Extended Abstracts of the 2018 International Conference on Solid State Devices and Materials, Tokyo, 2018, pp727-728

Investigation of Nanoscale Voids in Sb-Doped p-Type ZnO Nanowires

Ken C. Pradel[1], Jun Uzuhashi[2], Toshiaki Takei[1], Tadakatsu Ohkubo[2], Kazuhiro Hono[2], Naoki Fukata[1]

[1] International Center for Materials Nanoarchitectronics (MANA)
National Institute for Materials Science (NIMS)
1-1 Namiki, Tsukuba, Ibaraki, 305-0044, Japan
Phone: +81-029-860-4769, E-mail: pradel.ken@nims.go.jp
[2] Research Center for Magnetic and Spintronic Materials
National Institute for Materials Science (NIMS)
1-2-1 Sengen, Tsukuba, Ibaraki, 305-0047, Japan

Abstract

While zinc oxide is an exciting material for research, its applications are limited by the absence of a stable p-type dopant. It was recently discovered that antimony can be used to grow stable p-type ZnO nanowires, but with a curious side effect that voids form inside the nanowire. Up until this point, these voids have only been used as a sign of successful doping, and research onto their formation and properties has been limited. In this work, a variety of characterization tools were used to probe these voids to learn more about their formation and makeup. It was found that a zinc antimony oxide phase forms at the bottom of the voids, which may help stabilize the dopant. More curiously though, it was found that water gets trapped inside the voids during growth, which presents new means of nanowire functionalization.

1. Introduction

Numerous papers have been published on zinc oxide and its applications due to its numerous advantageous properties. It is a cheap, abundant material, and easy to form nanomaterials with techniques such as MOCVD and the hydrothermal method. However, one curious point has been the difficulty in finding a stable p-type dopant. While there are numerous reports on p-type ZnO, few mention the long-term stability, making its reproducibility questionable.

One of the few exceptions has been antimony doping, where one group reported ZnO that remained p-type for over 18 months. ZnO was doped with an antimony glycolate using a low temperature hydrothermal method, to grow arrays of p-type nanowires. This method has proven to be reproducible, and has been adapted for both piezoelectric and optoelectronic devices. The material could be easily grown to form both homojunctions with naturally n-type ZnO, or heterojunctions with silicon, and proved to be an effective photodetector in both cases.

Despite the numerous investigations into its applications, relatively little work has been done on the fundamental properties of this material. A follow-up to the original report on this method demonstrated that voids form inside the nanowire as a result of doping. They reported that an Sb precipitate forms during growth that forms an inversion domain boundary. As the growth of ZnO is slower on the precipitate than the surrounding nanowire matrix, the nanowire continues growing normally around it, eventually forming a void. The Sb planar defect stabilizes an extra plane of oxygen atoms, which was found to act as electron acceptors via density functional theory calculations. This runs contrary to previous reports on Sb doped ZnO which explained p-type conductivity via a SbZn-2VZn complex. These voids are a peculiar defect, and up until now has been used as little more than a telltale sign of successful doping. In this work, we use a variety of characterization techniques to investigate the fundamental properties of Sb-doped p-type ZnO. In addition to the standard measurement tools such as scanning electron microscopy, transmission electron microscopy, and x-ray diffraction, Raman spectroscopy and atom probe tomography were employed. By combining all the information gained from these methods, a more complete picture of the properties of the Sb-doped ZnO was made, especially with regards to the void structures.

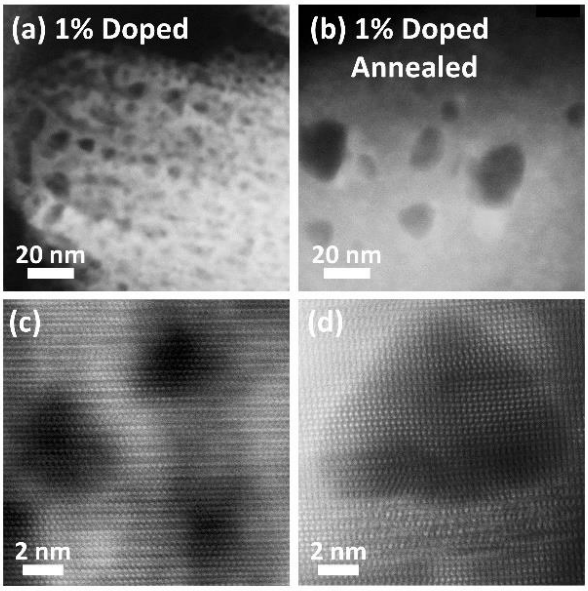

Fig. 1 HRTEM images of Sb-doped ZnO nanowires before and after annealing.

2. Methods

Zinc oxide nanowires were grown using a hydrothermal method. The substrate of choice was an n-type Si wafer etched in a hydrofluoric acid buffer solution to remove the native oxide layer. The substrate was sputtered with 100 nm of ZnO which served as a seeding layer for nanowire growth. The growth solution consisted of 25 mM zinc nitrate, 12.5 mM of hexamethylenetetramine (HMTA), 0.7 mM sodium citrate, and 0.5 M ammonium hydroxide. To make p-type nanowires, 0.25 mM of an antimony glycolate solution was added, corresponding to 1% doping. The preparation of this solution is described in detail in previous reports. Sodium citrate is added to the solution to encourage lateral growth in the nanowires, causing them to grow into densely packed films. The substrate was placed floating on the solution surface with the seed layer side down, and heated in an oven at 75°C for 1 hour to allow the nanowires to grow. The substrate was floated to prevent homogeneously nucleated waste material in the solution from precipitating on the substrate and interfering with growth. Following growth, nanowires were annealed at 950°C for 30 minutes in an oxygen environment in a rapid thermal annealing furnace to activate the dopant.

2. Results and Discussion

Scanning transmission electron microscopy was used to image the nanowires (Fig. 1a&b), with high angle annular dark field (HAADF) imaging used to obtain high resolution views of the microstructure (Figure 1c&d). A large number of dark areas can be observed, showing that the sample is thinner in these areas. From the HAADF images these clearly take the form of spots 2-5 nm in diameter. This is caused by the interference of the dopant with normal nanowire growth. The proposed theory is that antimony precipitates on the growth surface of the nanowire, forming an inversion domain boundary, which reverses the ZnO polarity at that point. As ZnO grows much slower along the $[000\bar{1}]$ direction compared to the [0001], normal ZnO growth occurs around the Sb precipitate, forming a void. Following annealing, the size of the voids increases, while their number decreases (Figure 2b). This suggests that at high temperatures, the voids migrate and coalesce. In the HAADF image (Figure 2d), a different crystal structure can be observed in the 2 nm region below the void. Because of how localized this phase change is, it is most likely caused by the Sb dopant, agreeing with previous observations. Electron diffraction patterns were taken of both the region below the void and the surrounding matrix to confirm what the makeup of this region is. We found the diffraction pattern to most closely match $Zn_7Sb_2O_{12}$. The presence of $Zn_7Sb_2O_{12}$ was also confirmed using Raman spectroscopy and x-ray diffraction, with characteristic peaks observed in both cases.

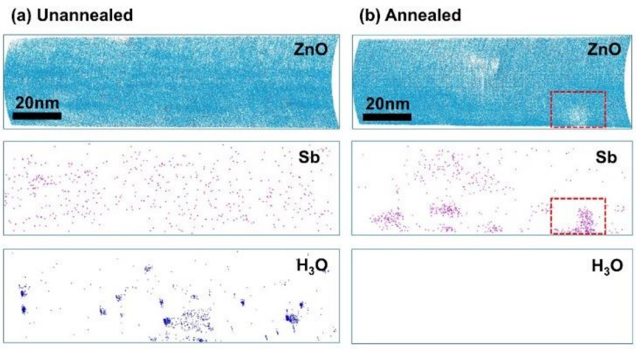

Fig. 2 Atom probe tomography scans of Sb doped ZnO nanowires before and after annealing.

Atom probe tomography is a powerful technique which can produce a three-dimensional reconstruction of atoms. These reconstructions provide information on solute clustering and segregation, making it a powerful tool for investigating the voids in Sb doped ZnO. Unannealed and annealed doped nanowires were analyzed. There are some noticeable differences in elemental distribution between the unannealed (Fig. 2a) and annealed wires (Fig. 2b). In the ZnO matrix, low density areas can be seen for the annealed sample, which correspond to the voids. For the unannealed sample, the antimony is uniformly distributed, while in the annealed sample, clustering of Sb is observed, which is consistent with the Zn-Sb-O precipitates observed in TEM. While many of the same peaks were observed in both spectra, and could be assigned to a variety of Zn compounds, there was one curious peak at 19 amu. Based on what compounds were present in the growth solution, the most likely candidate for this peak is water in the form of H_3O^+. Furthermore, in the reconstructed nanowire, the signal segregated out into distinct clusters of several nanometers in diameter, similar to the voids observed in TEM. For the annealed nanowire, the peak disappears completely, suggesting that the water evaporated out. To further verify that this is water, Raman spectroscopy was used in the range from 2800-3800 cm^{-1}. The peak disappears following annealing confirming that the water evaporates out during the annealing process.

3. Conclusions

In conclusion, we have performed a thorough investigation into the microstructure of hydrothermally grown Sb-doped ZnO nanowires using TEM, XRD, Raman spectroscopy and atom probe tomography. The void structures, once considered to have a simple structure, are actually more complicated. We have demonstrated that these voids are coarsened when the nanowires are annealed. A $Zn_7Sb_2O_{12}$ phase is clearly visible at the bottom of the void following annealing, which may provide a hint as to how the conduction is stabilized. The ability to trap water in the void is also of interest as it may provide a means of functionalizing ZnO with water soluble materials such as organic dyes and quantum dots, increasing its applicability.

Acknowledgements

This work was supported by JSPS KAKENHI Grant Numbers 26246021 and 26600049, and the World Premier International Research Center Initiative (WPI Initiative), MEXT, Japan.

References

[1] Wang, F.; Seo, J.-H.; Bayerl, D.; Shi, J.; Mi, H.; Ma, Z.; Zhao, D.; Shuai, Y.; Zhou, W.; Wang, X. *Nanotechnology* **2011,** 22, (22), 225602.
[2] Yankovich, A. B.; Puchala, B.; Wang, F.; Seo, J. H.; Morgan, D.; Wang, X. D.; Ma, Z. Q.; Kvit, A. V.; Voyles, P. M. *Nano Letters* **2012,** 12, (3), 1311-1316.
[3] Pradel, K. C.; Wu, W. Z.; Zhou, Y. S.; Wen, X. N.; Ding, Y.; Wang, Z. L. *Nano Letters* **2013,** 13, (6), 2647-2653.