

Dynamic Observation of Functional Metal Oxide Conversion Behaviors in Fe/ZnO Interfaces

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Abstract

Atomic-oriented heterostructures improve the performance of transition metal oxide-based devices. An in-depth understanding of the solid-state reaction mechanism at the atomic scale via in situ transmission electron microscopy (TEM) can help us to controllably synthesize the oriented heterostructure. In this work, the solid-state reaction process was directly observed. It was demonstrated that electron beam irradiation (EBI) could impel the reaction at a relatively low temperature. Significantly, a special two-step process of solid-state reaction was demonstrated, which Fe diffused along boundaries of ZnO and then reacted along the slip system of ZnO. The microstructure of reactant and products could be precisely controlled. Moreover, controllable Fe₃O₄ twins in the same direction through the (11 $\bar{1}$) plane could methodically solve the random-orientation problem of twins. This work provided a novel nanofabricated approach to produce oriented transition metal oxide heterostructures while visualizing the mechanism of solid-state reaction forming process, which allows for further investigation of transition metal oxide applications.

1. Introduction

Recently, transition metal oxides are of great interest due to their wide physical characteristics.[1, 2] However, at the age of pursuing the devices further scaling down and better performance, transition metal oxide heterostructure plays an important role to obtain the multifunction devices with the same, even smaller volume. Previous works showed that heterostructures could combine or improve the functions of two different materials, which could be able to enhance the performance of devices.[3] Besides, the performance of devices is highly correlated with microstructure and defects. Among the various defects, twin attracts great attention due to its wide range applications because of its excellent physical and mechanical properties.[4] Therefore, taking control of the twins has become an important issue.

The fundamental transformation of twins and heterostructures would lead from atomic diffusion.[5] Therefore, a detailed understanding of the transformation process at the atomic scale is necessary. Among the various analysis

methods, *in-situ* TEM could capture the whole process during the transformation and revealing the atomic-scaled microstructure. Therefore, in-situ TEM is the most powerful approach for revealing the phase transformation, the dynamics at the interface of two materials and the growth of the microstructure.[6]

Recently, ZnO and Fe₃O₄ have been widely used in many electronic devices.[7, 8] ZnO/Fe₃O₄ heterostructure could develop spintronics. Previous research also demonstrated that Fe/ZnO bilayer could improve the performance of magnetic devices.[9] However, the solid-state reaction process of ZnO based heterostructures is still not discussed in detail. In this work, the details of solid-state reaction process were clearly revealed. And based on the mechanism, a new approach to control the microstructure was provided.

2. Methods, Results and Discussion

Methods

Oriented ZnO thin film was produced by Pulsed Laser Deposition (PLD) system, which grew on Si (001) substrate. Fe and SiO₂ (anti-oxidized protection layer) were deposited by Electron Beam Evaporation. TEM sample was produced by Focus Ion Beam (FIB), and then transferred on the heating chips, which was mounted on an *in-situ* TEM holder (Protochips Aduro300). The TEM images is carried out in JOEL F200. And Fe/ZnO bilayer was performed at the temperature of 650 degree C.

Results and Discussion

Figure.1a shows the cross-section of the sample. The microstructure of the oriented ZnO thin film was composed of nano column. Each column was slightly rotated along [0001]_{ZnO}, which makes all the ZnO thin film maintain the same out-plane direction. The sample was annealed at the temperature of 650 degree C, and the TEM image of annealed sample was shown in figure.1c. According to the images and the corresponding FFTs shown in figure.1 d-e, we could find that the closest packing planes of ZnO and Fe₃O₄ were parallel to each other. The point analysis of energy dispersive spectrometer (EDS) shown in Figure.1f also shows that Fe₃O₄/ZnO heterostructure was formed after annealing process.

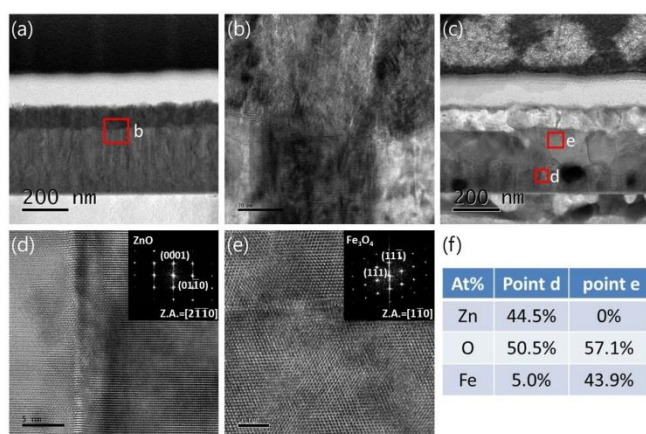
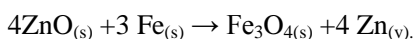


Fig. 1 TEM images and EDS point analysis of the sample.

The transformation could be described as follow:



Because the atomic packing factor of Fe_3O_4 (69%) is higher than ZnO (55.4%), voids would appear after annealing process. The driving force in this work was different from the oxidation-reduction. This is because thermodynamics of oxidation-reduction potential would be different at high temperature, which could be determined by *Nernst equation*. The details were shown in the previous research of our group.[10]

To realize the details during transformation process, we performed a high magnification experiment. A series of TEM images during the *in-situ* experiment was shown in figure.2. We could find that the reaction was along the horizontal direction in every atomic layer. This direction is parallel to the closest packing plane of ZnO . The slip system on closet packing plane has higher atomic density, which makes the reaction need lower energy. So we supposed that the reaction was along $\langle 2\bar{1}10 \rangle$ of ZnO . And TEM observation would let the vectors be projected on the screen, which made the vector look like the horizontal direction.

3. Conclusions

In summary, the $\text{Fe}_3\text{O}_4/\text{ZnO}$ heterostructure was successfully synthesized, and the solid-state reaction process was directly observed via *in-situ* TEM. A unique two-step process was demonstrated, which Fe diffused along the boundaries of ZnO , and react along the slip system of ZnO . Based on this mechanism, the closest packing planes of reactant and product could be precisely controlled. Therefore, twins could also be controlled in the same direction. And this made ZnO and Fe_3O_4 in a specific orientation relationship of $[0001]_{\text{ZnO}} // [11\bar{1}]_{\text{Fe}_3\text{O}_4}$. This work provided a novel nanofabricated approach to produce oriented transition metal oxide heterostructures while visualizing the mechanism of solid-state reaction forming process, which allows for further investigation of transition metal oxide applications.

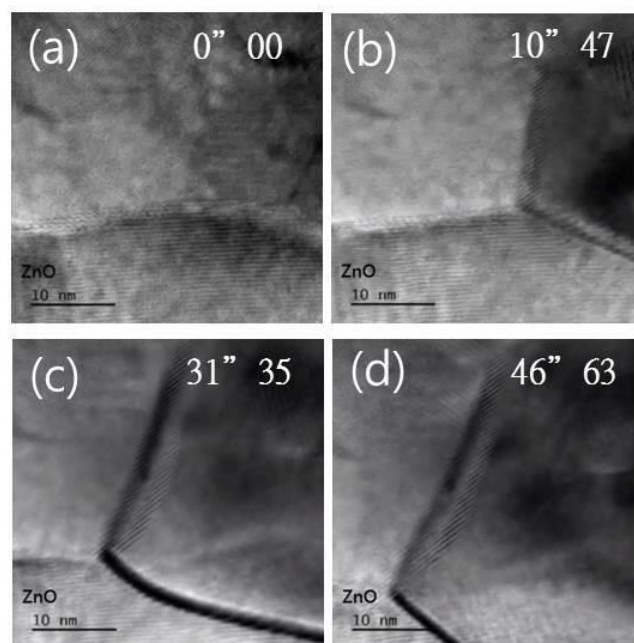


Fig. 2 Series of TEM images during reaction process

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References

- [1] J. Baumgartner, A. Dey, P.H.H. Bomans, C. Le Coadou, P. Fratzl, N.A.J.M. Sommerdijk, D. Faivre, *Nature Materials* 12 (2013) 310.
- [2] J.-Y. Chen, C.-W. Huang, C.-H. Chiu, Y.-T. Huang, W.-W. Wu, *Advanced Materials* 27(34) (2015) 5028-5033.
- [3] M. Lee, J.-W. Jo, Y.-J. Kim, S. Choi, S.M. Kwon, S.P. Jeon, A. Facchetti, Y.-H. Kim, S.K. Park, *Advanced Materials* 30(40) (2018) 1804120.
- [4] B. Wang, Z. Zhang, J. Cui, N. Jiang, J. Lyu, G. Chen, J. Wang, Z. Liu, J. Yu, C. Lin, F. Ye, D. Guo, *ACS Applied Materials & Interfaces* 9(35) (2017) 29451-29456.
- [5] L. Zou, C. Yang, Y. Lei, D. Zakharov, J.M.K. Wiezorek, D. Su, Q. Yin, J. Li, Z. Liu, E.A. Stach, J.C. Yang, L. Qi, G. Wang, G. Zhou, *Nature Materials* 17 (2017) 56.
- [6] K.-C. Chen, W.-W. Wu, C.-N. Liao, L.-J. Chen, K.N. Tu, *Science* 321(5892) (2008) 1066-1069.
- [7] Y.-J. Chen, F. Zhang, G.-g. Zhao, X.-y. Fang, H.-B. Jin, P. Gao, C.-L. Zhu, M.-S. Cao, G. Xiao, *The Journal of Physical Chemistry C* 114(20) (2010) 9239-9244.
- [8] D. Gilks, K.P. McKenna, Z. Nedelkoski, B. Kuerbanjiang, K. Matsuzaki, T. Susaki, L. Lari, D. Kepaptsoglou, Q. Ramasse, S. Tear, V.K. Lazarov, *Scientific Reports* 6 (2016) 29724.
- [9] W.-C. Lin, P.-C. Chang, C.-J. Tsai, T.-C. Hsieh, F.-Y. Lo, *Applied Physics Letters* 103(21) (2013) 212405.
- [10] J.-Y. Chen, C.-W. Huang, W.-W. Wu, *Small* 14(6) (2018) 1702877.