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ABSTRACT

We report on neutron transmutation doping (NTD) of isotopically (^{64}Zn) enriched ZnO nanorods to produce material with holes as the majority mobile carrier. Nanorods of ZnO enriched with ^{64}Zn were synthesised and the abundance of ^{64}Zn in these samples is ~ 71%, compared to the natural abundance of ~ 49 %. The enriched material was irradiated with thermal neutrons which converts some ^{64}Zn to ^{65}Zn. The ^{65}Zn decays to ^{65}Cu with a half-life of 244 days and the Cu can act as an acceptor dopant. After 690 days, a hot probe technique was used to determine the majority charge carriers in non-irradiated and neutron irradiated nanorod samples. Non-irradiated samples were measured to be to have electrons as the majority mobile carrier and the irradiated samples were measured to have holes as the majority mobile carrier.

Because of its wide band-gap (3.4e V) and large exciton energy (60meV)[1] ZnO is a promising material for a range of optoelectronic applications such as UV lasers and light emitting diodes. However, ZnO technology has been held back by the lack of a reliable process for reproducibly synthesizing stable p-type material. There are have been many attempts to address this outstanding problem in ZnO technology.[2,3] Closest to the work reported here are studies on Neutron Transmutation Doping (NTD) carried out on n-type ZnO with a natural abundance of Zn isotopes.[4–7] The distribution Zn isotopes in natural abundance material[8] is 49.28% ^{64}Zn, 27.83% ^{66}Zn, 4.20% ^{67}Zn; 18.3% ^{68}Zn and 0.5% ^{70}Zn. For NTD, ^{66}Zn and ^{67}Zn are not of interest because neutron irradiation results in other stable Zn isotopes. Neutron irradiation of ^{64}Zn results in ^{65}Zn which radioactively decays to ^{65}Cu on a Zn lattice site. $^{65}Cu_{Zn}$ is an acceptor dopant[9] that promotes p-type doping.[4] However, neutron irradiation of ^{68}Zn and ^{70}Zn produces ^{69}Ga and ^{71}Ga on a Zn site. Ga_{zn} can act as a donor dopant[1] and can partially compensate p-type dopants and hence mitigate against majority carrier type conversion to holes. Thus the relative concentrations of ^{64}Zn versus $^{68}Zn+^{70}Zn$ isotopes controls whether or not NTD will change the charge carrier type of the ZnO. In the work presented here we use ^{64}Zn enriched[10] ZnO

which has relatively less ^{68}Zn and ^{70}Zn, and, by employing NTD, are able to demonstrate conversion to material with holes as the majority mobile carrier.

It should be noted that in addition evidence that Cu_{Zn} can act as acceptor[2,9,11] there are also reports[6,12] that Cu_{Zn} site in ZnO produces a trap too deep to produce mobile holes at room temperature. There is also some evidence[13] that the depth of Cu_{Zn} site can be reduced by alloying with S.

The synthesis and properties of the isotopically enriched ZnO nanorod samples were described previously;[8,14] the ^{64}Zn enriched sample used in this work had the following relative concentration of Zn isotopes: 71.5% ^{64}Zn, 15.6% ^{66}Zn, 2.3% ^{67}Zn; 10.3% ^{68}Zn and 0.08% ^{70}Zn. A ^{64}Zn enriched nanorod sample was irradiated with neutrons using the thermal reactor of the Australian Nuclear Science and Technology Organization (ANSTO) under a flux of 2.8×10^{13} $cm^{-2}s^{-1}$ for 6 hours. This means that the fluence is 6×10^{17} cm^{-2}. After neutron irradiation the sample emitted 135 kBq of ^{65}Zn decay radiation.

In previous NTD studies[4,6,12] of ZnO the samples were both annealed (under varying conditions) and unannealed. The annealing was undertaken to mitigate the effects of neutron damage to

the material. In the investigation reported here the samples were unannealed.

The Zn isotope nuclear reactions are well known and have been reported in detail.[12,6] Neutron irradiation converts some of the ^{64}Zn to ^{65}Zn - an unstable isotope with a half-life of 244 days that converts to ^{65}Cu$_{Zn}$ by a variety of routes. After absorbing a neutron ^{68}Zn isotope converts to ^{69}Zn which converts to ^{69}Ga$_{Zn}$ on a time scale of around 14 hours. Because of the residual ^{68}Zn (10.3%) in the enriched ^{64}ZnO, a few days after neutron irradiation of the enriched ^{64}ZnO it can be expected to be more n-type because of the new ^{69}Ga$_{Zn}$ donor dopants that arise from the transmutation process of the ^{68}Zn to ^{69}Ga$_{Zn}$. But as the ^{65}Zn converts to acceptor dopant ^{65}Cu$_{Zn}$ we expect the ^{64}Zn enriched material to become less n-type and eventually convert to holes as the majority mobile charge carrier. The neutron irradiated ^{64}ZnO nanorod samples were electrical characterized more than 690 days after the neutron irradiation by which time >85% of the ^{65}Zn created by the neutron irradiation had converted to ^{65}Cu$_{Zn}$.

A hot probe technique[15] adapted for nanorod samples was used to establish the majority carrier type in the irradiated and non-irradiated ^{64}ZnO nanorod samples. In the hot probe technique, a temperature difference, ΔT, is produced across a sample. The mobile charge carriers acquire thermal energy from the hot side of the sample and preferentially thermally diffuse from the hot to the cold part of the sample. Therefore, the mobile charge carriers accumulate at the cold side of the sample this gives rise to unbalanced charge distribution thereby an electric field and a voltage difference between the hot and cold parts of the sample. If the mobile charge carriers are electrons, then the cold part is negative with respect to the hot part and if the mobile charge carriers are holes, then the cold part is positive with respect to the hot part.

The conventional hot probe technique was adapted to characterize our ZnO nanorod samples – a technique we call the micro-hot probe. For the micro-hot probe technique, the first step was to fabricate a sample holder that could be used to generate a temperature difference, ΔT, and measure a thermal voltage across a ZnO nanorod (which typically had the morphology of a hexagonal column 1–10μm long and 0.1-0.5μm wide). The next step was to place the nanorod in the sample holder using a Focused Ion Beam–Scanning Electron Microscope (FIB-SEM). The ΔT was generated across the sample by cooling one side of the sample holder with dry (CO$_2$) ice at -78.5 degrees C (~194 K). The sample holder has electrodes designed to allow the voltage difference across the cooled sample to be measured. Figure (1) shows a schematic of the physical layout of the sample holder and of the electrical circuit.

The sample holder has a platinum thin film pattern deposited on a glass substrate. The Pt film provides electrical contacts to a ZnO nanorod and a means of temperature measurement because the resistivity of Pt thin film is very close to linearly dependent on the temperature (an effect used in thin film Pt resistance thermometers[16]). In our experiments we only used the measurement of the R_{12} and R_{34} resistances to confirm that a temperature difference was achieved; we did not make calibrated measurements of temperature difference, ΔT, as that is not required to establish the carrier type.

The gap between the two electrodes was created using the ion beam in the FIB-SEM to mill away the Pt thin film at the junction of the electrodes (see Figure (2)). The nanorod is manipulated into place using a similar technique to that described in a previous paper.[8,17] Finally, ion beam deposition of a thin line of Pt was performed to electrically contact and mechanically bind the nanorod to the electrodes. Figure (2) shows a SEM micrograph of the mounted nanorod.

Both neutron irradiated and non-irradiated ^{64}ZnO nanorods were mounted in sample holders. Before the substrate with nanorods grown on it was neutron irradiated, a nanorod sample was extracted and was measured using the micro-hot probe to confirm that non-irradiated (as-grown) ^{64}ZnO nanorods were n-type (as is always the case).

To carry out the hot probe technique with these samples one side of the sample holder is cooled using a dry ice pellet at -78.8 degrees C, the dry ice pellet is located in thermal contact with one electrode and the temperature is monitored by measuring the change in the resistances R_{12} and R_{34}. The resistance measurements confirms the cooling of the electrode in thermal contact with the dry ice pellet but it does not give the temperature at either end of the nanorod, rather the measurement gives an average over the whole electrode. The thermally generated voltage is then measured between contact pads 1+2 and 3+4. The resistance and voltage measurements are carried out using standard (Digitech Model QM1325) multimeters. Part of the experimental procedure involves reversing the cooling by changing the electrode that is cooled with the dry ice pellet. The results are reported in Table I.

In this micro-hot probe technique, we are concerned with the sign rather than the magnitude of the thermally generated voltage.
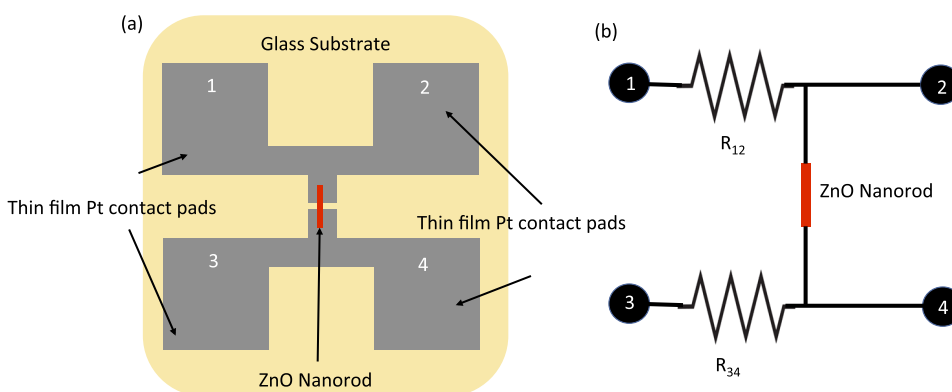

FIG. 1. (a) shows a schematic of the physical layout of the sample holder; the thin film platinum is deposited on a glass substrate (b) shows the equivalent electrical circuit; resistances R_{12} and R_{34} are measured to indicate the temperature on either side of the ZnO nanorod, while the thermally generated voltage is measured between contact pad12 and contact pad34.
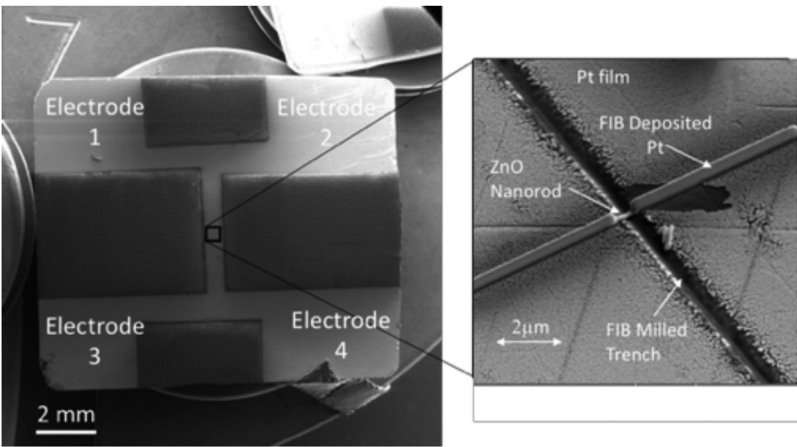
FIG. 2. SEM of sample holder the insert shows a single ^{64}ZnO nanorod mounted across the gap that provides electrical and thermal insulation. The Pt thin film has a trench milled by the FIB and the nanorod is placed across the gap using a nanomanipulator. Electrical and thermal contact and mechanical binding are provided at either end of the nanorod by FIB deposited Pt.

We consistently obtained results that show that the neutron irradiated ^{64}ZnO nanorods give positive voltages for the cold electrode relative to the hot electrode, indicating material with holes as the majority mobile carrier, and the non-irradiated ^{64}ZnO nanorods give negative voltages for the cold electrode relative to the hot electrode, indicating n-type material.

The magnitude of the thermal voltage depends on the material properties such as the magnitude of the Seebeck coefficient for isotopically enriched ^{64}ZnO nanorods. The Seebeck coefficient for isotopically enriched ^{64}ZnO nanorods has not previous been measured but values for natural abundance n-type ZnO nanorods have been measured to be $-400 \mu V/K$.[18] If we take this value and use the magnitude of the thermally generated voltage that we measure for the n-type nanorod then we estimate that the actual temperature difference across the nanorod is $\Delta T \approx 2K$.

In our experimental set-up the electrical contact between the FIB deposited Pt and the nanorod is unlikely to be a perfect ohmic contact and may well display some rectifying characteristics[19,20] and that could account for the asymmetry in the magnitude of the thermally generated voltage that is measured when the dry ice pellet is moved between the electrodes.

The evidence presented here is consistent with previous work[4] on NTD of ZnO with a natural abundance isotopic distribution which demonstrated that that Cu on a Zn lattice site, Cu_{zn}, acts as an acceptor dopant and reduces the majority (n-type) carrier concentration. But compared to natural abundance ZnO, our enriched ^{64}Zn isotope material has its ^{64}Zn isotope concentration increased by ~1.5 and so after neutron irradiation the concentration of Cu_{zn} acceptor sites has increased by ~1.5. Furthermore, comparing the natural abundance with the isotopically enriched material the concentration of the ^{68}Zn isotope in enriched material is reduced by a factor of 1.8. After neutron irradiation the ^{68}Zn isotope is converted to ^{69}Ga$_{zn}$ which can act as donor dopant and mitigate against p-type doping. After neutron irradiation the isotopically enriched material thus has 1.8 times less ^{69}Ga$_{zn}$ concentration compared to the natural abundance material. Compared to natural abundance ZnO, NTD of isotopically enriched ZnO material produces an increased concentration of Cu_{zn} acceptor sites and a reduced concentration of ^{69}Ga$_{zn}$ donor sites, resulting material, whereas following NTD the natural abundance ZnO material shows only a reduced concentration of mobile electrons and the material remains n-type.[4]

In summary, in ZnO with natural abundance of isotopes there are two important NTD processes (^{64}Zn transforming to ^{65}Cu$_{zn}$ with a half-life of 244 days, and ^{68}Zn transforming to ^{69}Ga$_{zn}$ with a half-life of ~ 14 hours). To induce holes as the majority charge carriers in ZnO material we have combined ^{64}Zn isotope enrichment of ZnO with NTD-this ^{64}Zn isotopic enrichment reduces the extent of the competing process of ^{68}Zn transformation to ^{69}Ga$_{zn}$. The micro-hot probe measurements presented here indicate that 690 days after thermal neutron irradiation the enriched ^{64}ZnO nanorods have sufficient Cu_{zn} acceptor dopants to compensate the original as grown

TABLE I. A summary of the micro-hot probe results for ^{64}ZnO nanorods. The cooling of the positive electrode is reversed by moving the dry ice pellet between the positive and negative electrodes.

Table of Hot probe results for isotopically enriched ^{64}ZnO nanorods			
Sample number	Sample description	Thermal Voltage (mV) Hot positive electrode	Thermal Voltage (mV) Cold positive electrode
1	Neutron Irradiated	-0.82 ± 0.14	1.24 ± 0.20
2	Neutron Irradiated	-25.47 ± 10.7	24.51 ± 7.26
3	Non-Irradiated	0.90 ± 0.19	-1.09 ± 0.18

n-type material and to convert to material with holes as the majority mobile carrier.

The results presented in this paper tend to support the recent reports[2,9,11] that a copper atom on the zinc atom site in ZnO, Cu_{Zn}, can act as an acceptor type dopant.

REFERENCES

[1] U. Ozgur, Y. I. Alivov, C. Liu, A. Teke, M. A. Reshchikov, S. Dogan, V. Avrutin, S. J. Cho, and H. Morkoc, Journal of Applied Physics **98**(4), 041301 (2005).

[2] M. Suja, S. B. Bashar, M. M. Morshed, and J. L. Liu, Acs Appl Mater Inter **7**(16), 8894 (2015).

[3] V. Avrutin, D. J. Silversmith, and H. Morkoc, Proc. IEEE **98**(7), 1269 (2010).

[4] F. A. Selim, M. C. Tarun, D. E. Wall, L. A. Boatner, and M. D. McCluskey, Appl Phys Lett **99**(20), 202109 (2011).

[5] H. Kim, K. Park, B. Min, J. S. Lee, K. Cho, S. Kim, H. S. Han, S. K. Hong, and T. Yao, Nucl Instrum Meth B **217**(3), 429 (2004).

[6] M. C. Recker, J. W. McClory, M. S. Holston, E. M. Golden, N. C. Giles, and L. E. Halliburton, Journal of Applied Physics **115**(24), 243706 (2014).

[7] G. K. Lindeberg, Journal of Applied Physics **38**(9), 3651 (1967).

[8] C. N. Ironside, D. W. Saxey, W. D. A. Rickard, C. Gray, E. McGlynn, S. M. Reddy, and N. A. Marks, AIP Advances **7**(2), 025004 (2017).

[9] C. Chen, W. Dai, Y. F. Lu, H. P. He, Q. Q. Lu, T. Jin, and Z. Z. Ye, Mater. Res. Bull. **70**, 190 (2015).

[10] E. E. Haller, Journal of Applied Physics **77**(7), 2857 (1995).

[11] J. B. Kim, D. Byun, S. Y. Ie, D. H. Park, W. K. Choi, J. W. Choi, and B. Angadi, Semicond. Sci. Technol. **23**(9) (2008).

[12] M. C. Recker, "Copper doping of zinc oxide by nuclear transmutation," M. Sc Thesis, Air Force Institute of Technology; http://oai.dtic.mil/oai/oai?verb=getRecord&metadataPrefix=html&identifier=ADA596866, 2014.

[13] H. L. Pan, B. Yao, T. Yang, Y. Xu, B. Y. Zhang, W. W. Liu, and D. Z. Shen, Appl Phys Lett **97**(14), 142101 (2010).

[14] C. Gray, J. Cullen, C. Byrne, G. Hughes, I. Buyanova, W. M. Chen, M. O. Henry, and E. McGlynn, J Cryst Growth **429**, 6 (2015).

[15] A. M. Alsmadi, N. Masmali, H. Jia, J. Guenther, H. Abu Jeib, L. L. Kerr, and K. F. Eid, Journal of Applied Physics **117**(15), 155703 (2015).

[16] K. G. Kreider, D. C. Ripple, and A. A. Kimes, Meas. Sci. Technol. **20**(4), 6 (2009).

[17] R. S. Chen, C. C. Tang, W. C. Shen, and Y. S. Huang, J. Vis. Exp. (106) (2015).

[18] C. H. Lee, G. C. Yi, Y. M. Zuev, and P. Kim, Appl Phys Lett **94**(2), 022106 (2009).

[19] K. Ip, Y. W. Heo, K. H. Baik, D. P. Norton, S. J. Pearton, S. Kim, J. R. LaRoche, and F. Ren, Appl Phys Lett **84**(15), 2835 (2004).

[20] L. J. Brillson and Y. C. Lu, Journal of Applied Physics **109**(12), 121301 (2011).