Hydrogen in red ZnO – defects or lattice expansion

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Abstract. The effect of hydrogen on ZnO while annealing at 1100 °C with Zn vapour or Ti metal is studied. ZnO turns red only when hydrogen is present in combination with oxygen deficiency. The coloration is reversible at 1100 °C by removing hydrogen either by evacuating or by gettering hydrogen with Ti at low temperature while annealing the ZnO at >950 °C. The latter is a simple method to lower the hydrogen impurity concentration. The annealing data are consistent with an activation energy >1.5 eV to reverse the coloration. Hall data on red ZnO reveal only a shallow donor level around 45 meV, too low for the colour change. Temperature dependent X-ray diffraction reveals a lattice expansion due to the presence of hydrogen which is sufficient to explain the colour change.

1. Introduction
ZnO is a promising wide bandgap semiconducting material with a large number of potential applications. A number of defects both intrinsic and due to impurities pose significant obstacles on the road to commercial applications. As-grown material is of n-type conductivity and no reliable method for p-type doping is known. Hydrogen is an almost omnipresent impurity and known to form a shallow donor when in an interstitial state [1-4]. Other states of hydrogen, some of which are not IR active, have been predicted and observed indirectly [5-7]. A practical method to reduce or even remove hydrogen from ZnO has to be devised in order to minimize the challenges in p-type doping.

ZnO turns red when it is annealed in the presence of Zn vapor at 1100 °C. The red colour has been linked to an excess in Zn [8-12]. Based on the ratio of Zn to O concentration, an excess in Zn is equivalent to a deficiency in oxygen. On an atomic scale, however, the presence of Zn interstitials (Zni) is very different from oxygen vacancies (VO). Stockmann noticed multiple options of accommodating excess Zn [13]. Halliburton et al. and Selim et al. pointed out that the same red colour was observed after annealing in the presence of phosphorous or titanium rather than zinc vapor, respectively, pointing to VO [10, 12]. Isolated zinc and oxygen vacancies anneal out below 200 °C and 400 °C, respectively, or merge to clusters which then anneal out below 700 °C [12,14-17]. The red coloration, however, persists suggesting a different defect. The potential contribution of hydrogen, OH ions or water to this effect was never tested and typically presumed insignificant. Here, it is shown that hydrogen in combination with VO or another form of oxygen deficiency, not interstitial zinc, Zni, is responsible for the red colour.

2. Experimental
ZnO from two suppliers and grown by two methods was studied. Hydrothermally grown ZnO was obtained from Tokyo Denpa Co., LTD (TEW) [18] and skull melt grown ZnO was purchased from Cermet Co. [19]. One sample was grown by seeded chemical vapour deposition. All samples were cut...
along the c-axis to 10×10 mm² squares and to 0.5 mm thickness. The supplier polished either on both sides (TEW) or on the Zn-face only (Cermet).

The samples were annealed in high purity low OH quartz ampoules (GE214) in a tube furnace under a variety of ambient conditions. The ampoules containing the samples were connected to an oil free vacuum system, evacuated to $\sim 10^{-7}$ torr and baked for $>12$ hrs at 120 °C to remove water vapour. The ampoule-sample assemblies were either sealed off with a hydrogen-oxygen torch for annealing in a closed system, or left connected to the pumping station in an open system to monitor partial pressures with a residual gas analyzer (RGA, Vacuum Generators). A schematic of the annealing system is shown in Figure 1.

The samples were annealed in the presence of Zn vapour (99.999% pure, 5N Plus Inc.) or Ti metal foil (99.6% pure, Goodfellow Corp.). The hydrogen and water content in the systems was controlled by preheating the ampoules, the Ti foil and the Zn metal pellets in the open system configuration. The evolution of hydrogen as a function of temperature and time was monitored with the RGA. Hydrogen was removed for ZnO by either pumping the evolving gases in the open-system configuration, or by gettering hydrogen with the Ti metal foil in the closed-system configuration. Prior to sealing, oxygen, hydrogen, or deuterium could be introduced into the ampoule through a leak-valve.

Positron annihilation experiments were carried out at the WSU positron beam with an energy range of 0.1 to 70 keV. A high efficiency high resolution (1.5 keV full width half maximum at 511 keV) germanium detector was used for the Doppler broadening experiments. The samples were annealed in situ for 30 minutes at up to 700 °C or in the tube furnace under nitrogen atmosphere above 700 °C. All positron measurements were carried out at room temperature.

3. Results
The release of hydrogen was monitored in the open-system configuration. In addition to the ZnO material [20], several sources of hydrogen may be present. As received Ti and the quartz ampoules may contain significant quantities of hydrogen. Titanium metal is an excellent getter for hydrogen as implemented in Ti-getter vacuum pumps. Ti absorbs hydrogen below $\sim$200 °C and releases it above 400 °C [21]. Ti foils were heated in ampoules to desorb and monitor hydrogen. The H₂ partial pressure rose to $5 \times 10^{-7}$ torr near 500 °C. The H₂ content in quartz ampoules is not evaluated or listed by manufacturers. Figure 2 shows the results of annealing an empty quartz ampoule twice. Hydrogen diffuses out of the near surface regions of the quartz. The second annealing shows about 10× lower partial pressures. Care must be taken not to heat the ampoule to higher temperatures to prevent further release from deeper in the material. If Zn vapour is present during the annealing, Zn atoms may crack water molecules and generate hydrogen by hydrolysis [22-24].
As received clear ZnO was annealed in a sealed ampoule in the presence of Zn vapour and Ti metal foil without any hydrogen treatment as discussed by Selim et al. [12]. In both cases, the ZnO turned reddish at room temperature. When the ampoule and the Ti foil were treated to remove or reduce the hydrogen content, no colour change occurred. ZnO remained clear. The Ti foil was maintained at a temperature sufficiently low to getter hydrogen. The surface roughness of the ZnO increased due to some loss of Zn. This transparent ZnO was then annealed in the presence of Zn vapour in an ampoule treated to lower the hydrogen and water vapour content. The sample remained clear just as with the previous experience with hydrogen depleted Ti. Figure 3 shows photos of the samples at room temperature after annealing. The arrows indicate the annealing step and reversibility. Also, hydrogen depleted ZnO (clear) was annealed in the presence of Ti metal that contained deuterium. This resulted in a yellow sample. Annealing any sample either in oxygen or under vacuum while pumping away any desorbed gases will remove the coloration and result in clear ZnO. Clearly, ZnO turns reddish only when hydrogen is present and oxygen deficient conditions are given. The former or latter alone does not lead to red ZnO.

Figure 3: Photos of ZnO samples after annealing at 1100 °C for 30 min in the presence of Ti metal (2nd row) Zn vapour (3rd row) and oxygen (4th row) either in the presence of hydrogen (in the ampoule, ZnO, and/or Ti) (left column) or after pre-treatment to remove or reduce the hydrogen content (middle column). In the right column, Ti was preloaded with some deuterium gas.
Positron annihilation depth profiles can be used to reveal vacancies. Typically, only neutral and negatively charged vacancies can be observed in semiconducting material. Neutral oxygen vacancies are not detectable at room temperature [15, 25]. As demonstrated by Selim et al. [12] and Weber et al. [26, 27], these oxygen vacancies can be revealed by adding zinc vacancies to the sample and then anneal at up to 700 °C. If oxygen vacancies are present in the original sample, they will become mobile and merge with the added Zn vacancies to form di-vacancies or larger vacancy clusters. In the as-prepared state, clear and red ZnO are indistinguishable and show a small (<3%) increase in S following annealing. When damage including V\textsubscript{Zn} is added, S rises in the damaged region by 6% and 4.5% for the red and clear ZnO samples respectively, somewhat above the 4% change associated with V\textsubscript{Zn} [28]. The specific values of saturation trapping of positrons in V\textsubscript{Zn} remain subject to debate until high quality ZnO similar to Si becomes available. Here, it is relevant only that V\textsubscript{Zn} and related defects were added and detected. S increases dramatically following annealing at 500 °C in the case of the damaged red ZnO sample only. Pre-existing open volume defects became mobile and merged with the V\textsubscript{Zn} related vacancies to larger clusters [12]. Oxygen vacancies must be present in the red ZnO. This is shown in Figure 4.

To detect any hydrogen in red ZnO, a sample was annealed in the open-system configuration at 5 °C/min to increasingly higher temperatures of 700, 850, 950 and 1050 °C. The ampoule was pre-treated to deplete hydrogen and water. The partial pressure of hydrogen was monitored with the RGA. Figure 5 shows the partial pressure of H\textsubscript{2} as a function of temperature. After each annealing step, the sample was cooled to room temperature and the colour noted. The sample became pale after 950 °C and whitish (due to surface roughness) after 1050 °C (see Figure 5). Hydrogen diffuses out around 400 °C without any affect on the sample colour. This is consistent with hydrogen bound at interstitial sites [29]. More hydrogen is released from 800 to 1000 °C and the red coloration disappeared. This hydrogen is more deeply bound at 1.5 eV and consistent with results by Nickel et al. [30-33] and calculations by Bang and Chang [34]. In addition to the effusion of hydrogen above 400 °C, Nickel et al. observed more molecular hydrogen well above 800 °C and found activation energies of about 1 eV. The former correlates with IR observations of OH vibrations while the latter is not visible to IR [35].

Preliminary low-temperature Hall measurements on a ZnO with hydrogen annealed red sample revealed a shallow donor level at 45±2 meV and no deep levels. This is consistent with observations by Lavrov et al. who identified this level with the H\textsubscript{O} defect [36]. Clearly, 45 meV are not sufficient to change the colour of ZnO. A different mechanism has to explain the colour change in the absence of a deep level. ZnO is thermochrome, i.e. the bandgap decreases sufficiently with increasing temperature to change the colour of ZnO from transparent at room temperature to dark yellow at ∼600 °C. X-ray
diffraction data (XRD) show this effect as a small change in the 2Θ diffraction. Preliminary XRD on clear and red ZnO reveal a similar shift in the 2Θ diffraction angles from 72.58° to 72.45° for clear and red ZnO, respectively. Loading of oxygen deficient ZnO with hydrogen exerts pressure on the c-axis and lowers the bandgap by the observed amount with the corresponding change in colour. In order to further verify this, temperature dependent X-ray diffraction measurements are ongoing.

4. Summary

The presence of hydrogen in oxygen deficient ZnO is responsible for the red coloration. A defect involving hydrogen and oxygen vacancies most likely causes H2O to form and the lattice to be expanded sufficiently to lower the bandgap of ZnO. The latter causes the change in colour.

Figure 5: Partial pressure of H2 as a function of temperature of red ZnO while heating at 5 °C/min to a) 700 °C, b) 850 °C, c) 950 °C, and d) 1050 °C. Heating to between 950 and 1050 °C is required to remove the red colour. Hydrogen diffuses out near 400 C without colour change and at >800 with the colour change. A base pressure of hydrogen after annealing was subtracted.

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References

[1] Mollwo E 1954 Z. Physik 138 478
[2] Thomas D G and Lander J J 1956 J. Chem. Phys. 25 1136
[3] Van de Walle C G 2000 Phys. Rev. Lett. 85 1012
[4] Hofmann D M, Hofstaetter A, Leiter F, Zhou H, Henecker F, Meyer B K, Orlinskii S B, Schmidt J, and Baranov P G 2002 Phys. Rev. Lett. 88 045504
[5] McCluskey M D, Jokela S D and Hlaing Oo W M 2006 Physica B 376-377 690
[6] Lavrov E V 2003 Physica B 340-342 195
[7] Lavrov E V, Börrnert F and Weber J 2005 Phys. Rev. B 71 035205
[8] Ehret W F and Greenstone A 1943 J. Am. Chem. Soc. 65 872
[9] de la Cruz R M, Pareja R, González R, Boatner L A and Chen Y 1992 Phys. Rev. B 45 6581
[10] Halliburton L E, Giles N C, Garces N Y, Luo M, Xu C, Bai L and Boatner L A 2005 Appl. Phys. Lett. 87 172108
[11] Jokela S J and McCluskey M D 2007 Physica B 401-402 395-398
[12] Selim F A, Weber M H, Solodovnikov D and Lynn K G 2007 Phys. Rev. Lett. 99 085502
[13] Stöckmann F 1950 Z. Physik 127 563
[14] Chen Z Q, Maekawa M, Kawasuso A, Sakai S and Naramoto H 2006 Physica B 376-377 722
[15] Tuomisto F, Saarinen K, Look D C and Farlow G C 2005 Phys. Rev. B 72 085206
[16] Vlasenko L S and Watkins G D 2005 Phys. Rev. B 71 125210
[17] Chen Z Q, Maekawa M, Kawasuso A, Sakai S and Naramoto H 2006 J. Appl. Phys. 99 093507
[18] Maeda K, Sato M, Niikura I and Fukuda T 2005 Semicond. Sci. Technol. 20 S49
[19] Nause J and Nemeth B 2005 Semicond. Sci. Technol. 20 S45
[20] Čižek J, Žaludová N, Vlach M, Daniš S, Kuriplach J, Procházka I, Brauer G, Anwand W, Grambo D, Skorupa W, Gemma R, Kirchheim R and Pundt A 2008 J. Appl. Phys. 103 053508
[21] Furuya Y, Takasaki A, Mizuno K and Yoshiie T 2007 J. Alloys Compd. 446-447 447
[22] Bazan J C, Gschaid M E and Alimenti G A 1999 J. Therm. Anal. 55 569
[23] Alimenti G A, Gschaid M E, Bazan J C and Ferreira M L 2004 J. Colloid Interface Sci. 276 24
[24] Melchior T, Piatkowski N and Steinfeld A 2009 Chem. Eng. Sci. 64 1095
[25] Takenaka H and Singh D J 2007 Phys. Rev. B 75 241102(R)
[26] Weber M H, Selim F A, Solodovnikov D and Lynn K G 2008 Appl. Surf. Sci. 255 68-70
[27] Weber M H, Parmar N S, Jones K A and Lynn K G 2010 J. Electron. Mater. 39 573-576
[28] Tuomisto F, Ranki V, Saarinen K and Look D C 2003 Phys. Rev. Lett. 91 205502
[29] Ip K, Overberg M E, Heo Y W, Norton D P, Pearton S J, Stutz C E, Kucheyev S O, Jagadish C, Williams J S, Luo B, Ren F, Look D C and Zavada J M 2003 Solid State Electron. 47 2255-2259
[30] Nickel N H and Fleischer K 2003 Phys. Rev. Lett. 90 197402
[31] Nickel N H and Brendel K 2003 Phys. Rev. B 68 193303
[32] Nickel N H 2006 Phys. Rev. B 73 195204
[33] Nickel N H 2007 Superlattices and Microstruct. 42 3-7
[34] Bang J and Chang K J 2008 Appl. Phys. Lett. 92 132109
[35] Shi G A, Saboktakin M, Stavola M and Pearton S J 2004 Appl. Phys. Lett. 85 5601
[36] Lavrov E V, Herklotz F and Weber J 2009 Phys. Rev. B 79, 165210