Fabrication of vertically aligned ferromagnetic ZnO nanopillar arrays on sapphire substrates by polymer-assisted deposition

Cite as: AIP Advances 10, 015337 (2020); https://doi.org/10.1063/1.5135332
Submitted: 05 November 2019 . Accepted: 03 January 2020 . Published Online: 23 January 2020

Jia Luo, Hongtao Ren, Xi Zhang, and Gang Xiang
Fabrication of vertically aligned ferromagnetic ZnO nanopillar arrays on sapphire substrates by polymer-assisted deposition

Jia Luo,1 Hongtao Ren,2,3 Xi Zhang,2 and Gang Xiang2,a)

AFFILIATIONS
1 School of Physical Science and Technology, Key Laboratory of Advanced Technology of Materials Ministry of Education of China, Southwest Jiao tong University, Chengdu 610031, China
2 College of Physics, Sichuan University, Chengdu 610064, China
3 China Key Laboratory for Nonequilibrium Synthesis and Modulation of Condensed Matter (MOE), School of Science, Xi’an Jiaotong University, Xi’an 710049, China

a) Author to whom correspondence should be addressed: gxiang@scu.edu.cn

ABSTRACT
Vertically aligned ferromagnetic ZnO nanopillar arrays have been fabricated on single-crystal sapphire substrates through polymer-assisted deposition. X-ray diffraction and transmission electron microscopy analysis show that the arrays are ZnO hexagonal crystal structure along the c-axial direction. The existence of room temperature ferromagnetism of the arrays was confirmed by the superconducting quantum interference device measurements. The enhancement of ferromagnetism in ZnO nanopillar arrays is found to be correlated with the increase in Zn vacancies and the decrease in oxygen interstitials, which was shown by photoluminescence measurements of the samples. Our results provide a viable way to fabricate ferromagnetic vertical arrays of ZnO nanopillars.

© 2020 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/). https://doi.org/10.1063/1.5135332

INTRODUCTION
ZnO is a versatile material that exhibits semiconducting, piezoelectric, photocatalytic, and ferromagnetic properties. ZnO nanostructures with different sizes, dimensions, and morphologies are highly correlated with emerging commercial applications and functional devices; vertically aligned ZnO nanowires (NWs) are a typical representative, which has a variety of applications, including nanowire dye-sensitized solar cells, photocatalysts, piezoelectric nanogenerators, and piezoelectric transistors. A variety of growth methods have been reported for the synthesis of vertical arrays of ZnO NWs. However, most of the previous studies focused on in situ growth conditions that required preparation of seed layers, incorporation of noble metal catalysts, or usage of expensive substrates, post-growth treatments. In addition, to the best of our knowledge, the ferromagnetism of pure ZnO nanopillar (NP) arrays has not been reported.

In this work, we explore a novel approach to produce ZnO nanopillar (NP) arrays. Based on previous work in which both room temperature ferromagnetism (RTFM) ZnO thin film (TF) and horizontal ZnO nanowire arrays have been synthesized by polymer-assisted deposition (PAD) and post-growth annealing, we will demonstrate that the vertical arrays of pure ZnO NPs can be fabricated by using post-growth annealing treatment on ZnO thin films prepared by PAD. Further magnetization measurements and photoluminescence (PL) measurements reveal that the existence and enhancement of RT ferromagnetism of the arrays are correlated with the defects in ZnO samples. Our results may have potential applications in ZnO-based magnetic and spintronic devices at the nanoscale.

EXPERIMENT
Vertically aligned ZnO NP arrays were fabricated on the basis of undoped ZnO thin films prepared by PAD with zinc nitrate
hexahydrate (purity ≥ 99.0%) and ethylene imine polymer (purity = 99%). The details of ZnO thin film growth process were described elsewhere. The as-grown films served as the precursors were then put into a double temperature zone tube furnace for annealing as follows: (1) annealing in oxygen atmosphere at 900 °C for 3 min with a heating and cooling rate of 75 °C/s and (2) annealing in oxygen atmosphere under 2800 Pa and 500 °C for 10 min.

The crystalline structure of vertically aligned ZnO NP arrays was then characterized by X-ray diffraction (XRD) with Cu Kα radiation and a transmission electron microscope (TEM). The morphology of the samples was observed by using a scanning electronic microscope (SEM). Magnetic measurements were performed using a superconducting quantum interference device (SQUID) with the magnetic field applied parallel to the sample surface at 300 K. The photoluminescence (PL) measurements were performed with an excitation wavelength of 325 nm at RT, and the results were obtained from the alcoholic solutions of the ZnO NP arrays scraped off from the substrate.

RESULTS AND DISCUSSION

The morphology of the sample on the substrate was examined by SEM. Figures 1(a) and 1(b) show the top view SEM images of the well-aligned ZnO NP arrays on the sapphire substrate. We can clearly observe hexagonal facet from the top of ZnO NPs. Figures 1(c) and 1(d) show that the diameters of the NPs are about 100 nm and the lengths are 200–400 nm.

To confirm the crystal structure and the growth direction of the ZnO nanopillars, TEM measurements were carried out. Figure 2(a) is the bright field TEM image of a NP with a diameter of around 100 nm. The electron diffraction spectroscopy (EDS) analysis in Fig. 2(b) reveals that the ZnO NPs are mainly composed of Zn and O, with the Cu signal from the Cu supporting grid. Figures 2(c) and 2(d) show the high-resolution TEM (HRTEM) image of ZnO NP and the FFT image of the HRTEM picture, respectively. The spacing of 0.26 nm between adjacent lattice planes corresponds to the distance between two (002) crystal planes, indicating that (0001) was the growth direction of the ZnO NPs. This (0001) preferential growth direction is also reflected in the high diffraction intensity of (002) peaks in Fig. 3(b).

Figure 3(a) depicts the magnetization vs the magnetic field curves of ZnO TF and NP arrays, which was measured by SQUID at room temperature. The samples exhibit clear hysteresis loops, indicating that ZnO TF and NP arrays are ferromagnetic at RT. The magnetization of ZnO NP arrays was 16.7 emu/cm³, stronger than 2.5 emu/cm³ of ZnO TF. It is known that the ferromagnetism observed in pure ZnO nanostructure has encouraged expectations for spintronics applications, and the origin of RTFM has been studied extensively, various defects considered to play a key role in RTFM of ZnO, such as anionic vacancy clusters, Zn interstitials (Zni), O vacancies (V_O), and zinc vacancy (V_Zn). It is interesting to note that post-annealing shows a robust effect on the enhancement of the ferromagnetic ordering of the sample. In order to explore the mechanism for the enhancement of ferromagnetism, we have performed the XRD and PL measurements. For all samples, XRD results indicate that ZnO TF and NP are polycrystalline wurtzite structures and no second phase was observed [see Fig. 3(b)]. After post-annealing, the (004) main peak in the as-grown sample disappears, indicating the formation of more defects in ZnO NP samples.

PL spectrum is an effective method to detect defects in ZnO such as oxygen vacancies, Zn interstitials, and Zn vacancies, and then it can be used to study magnetism. Figure 4(a) is the PL spectra for ZnO TF and ZnO NP samples measured at RT. We can see a few emission peaks in the PL spectra of ZnO TF and ZnO NP.
samples: a UV band-edge emission at about 3.27 eV is caused by the band-to-band transition and free exciton recombination, a peak around 2.68 eV attributed to Zn\(^{1+}\) vacancies, and a visible emission centered around 1.83 eV that is generally related to oxygen interstitials (O\(_i\)). The CIE diagram of our samples is shown in Fig. 4(b), and the corresponding Commission Internationale de L’Eclairage \(x, y\) coordinates are (0.21, 0.20) and (0.23, 0.23) for ZnO TF and ZnO NP, respectively. From the PL spectrum, we can see that compared with the thin film, the position of nanopillar arrays’ characteristic peak was redshifted from 379 nm to 384 nm; corresponding to the CIE diagram, we can see ZnO TF and ZnO NP have different emission colors, and the color coordinates of ZnO NP deviate from blue-purple regions. In addition, it can be seen from the PL spectrum that the characteristic peak of ZnO NP is stronger than the thin film, and the peak caused by defects (at 678 nm) is weakened, which indicates a better potential of optical applications of the ZnO NP samples. It is worth noting that the peak at 2.68 eV corresponding to Zn\(^{1+}\) vacancies of ZnO NP is obviously higher than that of ZnO TF, while the peak attributed to O\(_i\) defects decreased significantly, indicating that the concentration of O\(_i\) in ZnO NP was lower than that in ZnO TF. These two observations are closely correlated with the fact that ZnO NP exhibits a higher magnetization than ZnO TF. The published experimental and theoretical works point out that the ferromagnetism of ZnO can be improved by an increase in the concentration of Zn vacancies due to the contribution of the unpaired 2p electrons of the O site around Zn vacancies. Since thermal annealing can not only make oxygen interstitials move to vacancy sites or escape but also result in more Zn vacancies in oxygen atmosphere, the potential mechanism of ferromagnetic enhancement can then be understood as follows: O\(_i\) defects in the ZnO NP samples were reduced after post-growth annealing in oxygen atmosphere, enhancing the ferromagnetism of the samples and facilitating the formation of Zn vacancies at the same time, and then the Zn vacancies made further contributions to the ferromagnetic ordering of the samples. As a result, the ZnO NP arrays obtained from post-growth annealing in oxygen atmosphere will have stronger ferromagnetic properties than ZnO TF.

**CONCLUSION**

In conclusion, we used the PAD method to realize the growth of vertically aligned ZnO NP arrays at a low temperature of 500 °C. During this process, no metal catalyst or ZnO seeds was used. The SEM images showed the distribution of diameter and length. Furthermore, the ZnO NP arrays are of high crystallinity and RTFM. Combining the analysis of PL spectrum and CIE diagram, we think that ZnO NP arrays have better luminescence properties than ZnO TF. Our study also shows that the improvement of ferromagnetism of the samples is related to the decrease in oxygen interstitials (O\(_i\)) and the increase in Zn vacancies (V\(_{Zn}^{1+}\)), while oxygen vacancies have no positive contribution to the ferromagnetic ordering in the samples. The discovery in our work provides a viable way to grow ferromagnetic ZnO NP arrays on a large scale, which would be very helpful for the fabrication of a facile and controlled nanometer array device.
ACKNOWLEDGMENTS

This work was supported by the National Key R&D Plan of China through Grant No. 2017YFB0405702.

REFERENCES

1. C. B. Ong, L. Y. Ng, and A. W. Mohammad, Renewable Sustainable Energy Rev. 81, 536 (2018).
2. P. Kumar, L. Panchakarla, S. V. Bhat, U. Maitra, K. Subrahmanyam, and C. Rao, Nanotechnology 21, 385701 (2010).
3. A. Qurashi, K. Subrahmanyam, and P. Kumar, J. Mater. Chem. C 3, 11995 (2015).
4. M. I. B. Utama, Q. Zhang, S. Jia, D. Li, J. Wang, and Q. Xiong, ACS Nano 6, 2381 (2012).
5. Y. Xia, P. Yang, Y. Sun, Y. Wu, B. Mayers, B. Gates, Y. Yin, F. Kim, and H. Yan, Adv. Mater. 15, 353 (2003).
6. C. Zhao, A. Chen, X. Ji, Y. Zhu, X. Gui, F. Huang, and Z. Tang, Mater. Lett. 154, 40 (2015).
7. L. E. Greene, M. Law, D. H. Tan, M. Montano, J. Goldberger, G. Somorjai, and P. Yang, Nano Lett. 5, 1231 (2005).
8. H. J. Fan, W. Lee, R. Scholtz, A. Dadgar, A. Krost, K. Nielsch, and M. Zacharias, Nanotechnology 16, 913 (2005).
9. Y. J. Kim, C.-H. Lee, Y. J. Hong, G.-C. Yi, S. S. Kim, and H. Cheong, Appl. Phys. Lett. 89, 163128 (2006).
10. H. Ren, G. Xiang, G. Gu, and X. Zhang, Mater. Lett. 122, 256 (2014).
11. H. Ren, G. Xiang, J. Luo, D. Yang, and X. Zhang, Mater. Lett. 234, 384 (2019).
12. H. Ren, G. Xiang, G. Gu, X. Zhang, W. Wang, P. Zhang, B. Wang, and X. Cao, J. Nanomater. 2012, 6.
13. S. Banerjee, M. Mandal, N. Gayathri, and M. Sardar, Appl. Phys. Lett. 91, 182501 (2007).
14. X. Zhang, Y. Cheng, L. Li, H. Liu, X. Zuo, G. Wen, L. Li, R. Zheng, and S. Ringer, Phys. Rev. B 80, 174427 (2009).
15. D. K. Mishra et al., Physica B 405, 2659 (2010).
16. S. Mal, J. Narayan, S. Nori, J. Prater, and D. Kumar, Solid State Commun. 150, 1660 (2010).
17. P. Zhan, W. Wang, C. Liu, Y. Hu, Z. Li, Z. Zhang, P. Zhang, B. Wang, and X. Cao, J. Appl. Phys. 111, 033501 (2012).
18. Q. Wang, Q. Sun, G. Chen, Y. Kawazoe, and P. Jena, Phys. Rev. B 77, 205411 (2008).
19. B. Das, P. Kumar, and C. Rao, J. Cluster Sci. 23, 649 (2012).
20. L. Zhuge, X. Wu, Z. Wu, X. Chen, and Y. Meng, Scr. Mater. 60, 214 (2009).
21. K. Vanheusden, W. Warren, C. Seager, D. Tallant, J. Voigt, and B. Gnade, J. Appl. Phys. 79, 7983 (1996).
22. Y. Heo, D. Norton, and S. Pearton, J. Appl. Phys. 98, 073502 (2005).
23. R. Cross, M. De Souza, and E. S. Narayanan, Nanotechnology 16, 2188 (2005).