Plasma analysis indicated that all the nanoparticles always contain unintentionally doped Mn^{2+} impurities at several ppm level [3], a pronounced sextet signal from those impurities was only expected to be identical for cubic and terraced nanoparticles.

Using Mn^{2+} as an EPR probe has been well known [4–6]. On the other hand, numerous papers report optical detection that demonstrates how a single Mn^{2+} ion influences the DMS exciton through the sp-d exchange field in a carrier-Mn complex in semiconductor single quantum dots [7–9]. The shift in the band edge energy leads to a great g -factor enhancement [10–12]. If LC defects trapped a charge carrier (as far as such a charge transfer was predicted for Mg and O surface ions) [1, 2] then an Mn^{2+} ion would also influence the nearby electron through the s-d exchange field.

Indeed, for both cubic and terraced nanoparticles we found the well-known hyperfine sextet of Mn^{2+} ions, usually for (001) MgO, yet for terraced ones we observed an additional broad feature with g -factor of 2.23 at room temperature (RT). Curiously, this feature moves downfield considerably when the temperature lowers to 4 K. Such lability makes it difficult to assign this feature to an isolated paramagnetic defect. The g -factor has nonmonotonous temperature dependence that may be interpreted as a shift from the electron free value that may be caused by the exchange field of nearby Mn^{2+} ions. Meanwhile, a low-field $g = 2.77$ feature has been known in GaAs: Mn^{2+} and was explained as the signal from the complex Mn^{2+} (d^5) plus the weakly coupled delocalized hole [13]. Note that an excited paramagnetic system in a triplet state with the exchange already showed a striking and unexplained nonmonotonous g shift (similar to what we observed) proportional to a quantity differing only slightly from the susceptibility [14].

Here we report the results of our EPR measurements on terraced and cubic MgO nanoparticles and correlate the temperature behavior of the low-field EPR feature with the

temperature behavior of the EPR signal from Mn^{2+} ions. By this correlation we conclude that the new EPR feature of terraced MgO nanoparticles may originate from trapped electrons/holes that were predicted to exist along the edges and ledges of the terraces being LC structural defects [1, 2]. The electrons may exchange/interact with nearby Mn^{2+} ions which provide an effective field that acts on the loosely trapped electrons as the EPR shows. Thus the puzzling EPR feature has been qualitatively explained and its existence can be considered as supporting the presence of loosely bound charge carriers along the edges of terraces that may find an application in nanoelectronics, based on the wide-gap oxide.

2. Experimental

MgO nanoparticles were produced in an oxyhydrogen flame and were distinguished by intensive terraced structure (say, of type I, Figure 1(b)) as described earlier in [3]. Type II nanoparticles (Figure 1(a)) were produced by burning Mg in dry air and were distinguished by exclusively cubic shape of nanoparticles (well-known MgO smoke). The powder samples were measured in a standard Bruker EPR spectrometer setup equipped with a helium flow cooling system with temperature stabilization. The measurements were performed in a sweeping mode in X-band of about 9.4 GHz.

3. Results and Discussion

Both types of nanoparticles contained similar amount of Mn^{2+} impurities of several tens ppm revealed by EPR as the characteristic sextet of hyperfine splitting (HFS) of Mn^{2+} ions in the cubic crystal field (Figure 2) with g -factors (of 1.88; 1.93; 1.98; 2.03; 2.09; 2.14). The sextet is known to have been widely used as a marker along with the famous DPPH for calibration of g -factors in EPR experiments. However, only for terraced samples of type I there appeared an additional broad EPR signal (temperature dependent linewidths of ca. 100–200 Oe) at low field with $g = 2.23$ at RT that was

FIGURE 2: EPR spectra of type II (a) and type I (c) MgO nanoparticles. ((b) and (d)) Temperature dependency of the EPR intensity of type II and type I nanoparticles, respectively.

not observed for type II samples. Moreover, the additional low-field EPR feature demonstrated a complex behavior with the temperature (Figure 3). The enhanced g -factor extracted from graphs in Figure 3 is shown in Figure 4 and is pronouncedly temperature dependent when g -factor changed up to $g = 2.7$ at 4 K (Figure 4). In parallel, one can observe a non-Curie temperature dependence of the HFS sextet intensity for both types of the samples (Figure 2); however, the specific temperature dependence was quite

different for type I and type II samples as presented in Figures 2(b) and 2(d), correspondingly.

A non-Curie behavior seems quite natural for the Mn^{2+} ion sextet because of the interplay between the thermal and radiofrequency energy population of the energy levels [15]. However, the difference between Figures 2(b) and 2(d) suggests that some Mn^{2+} ions in type I samples participate in the resonance differently just because they may lie in the vicinity of the LC structural defects that may modify the

FIGURE 3: EPR of type I MgO nanoparticles measured at different temperatures. (a) the EPR spectra; (c) a magnified region encircled in (a) and (b) replotted (c) with the g -factor instead of the field; (d) EPR absorption as the integrated signal from (c). The lines are vertically shifted for better comprehension.

charge state of the surrounding oxygen ion. Therefore, as we mentioned before, there is a need in charge compensation, so similar to Mg^{1+} ion on the surface an Mn^{1+} ion could be created. However, if all ions were such, the Mn^{1+} ions (being a d^6 non-Kramers ion) would be nearly EPR silent. Thus instead one may rather expect a number of complexes electron $-\text{Mn}^{2+}$, such that the electron may be donated to a

nearby LC defect and be loosely bound. Analogous charge compensation by a hole was discussed in [8]. It is intriguing to notice that in GaAs: Mn the bound hole produced a broad low-field EPR feature at $g = 2.77$ along with the Mn^{2+} signal [13]. Additionally, a flip-flop in two resonant forms $\text{Fe}^{3+}-\text{O}^{2-} \leftrightarrow \text{Fe}^{2+}-\text{O}^{1-}$ (it could be realized in the $\text{Mn}^{2+}-\text{O}^{1-}$ state jumping into the $\text{Mn}^{3+}-\text{O}^{2-}$ state and back) was reported in

FIGURE 4: g -factor dependence of the low-field EPR signal on temperature (points). The line is drawn according to (3).

[16] as the main reason for EPR feature (the radiation dose dependent) at $g \approx 2.54$ in feldspars.

We suggest a simple semiquantitative analysis of our experimental findings based on the analogy with DMS. A loosely trapped electron brought to an LC defect is in the field of a nearby Mn^{2+} ion which magnetic moment relaxes relatively slow. The local field induced by the exchange between the electron and the ion influences the carrier [12]. The local field from the magnetic ion makes magnetization $M = \chi(T)H$ leading to a shift in a resonance field of the nearby loosely trapped electron, thus producing a temperature dependent g -factor. It is similar to what happens when an Mn^{2+} ion acts on an exciton in a quantum dot with a so-called giant Zeeman effect [10–12].

We can write down the equation for the effective g -factor of the electron that explicitly expresses it through magnetization and the susceptibility in analogy with [12]:

$$g = g_e + \frac{\alpha M}{g_{\text{Mn}} \mu_B^2 H} = 2 + \frac{\alpha \chi}{2 \mu_B^2}, \quad (1)$$

where $g_e \approx 2$ is the loosely trapped electron g -factor (this is quite different from the DMS where instead of g_e in (1) there is g^* , the negative g -factor of the band electron) and $g_{\text{Mn}} \approx 2$ is the Mn^{2+} g -factor, α is the exchange integral, positive for ferromagnetic interaction between the electron and Mn^{2+} ion, μ_B is the Bohr magneton, and χ is the static magnetic susceptibility.

Instead of χ , in (1) we deal with the EPR susceptibility $\chi(T)$ which is proportional to the EPR response of the Mn^{2+} ions residing at the LC defects and which can be obtained by subtracting the appropriately rescaled EPR susceptibility $\chi_C(T)$ of cubic samples (calculated in the usual way from the linewidth and the intensity of the signal in arbitrary units) taken from Figure 2(b), from the EPR susceptibility $\chi_T(T)$ of terraced samples (taken from Figure 2(d)):

$$\chi(T) = \chi_T(T) - A \chi_C(T), \quad (2)$$

where $A > 0$ is a constant. Finally, the g -factor is the sum of the free electron value and the shift:

$$g(T) = 2 + B [\chi_T(T) - A \chi_C(T)], \quad (3)$$

where $B > 0$ is another constant. Both A and B can be obtained from comparing $g(T)$ with the experimental dependence in Figure 4. The line with the fitting parameters $A = 0.25$ and $B = 7 \times 10^{-5}$ is rather close to the experimental data. Finally, it also qualitatively reproduces the otherwise puzzling nonmonotonous behavior of $g(T)$.

4. Conclusion

In conclusion, we presented unusual EPR data of a nanostructured material, based on MgO terraced nanoparticles, that demonstrated a possibility of manipulating the electronic properties of the wide-gap oxide by magnetic Mn^{2+} ions similar to the well-established manipulation with DMS quantum dots. An encouraging example of such manipulation is room temperature magnetism found in $\text{ZnO}:\text{Mn}^{2+}$ [17].

Competing Interests

The authors declare that they have no competing interests.

Acknowledgments

This work was done by financial support from the Global Frontier Center for Multiscale Energy Systems (2011-0031561) supported by the Korean Ministry of Science and Technology. The authors thank Korea University and Sunhee Kim from KBSI for the EPR measurements.

References

- [1] M. Chiesa, M. C. Paganini, E. Giamello, D. M. Murphy, C. Di Valentin, and G. Pacchioni, “Excess electrons stabilized on ionic

- oxide surfaces,” *Accounts of Chemical Research*, vol. 39, no. 11, pp. 861–867, 2006.
- [2] K. P. McKenna, P. V. Sushko, and A. L. Shluger, “Inside powders: a theoretical model of interfaces between MgO nanocrystallites,” *Journal of the American Chemical Society*, vol. 129, no. 27, pp. 8600–8608, 2007.
- [3] P. V. Pikhitsa, C. Kim, S. Chae et al., “Two-band luminescence from an intrinsic defect in spherical and terraced MgO nanoparticles,” *Applied Physics Letters*, vol. 106, no. 18, Article ID 183106, 2015.
- [4] T. Yamamura, A. Hasegawa, Y. Yamada, and M. Miura, “The electron spin resonance of the Mn^{2+} ion on the surface of magnesium oxide,” *Bulletin of the Chemical Society of Japan*, vol. 43, no. 11, pp. 3377–3382, 1970.
- [5] E. G. Derouane, J. Thelen, and V. Indovina, “Manganese ions as paramagnetic probes in magnesium oxide. II. Crystal growth and ionic diffusion,” *Bulletin des Sociétés Chimiques Belges*, vol. 82, no. 9-10, pp. 657–671, 1973.
- [6] T. Story, C. H. W. Swüste, P. J. T. Eggenkamp, H. J. M. Swagten, and W. J. M. De Jonge, “Electron paramagnetic resonance knight shift in semimagnetic (diluted magnetic) semiconductors,” *Physical Review Letters*, vol. 77, no. 13, pp. 2802–2805, 1996.
- [7] M. Goryca, M. Koperski, T. Smolenski et al., “Spin-lattice relaxation of an individual Mn^{2+} ion in a CdTe/ZnTe quantum dot,” *Physical Review B*, vol. 92, no. 4, Article ID 045412, 2015.
- [8] A. Kudelski, A. Lemaître, A. Miard et al., “Optically probing the fine structure of a single Mn atom in an InAs quantum dot,” *Physical Review Letters*, vol. 99, no. 24, Article ID 247209, 2007.
- [9] L. Besombes, Y. Léger, L. Maingault, D. Ferrand, H. Mariette, and J. Cibert, “Probing the spin state of a single magnetic ion in an individual quantum dot,” *Physical Review Letters*, vol. 93, no. 20, Article ID 207403, pp. 1–4, 2004.
- [10] J. A. Gaj, R. Planel, and G. Fishman, “Relation of magneto-optical properties of free excitons to spin alignment of Mn^{2+} ions in $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$,” *Solid State Communications*, vol. 29, no. 5, pp. 435–438, 1979.
- [11] F. J. Teran, M. Potemski, D. K. Maude et al., “Collective character of spin excitations in a system of Mn^{2+} spins coupled to a two-dimensional electron gas,” *Physical Review Letters*, vol. 91, no. 7, Article ID 077201, 2003.
- [12] J. K. Furdyna, “Diluted magnetic semiconductors,” *Journal of Applied Physics*, vol. 64, no. 4, pp. R29–R64, 1988.
- [13] J. Schneider, U. Kaufmann, W. Wilkening, M. Baeumler, and F. Köhl, “Electronic structure of the neutral manganese acceptor in gallium arsenide,” *Physical Review Letters*, vol. 59, no. 2, pp. 240–243, 1987.
- [14] B. R. Cooper, R. C. Fedder, and D. P. Schumacher, “Paramagnetic-resonance study of crystal-field and exchange effects in an excited state of Tm^{3+} ,” *Physical Review*, vol. 163, no. 2, pp. 506–517, 1967.
- [15] M. Godlewski, S. Yatsunenko, and V. Y. Ivanov, “Recombination processes in nanoparticles of H-Mn-VI compounds-magnetic resonance study,” *Israel Journal of Chemistry*, vol. 46, no. 4, pp. 413–421, 2006.
- [16] M. D. Sastry, Y. C. Nagar, B. Bhushan, K. P. Mishra, V. Balaram, and A. K. Singhvi, “An unusual radiation dose dependent EPR line at $g_{\text{eff}} = 2.54$ in feldspars: possible evidence of $\text{Fe}^{3+}\text{O}^{2-} \leftrightarrow \text{Fe}^{2+}\text{O}^-$ and exchange coupled $\text{Fe}^{3+}\text{-Fe}^{2+}\text{-nO}^-$,” *Journal of Physics Condensed Matter*, vol. 20, no. 2, Article ID 025224, 2008.
- [17] N. S. Norberg, K. R. Kittilstved, J. E. Amonette, R. K. Kukkadapu, D. A. Schwartz, and D. R. Gamelin, “Synthesis of colloidal $\text{Mn}^{2+}:\text{ZnO}$ quantum dots and high- T_C ferromagnetic nanocrystalline thin films,” *Journal of the American Chemical Society*, vol. 126, no. 30, pp. 9387–9398, 2004.