Materials Letters 144 (2015) 12–14

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Surface-polarity-dependent ferromagnetism in arsenic-implanted ZnO films prepared by MBE

Minju Ying [a,*], Wei Cheng [a], Xiaoxiao Wang [a], Bin Liao [a], Xu Zhang [a], Zengxia Mei [b], Xiaolong Du [b], Steve M Heald [c], Harry J. Blythe [d], A. Mark Fox [d], Gillian A. Gehring [d,**]

[a] Key Laboratory of Beam Technology and Material Modification of Ministry of Education, College of Nuclear Science and Technology, Beijing Normal University, Beijing 100875, P. R. China
[b] Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, P. R. China
[c] Advanced Photon Source, Argonne National Laboratory, Argonne, IL 60439, United States of America
[d] Department of Physics and Astronomy, Hicks Building, University of Sheffield, Sheffield S3 7RH, United Kingdom

ARTICLE INFO

Article history:
Received 8 November 2014
Accepted 2 December 2014
Available online 9 December 2014

Keywords:
Semiconductors
Thin films
RT Ferromagnetism
Ion implantation

ABSTRACT

O-polar and Zn-polar ZnO films were prepared by rf-plasma assisted molecular beam epitaxy (MBE) on sapphire substrates. Arsenic ions have been implanted into high quality ZnO with a definite polarity. Substantial temperature-independent ferromagnetism has been observed for both films, with the O-polar film having approximately twice the magnetization as the Zn-polar film. The saturation magnetization is shown to be due to the defects introduced during implantation, rather than to local moments associated with the As ion. Rutherford Backscattering/Channeling and optical absorption measurements confirm that the implantation introduces more defect states in the O-polar films, while X-ray absorption near-edge structure measurements show that the environment of the arsenic ions was similar for both polarities.

1. Introduction

ZnO-based dilute magnetic semiconductors have attracted much attention over the past decade as promising materials for application in spintronic devices[1]. Numerous papers report that the inclusion of transition metal (TM) dopants in ZnO leads to room temperature (RT)ferromagnetism[2,3], but RT ferromagnetism has also been observed in non-TM or un-doped ZnO, which implies that defects play an important role in establishing the long-range ferromagnetism in these materials [4–7]. Theoretical predictions indicate that ferromagnetism can occur as a result of the formation of *p*–type As_{Zn}-2 V_{Zn} complexes [8], but the doping process also creates many vacancies, interstitials and antisites [9], and the contribution of these lattice defects has to be considered as well.

In this article we investigate the relative importance of *p*–type complexes and lattice defects in producing magnetism in As implanted ZnO films. There is no inversion symmetry along the c-axis in wurtzite ZnO, so that Zn-polar ZnO(0001) and O-polar ZnO(000–1) have opposite polarizations and differ both structurally and chemically [10–12]. The influence of ZnO surface polarity on introducing defects during As implantation process and on the resulting magnetism has been considered in this work. To the best of our knowledge, there are no reports on this issue so far.

We report on measurements on high quality polar ZnO films doped with As by ion implantation. We measure substantial saturation moments in As doped films of both polarities, with the O-polar films having approximately twice the magnetization as the Zn-polar films. We conclude that the lattice disorder introduced by implantation, rather than local moments on the As sites, is primarily responsible for the observed magnetization, with the difference between the O-polar and Zn-polar films being caused by differing defects densities.

2. Experimental details

A radio-frequency plasma-assisted MBE system (OmniVac) was used to grow single crystal ZnO films of thickness 400 nm on sapphire substrates. The controlled growth of unipolar ZnO films was realized by interface engineering using an MgO buffer layer on α-Al_2O_3 (0001) [13]. High purity As ions were introduced into both O-polar and Zn-polar ZnO films by ion implantation. A sequence of four implantation energies (400KeV, 200KeV, 100KeV, and 30KeV)

* Corresponding author. Tel.: +86 10 6220 8249.
** Corresponding author. Tel.: +44 114 222 4299.
E-mail addresses: mjying@bnu.edu.cn (M. Ying), g.gehring@sheffield.ac.uk (G.A. Gehring).

http://dx.doi.org/10.1016/j.matlet.2014.12.017
0167-577X/

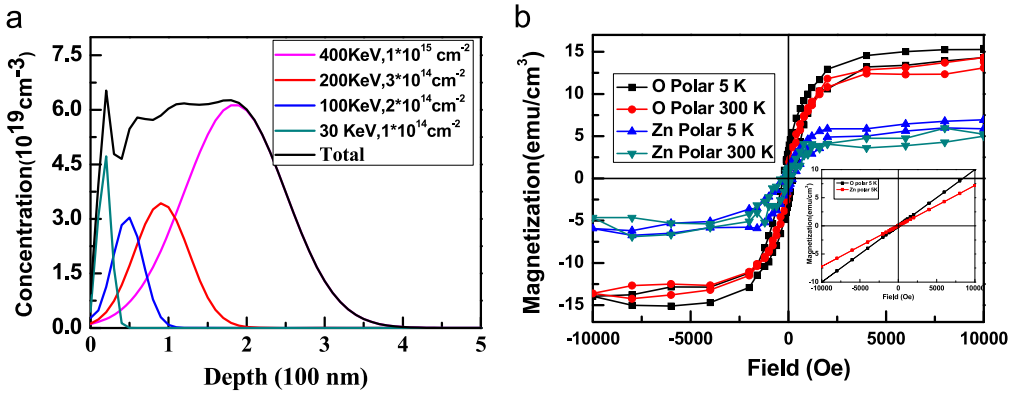

Fig. 1. (Color on line) (a) SRIM simulated As distribution in ZnO (b) Magnetization data for As doped O polar and Zn polar ZnO films at 5 and 300 K.The inset shows the paramagnetism at 5 K.

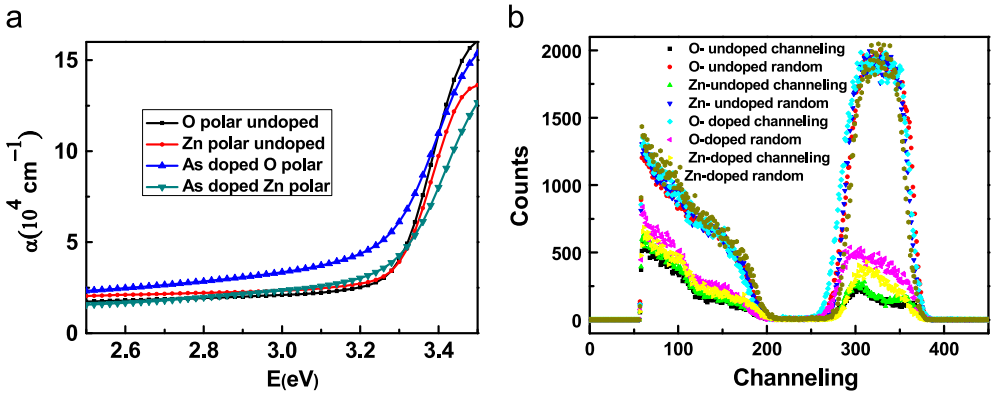

Fig. 2. (Color on line)(a) Optical loss coefficient α of the O- and Zn-polar films before and after implantation. (b) Rutherford backscattering/channeling spectra for As-doped O-polar and Zn-polar ZnO films.

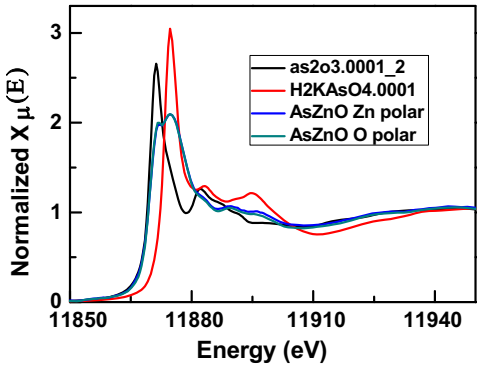

Fig. 3. (color on line) The XANES data for the As-doped samples compared with some As^{3+} and As^{5+} standards.

was used to produce a nearly even distribution of As ions throughout the films. SRIM simulations reveal that an As concentration of about 6×10^{19} cm^{-3} was obtained from the film surface to a depth of more than 200 nm, as shown in Fig. 1(a). Rutherford Backscattering/Channeling (RBS/C) measurements were carried out to characterize the implantation-induced disorder, while information about the As sites in the ZnO films was obtained by X-ray absorption near-edge structure (XANES).

The As-doped films should in principle have p-type conductivity, but electrical measurements show that both the as-grown and ion-implanted ZnO films are all highly resistive, indicating a lack of mobile carriers. Optical transmission spectra were measured to find the band gaps and to check for the film quality after implantation. Hysteresis loops were taken with a superconducting quantum interference device (SQUID) at 5 K and 300 K. The magnetizations of the doped films were found by subtracting the diamagnetic signal measured for the undoped ZnO films on the substrate.

3. Results and discussion

Magnetization hysteresis loops for the O-polar and Zn-polar films at 5 K and 300 K are shown in Fig. 1(b), after separating the ferromagnetic and paramagnetic contributions. The saturation magnetizations measured for both the O-polar and Zn-polarfilms are substantial: ~15 emu cm^{-3} and ~6 emu cm^{-3} at 4 K respectively. These large magnetizations could be related either to the local moments associated with the implanted As ions or to the lattice defects produced by the implantation process. In the former case we can estimate a lower bound for the magnetization of ~30 μ_B and ~12 μ_B per As-ion for the O-polar and Zn polar films respectively by assuming that the As doping level is as high as 6×10^{19} cm^{-3} throughout the whole 400 nm thickness of the film. These values seem unrealistic and are very much higher than the value of 1 μ_B predicted for the As_{Zn}-2 V_{Zn} center [8]. Hence we deduce that polarized lattice defects are primarily responsible for the large magnetizations, with the weak temperature dependence observed for our films being typical for defect-induced ferromagnetism [14]. The larger ferromagnetic and the paramagnetic responses of the O-polar film can then be explained by its larger defect density, confirmed by the optical transmission and RBS/C data presented below.

The optical loss coefficients for the undoped and As-doped O-polar and Zn-polar films are shown in Fig. 2(a). It is clear that the implantation has led to the introduction of many defects that have caused an increase in the scattering losses below the band gap and less sharp absorption edges for both films, with significantly more for the O-polar film. The energy band gap is 3.34 eV for both the undoped films but after As implantation the gap for the Zn-polar film is almost unchanged whereas that for the O polar film is reduced to 3.31 eV due to defect states formed near the band edge.

Fig. 2(b) shows the random and aligned Rutherford backscattering spectra for the undoped and As-doped O-polar and Zn-polar ZnO samples. Extensive dechanneling is observed for both films after As implantation, which is primarily attributed to implantation-induced lattice disorder. The larger back scattering signal observed in the aligned spectra of the As-implanted O-polar film implies that much more lattice disorder is induced in the implantation process for that film, in agreement with its larger optical loss coefficient. The ratio of the backscattering yields of aligned and random spectra in the near-surface region (i.e. the minimum yield) increases from 9.8% to 24.5% for the O-polar ZnO and from 11.3% to 17.3% for the Zn-polar films this indicates that the Zn polar films were initially more disordered but that the increase in the disorder after implantation was very significantly higher for the O-polar films. Hence the As doped O-polar films contain more vacancies, interstitials and antisites.

Fig. 3 shows the As XANES data compared with some As^{3+} and As^{5+} standards showing that there is an approximately equal mixture of As^{3+} and As^{5+} for both films. The XANES data shows little difference between the O-polar and Zn-polar films, which confirms that the larger magnetism observed in the O-polar film is caused by its larger lattice disorder, as discussed above.

4. Conclusions

Arsenic ions have been implanted into high quality O-polar and Zn-polar ZnO films prepared by rf-plasma assisted MBE on sapphire substrates. Substantial room temperature ferromagnetism has been observed for both films, but the saturation magnetism for O-polar ZnO is more than twice as large as that of Zn-polar ZnO. The values of the observed saturation magnetizations are considerably larger than the values expected from As point defects, and the origin of the magnetism is therefore attributed to lattice defects introduced by the ion implantation process. RBS/Channeling and optical transmission measurements confirm that much more lattice disorder is introduced by implantation in the O-polar ZnO film.

This work demonstrates that ion implantation, without annealing, is a good method to introduce magnetic defects into insulating ZnO films and that in this case the implantation process itself may be more important than the atomic specie implanted.

Acknowledgments

This work is financially supported by National Natural Science Foundation of China under Grant Nos. 10604007, 10975020, 51171028.Use of the Advanced Photon Source, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science by Argonne National Laboratory, was supported by the U.S. DOE under Contract No. DE-AC02-06CH11357.

References

[1] Ohno H. Making nonmagnetic semiconductors ferromagnetic. Science 1998 951–6.
[2] Pan F, Song C, Liu XJ, Yang YC, Zeng F. Ferromagnetism and possible application in spintronics of transition-metal-doped ZnO films. Mater Sci Eng 2008;62:1–35.
[3] Behan AJ, Mokhtari A, Blythe HJ, Score D, Xu XH, Neal JR, et al. Two Magnetic regimes in doped ZnO corresponding to a dilute magnetic semiconductor and a dilute magnetic insulator. Phys Rev Lett 2008;100:047206.
[4] Zhan P, Wang WP, Liu C, Hu Y, Li ZC, Zhang ZJ, et al. Oxygen vacancy–induced ferromagnetism in un-doped ZnO thin films. J Appl Phys 2012;111:033501.
[5] Xing GZ, Lu YH, Tian YF, Yi JB, Lim CC, Li YF, et al. Defect-induced magnetism in undoped wide band gap oxides: zinc vacancies in ZnO as an example. AIP Adv 2011;1:022152.
[6] Straumal BB, Mazilkin AA, Protasova G, Myatiev AA, Straumal PB, Goering E, et al. Amorphous grain boundary layers in the ferromagnetic nanograined ZnO films. Thin Solid Films 2011;520:1192–4.
[7] Zhang X, Cheng YH, Li LY, Liu H, Zuo X, Wen GH, et al. Evidence for high-T_c ferromagnetism in $Zn_x(ZnO)_{1-x}$ granular films mediated by native point defects. Phys Rev B 2009;80:174427.
[8] Lu YB, Dai Y, Guo M, Lin Y., Huang BB. Investigation of magnetic properties induced by group-V element in doped ZnO. Phys Chem Chem Phys 2013;15:5208–14.
[9] Zhou SQ. Defect-induced ferromagnetism in semiconductors: a controllable approach by particle irradiation. Nucl Instr Meth B 2014;326:55–60.
[10] Dulub O, Diebold U, Kresse G. Novel stabilization mechanism on polar surfaces: ZnO(0001)-Zn. Phys Rev Lett 2003;90:016102.
[11] Lautenschlaeger S, Sann J, Volbers N, Meyer BK, Hoffmann A, Haboeck U, et al. Asymmetry in the excitonic recombinations and impurity incorporation of the two polar faces of homoepitaxially grown ZnO films. Phys Rev B 2008;77:144108.
[12] Allen MW, Zemlyanov DY, Waterhouse GIN, Metson JB, Veal TD, McConville CF, et al. Polarity effects in the x-ray photoemission of ZnO and other wurtzite semiconductors. Appl Phys Lett 2011;98:101906.
[13] Liu ZL, He X, Mei ZX, Liang HL, Gu L, Duan XF, et al. Polarity-manipulation based on nanoscale structural transformation on strained 2D MgO. J Phys 2014;47:105303 D:Appl Phys 2014;47:105303.
[14] Kopnov G, Vager Z, Naaman R. New magnetic properties of silicon/silicon oxide interfaces. Adv Mater 2007;19:92.