

Crucial role of interdiffusion on magnetic properties of *in situ* formed MgO/Fe_{3-δ}O₄ heterostructured nanowires

Aurelian Marcu,¹ Takeshi Yanagida,^{2,a)} Kazuki Nagashima,² Keisuke Oka,² Hidekazu Tanaka,² and Tomoji Kawai²

¹National Institute of Laser Plasma and Radiation Physics, Laser Department, P.O. Box MG-36, Atomistilor 409, Bucharest-Magurele, Romania

²Institute of Scientific and Industrial Research, Osaka University, 8-1 Mihogaoka Ibaraki, Osaka 567-0047, Japan

(Received 23 March 2008; accepted 10 April 2008; published online 1 May 2008)

Although a heterointerface in oxides plays a crucial role on the properties, such heterointerface effects on oxide nanowires have not been well understood. Here, we demonstrate the crucial role of atomic interdiffusion on the magnetic properties of *in situ* formed MgO/Fe_{3-δ}O₄ heterostructured nanowires. The wide variation of nanowire heterointerfaces was found when varying the growth atmosphere. The occurrence of the interdiffusion and the large interface area of nanowires strongly affect the magnetism via forming mixed spinel structures at the heterointerface. Thus, it is crucial to precisely control the atomic interdiffusion at the heterointerface for the desired properties of heterostructured oxide nanowires. © 2008 American Institute of Physics.

[DOI: [10.1063/1.2918132](https://doi.org/10.1063/1.2918132)]

Transition metal oxide nanowires are potential candidates to incorporate the rich functionalities of the physical properties, including ferromagnetism, superconductivity, and ferroelectricity, into nanowire-based devices.¹⁻⁴ However, there is a fundamental limitation to fabricate nanowires of various transition metal oxides due to the one-dimensional crystal growth mechanism such as vapor-liquid-solid mechanism.^{5,6} Use of a core-shell heterostructured oxide nanowire might overcome such critical issue, since the methodology essentially allows us to explore a wide range of oxide materials.⁷⁻⁹ In oxide heterostructures, a heterointerface plays an important role on the physical properties.¹⁰⁻¹² Therefore a well-defined heterointerface in core-shell heterostructured nanowires is strongly desired. Although the feasibility of *ex situ* formations of heterostructured oxide nanowires has been demonstrated,⁷⁻⁹ an *in situ* formation of heterostructured nanowires without atmospheric exposure would be one of powerful methods to create a well-defined oxide heterointerface. However, such *in situ* formations of oxide heterostructured nanowires have not been reported so far. We have reported the feasibility of MgO nanowires as a nanoscale oxide substrate by using pulsed laser deposition (PLD), which in principle allows us to form *in situ* core-shell heterostructured oxide nanowires.¹³⁻¹⁶ Ferrites, including Fe₃O₄, α-Fe₂O₃ and γ-Fe₂O₃, have been intensively investigated for the magnetic applications,¹⁷⁻²² and recently the spintronics applications^{2,3,23} and the nonvolatile memory²⁴ have renewed the interests. Thus it would be an interesting issue to fabricate the oxide heterostructured nanowires using ferrite toward miniaturizing the ferrite-based device applications. Here, we report the *in situ* formation of MgO/Fe_{3-δ}O₄ core-shell heterostructured oxide nanowires by PLD and the effect of heterointerface on the magnetic properties. We found a significant role of the atomic interdiffusion at the heterointerface on the magnetic properties of MgO/Fe_{3-δ}O₄ heterostructured nanowires.

MgO/Fe_{3-δ}O₄ core-shell heterostructured nanowires were fabricated using *in situ* PLD method. Firstly, MgO nanowires were grown on MgO (100) single crystal substrate by Au catalyst-assisted PLD, and the details can be seen elsewhere.¹³⁻¹⁶ Secondly, Fe_{3-δ}O₄ shell layer was deposited onto the MgO nanowire without atmospheric exposure. Fe₂O₃ pellet was used as the target, which was obtained by milling Fe₂O₃ (99.9% pure) powder for 1 h and then sintered at 1000 °C for 24 h. The repetition rate, the laser energy, and the substrate-to-target distance were 10 Hz, 15 mJ, and 45 mm, respectively. The substrate temperature and oxygen pressure during the shell depositions were varied from room temperature (RT) to 800 °C and 10⁻⁴–10 Pa, respectively. Field emission scanning electron microscopy (FESEM) (JEOL JSM-6330FT) at an accelerating voltage of 30 kV was used to characterize the macroscopic morphology. Prior to the FESEM observation, Pt was sputtered on the samples to prevent the charging. The thickness of Pt was nearly 5 nm. High-resolution transmission electron microscopy (HRTEM) (JEOL JEM-3000F) coupled with energy dispersive spectroscopy (EDS) was used to evaluate the microstructure at the interface, and the composition of the fabricated nanowires. Samples for HRTEM were prepared by placing a drop of the sample suspension on a copper microgrid (JEOL 7801-11613). HRTEM measurements were performed at an accelerating voltage of 300 kV. The magnetic properties of heterostructured nanowires were evaluated by a superconducting quantum interference device.

Figure 1 shows the FESEM images of MgO/Fe_{3-δ}O₄ heterostructured nanowires grown under 400 °C substrate temperature and 10 Pa oxygen pressure. The smooth covering surface can be seen in the image. The variation of the laser energy drastically changes the heterostructured nanowire morphology. Above the laser energy of 15 mJ, the preferential crystal growth of shell layers near the tips tends to appear as the laser energy tends to increase. The similar trend was found when varying the distance between the target and the substrate, indicating the significant role of the ablated particle flux on the shell covering formation process. The

^{a)}Electronic mail: yanagi32@sanken.osaka-u.ac.jp.

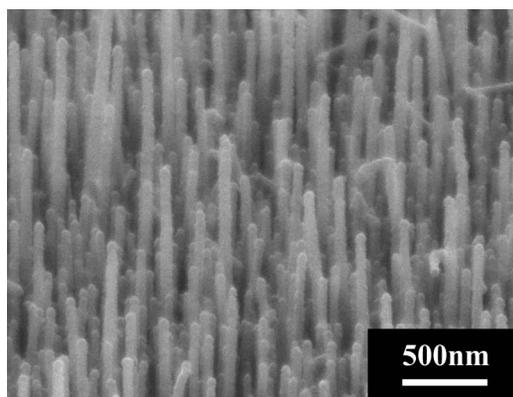


FIG. 1. FESEM images of MgO/Fe_{3-δ}O₄ core-shell nanowires grown under 400 °C growth temperature and 10 Pa oxygen pressure.

preferential crystal growth at the tip when increasing the ablated particle flux can be understood in terms of the plume penetration depth variation in between nanowires.²⁵ Thus, the dominant factor for the heterostructured nanowire formation using *in situ* PLD technique is rather dependent on the ablated particle flux.

Although the macroscopic uniformity of heterostructured oxide nanowires can be achieved via controlling the ablated particle flux, the magnetic properties might be altered by varying the ambient atmosphere during the *in situ* formation of the heterostructures. Figure 2 shows the *M-H* data measured at 300 K for two heterostructured nanowires grown at 300 and 600 °C growth temperatures under 10⁻⁴ Pa oxygen pressures. The ferromagnetic behavior can be seen in both samples. All fabricated heterostructured nanowires exhibited such ferromagnetic behavior. Figure 3 shows the variation of the saturation magnetizations when varying the oxygen pressure and the growth temperature. According to a thermodynamic law in spinel ferrites,²⁶ the saturation magnetization should increase when the ambient atmosphere tends to be reduced, i.e., decreasing the ambient oxygen pressure and increasing the growth temperature within the range of this study. This is simply due to an increase of Fe²⁺ ions within the spinel structure.²⁶ Although such general magnetic trend can be seen in Fig. 3, there is a drastic reduction of the saturation magnetization around 300–400 °C. This effect cannot be interpreted in terms of only thermodynamic law of ferrites.

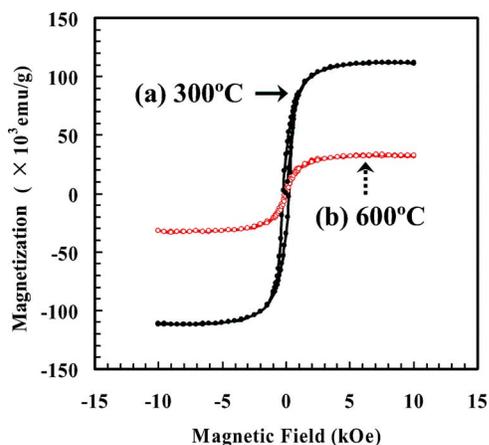


FIG. 2. (Color online) *M-H* data of heterostructured nanowires grown under 10⁻⁴ Pa oxygen pressure with the varying grown temperature.

Author complimentary copy. Redistribution subject to AIP license or copyright, see <http://apl.aip.org/apl/copyright.jsp>

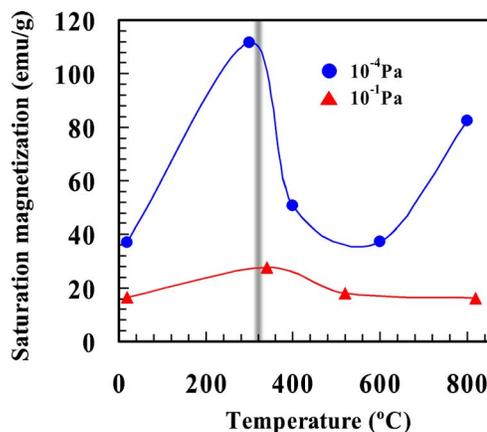


FIG. 3. (Color online) Variation of saturation magnetizations when varying the growth atmosphere including the growth temperature and the oxygen pressure.

The possible mechanism for the observed magnetic reduction might be due to the microstructure variation at the heterointerface. Figure 4 shows the microstructure variation at the heterointerface when varying the ambient temperature under 10⁻⁴ Pa oxygen pressure. The wide variation of the heterointerfaces can be seen in the HRTEM images. As the growth temperature it is increased, the shell layer at the heterointerface tends to show (i) the polycrystallinelike structure, (ii) the single crystal core-shell heterostructures, and (iii) the mixed crystal structure without observable heterointerfaces. This trend was found to be similar even when varying the oxygen pressure. The variation from the polycrystallinelike structures to the well-defined core-shell interfaces below 300 °C can be interpreted in terms of the enhancement of crystallization at the heterointerface. In the magnetic properties, the saturation magnetization increased with increasing the growth temperature due to reduced atmosphere, i.e., increased Fe²⁺ ions. In addition, the results also indicate that the spinel ferrite structure exists even for RT grown heterostructured nanowires.

When further increasing the growth temperature above 300 °C, the heterointerface between the core and the shell layers tends to disappear, as shown in the HRTEM images. At 800 °C of the growth temperature, the heterointerface is no longer visible at all. These results may indicate the occurrence of the atomic interdiffusion at the heterointerfaces formed above 300 °C. In a spinel ferrite, Mg ions can be incorporated at mainly *B* site via forming MgFe₂O₄.^{27,28} The saturation magnetization of MgFe₂O₄ is almost 1 bohr magnetron that is nearly one-fourth compared with Fe₃O₄.^{29,30} Thus, the formation of MgFe₂O₄ at the heterointerface can rigorously explain the observed reduction of the saturation

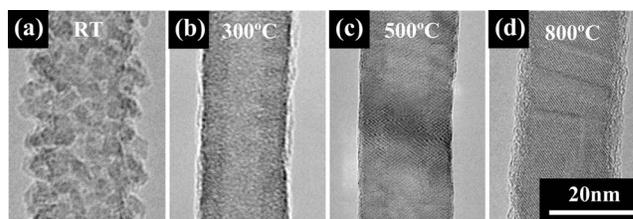


FIG. 4. HRTEM images of MgO/Fe_{3-δ}O₄ core-shell nanowires. [(a)–(d)] images show the heterostructured nanowires grown at RT up to 800 °C under 10⁻⁴ Pa oxygen pressure.

magnetization around 300–400 °C growth temperatures. Although the presence of MgFe₂O₄ structures at the heterointerface should be justified, the direct identification of MgFe₂O₄ structures was unfortunately not feasible using our HRTEM-EDS technique since the lattice constants of spinel Fe₃O₄, γ-Fe₂O₃, and MgFe₂O₄ are too close. The composition of mixed spinel structure at the heterointerface should be (Mg, Fe)₃O₄ and differ from the nominal MgFe₂O₄, depending on the core-shell volume ratio. The space distribution of interdiffusion should also affect the magnetic properties, which is dependent on the diffusion length of Mg with spinel ferrites. It should be noted that the magnetic properties of heterostructured nanowires grown at 500 °C was indeed affected by the presence of the atomic interdiffusion, although the HRTEM image shows relatively clear core-shell heterointerface. Therefore, above results highlight the significant role of the atomic interdiffusion on the magnetic properties of oxide heterostructured nanowires. The reason why the physical events at the heterointerface strongly dominate the measured magnetic properties is due to the huge specific surface area of heterostructured nanowires. For example, we can roughly estimate that the interface area per unit area of the heterostructured nanowires is at least 10⁴ times larger than the thin film case. The interface effects must be much more significant on the measured physical properties when compared with thin films. In other words, the use of heterostructured nanowires offers a good tool to detect the physical events at the oxide heterointerface. Overall, this study demonstrates that the *in situ* formation of oxide heterostructured nanowires and the precise control of heterointerfaces are important toward not only the fundamental investigations of nanoscale properties but also the applications of oxide heterostructured nanowires.

In conclusion, we have demonstrated the crucial role of interdiffusion on the magnetic properties of MgO/Fe_{3-δ}O₄ core-shell heterostructured nanowires *in situ* formed by PLD. The wide variation of nanowire heterointerfaces was found when varying the ambient atmosphere. Especially the presence of interdiffusion was demonstrated for growth temperature range above 300 °C. The occurrence of the interdiffusion strongly affects the magnetic properties of heterostructured due to the huge interface area of heterostructured nanowires. Thus, it is crucial to precisely control the atomic interdiffusion at the oxide heterointerface for the desired oxide heterostructured nanowire properties.

¹W. Ramadan, S. B. Ogale, S. Dhar, L. F. Fu, S. R. Shinde, D. C. Kundaliya, M. S. R. Rao, N. D. Browning, and T. Venkatesan, *Phys. Rev.*

B **72**, 205333 (2005).

²J. Takaobushi, H. Tanaka, T. Kawai, S. Ueda, J.-J. Kim, M. Kobata, E. Ikenaga, M. Yabashi, and K. Kobayashi, *Appl. Phys. Lett.* **89**, 242507 (2006).

³M. Ishikawa, H. Tanaka, and T. Kawai, *Appl. Phys. Lett.* **86**, 222504 (2005).

⁴W. Eerenstein, M. Wiora, J. L. Prieto, J. F. Scott, and N. D. Mathur, *Nat. Mater.* **6**, 348 (2007).

⁵R. S. Wagner and W. C. Ellis, *Appl. Phys. Lett.* **4**, 89 (1964).

⁶R. S. Wagner and W. C. Ellis, *Trans. Metall. Soc. AIME* **233**, 1053 (1965).

⁷S. Han, C. Li, Z. Liu, B. Lei, D. Zhang, W. Jin, X. Liu, T. Tang, and C. Zhou, *Nano Lett.* **4**, 1241 (2004).

⁸D. Zhang, Z. Liu, S. Han, C. Li, B. Lei, M. P. Stewart, J. M. Tour, and C. Zhou, *Nano Lett.* **4**, 2151 (2004).

⁹B. Lei, C. Li, D. Zhang, S. Han, and C. Zhou, *J. Phys. Chem. B* **109**, 18799 (2005).

¹⁰K. Nagashima, T. Yanagida, H. Tanaka, and T. Kawai, *J. Appl. Phys.* **100**, 063714 (2006).

¹¹K. Nagashima, T. Yanagida, H. Tanaka, and T. Kawai, *Phys. Rev. B* **74**, 172106 (2006).

¹²K. Nagashima, T. Yanagida, H. Tanaka, and T. Kawai, *J. Appl. Phys.* **101**, 026103 (2007).

¹³K. Nagashima, T. Yanagida, H. Tanaka, and T. Kawai, *J. Appl. Phys.* **101**, 124304 (2007).

¹⁴K. Nagashima, T. Yanagida, H. Tanaka, and T. Kawai, *Appl. Phys. Lett.* **90**, 233103 (2007).

¹⁵A. Marcu, T. Yanagida, K. Nagashima, H. Tanaka, and T. Kawai, *J. Appl. Phys.* **102**, 016102 (2007).

¹⁶T. Yanagida, K. Nagashima, H. Tanaka, and T. Kawai, *Appl. Phys. Lett.* **91**, 061502 (2007).

¹⁷S. Tiwari, R. J. Choudhary, R. Prakash, and D. M. Phase, *J. Phys.: Condens. Matter* **19**, 176002 (2007).

¹⁸C. Baratto, P. P. Lottici, D. Bersani, G. Antonioni, G. Gnappi, and A. Montenero, *J. Sol-Gel Sci. Technol.* **13**, 667 (1998).

¹⁹K. Shi, L. M. Peng, Q. Chen, R. Wang, and W. Zhou, *Microporous Mesoporous Mater.* **83**, 219 (2005).

²⁰Y. Peng, C. Park, and D. E. Laughlin, *J. Appl. Phys.* **93**, 7957 (2003).

²¹M. Aronniemi, J. Lahtinen, and P. Hautajarvi, *Surf. Interface Anal.* **36**, 1004 (2004).

²²M. T. Johnson, J. R. Michel, S. R. Gillis, and C. B. Carter, *Philos. Mag. A* **79**, 2887 (1999).

²³J. Takaobushi, M. Ishikawa, S. Ueda, E. Ikenaga, J.-J. Kim, M. Kobata, Y. Takeda, Y. Saitoh, M. Yabashi, Y. Nishio, D. Miwa, K. Tamasaku, T. Ishikawa, I. Satoh, H. Tanaka, K. Kobayashi, and T. Kawai, *Phys. Rev. B* **76**, 205108 (2007).

²⁴H. Inonue, S. Yasuda, H. Akinaga, and H. Takagi, *Phys. Rev. B* **77**, 035105 (2008).

²⁵K. Nagashima, T. Yanagida, H. Tanaka, S. Seki, A. Saeki, S. Tagawa, and T. Kawai, *J. Am. Chem. Soc.* **130**, 5378 (2008).

²⁶Y. Goto, *Jpn. J. Appl. Phys.* **3**, 739 (1964).

²⁷L. M. Corliss and J. M. Hastings, *Phys. Rev.* **90**, 1013 (1953).

²⁸S. V. Kumari, V. K. Vaidyan, and K. G. Sathyanarayana, *J. Mater. Sci.* **27**, 5504 (1992).

²⁹H. S. Belson and C. J. Kriessman, *J. Appl. Phys.* **30**, 170S (1959).

³⁰E. Banks, N. H. Riederman, H. W. Schleunig, and L. M. Silber, *J. Appl. Phys.* **32**, 44S (1961).