High-resolution photoluminescence spectroscopy of Sn-doped ZnO single crystals

E. Senthil Kumar¹, F. Mohammadbeigi¹, L. A. Boatner² and S. P. Watkins¹

¹Department of Physics, Simon Fraser University, Burnaby, BC, Canada-V5A1S6

²Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA

E-mail: simonw@sfu.ca

Abstract.

Group IV donors in ZnO are poorly understood, despite evidence that they are effective n-type dopants. Here we present high-resolution photoluminescence (PL) spectroscopy studies of unintentionally doped and Sn-doped ZnO single crystals grown by the chemical vapor transport method. Doped samples showed greatly increased emission from the I_{10} bound exciton transition that was recently proven to be related to the incorporation of Sn impurities based on radio-isotope studies. The PL linewidths are exceptionally sharp for these samples, enabling a clear identification of several donor species. Temperature-dependent PL measurements of the I_{10} line emission energy and intensity dependence reveal a behavior that is similar to other shallow donors in ZnO. Ionized donor bound-exciton and two-electron satellite transitions of the I_{10} transition are unambiguously identified and yield a donor binding energy of 71 meV. In contrast to recent reports of Ge-related donors in ZnO, the spectroscopic binding energy for the Sn-related donor bound exciton follows a linear relationship with donor binding energy (Haynes rule) similar to recently observed carbon related donors, and confirming the shallow nature of this defect center, which was recently attributed to a Sn_{Zn} double donor compensated by an unknown single acceptor.

Keywords: zinc oxide, photoluminescence, electrical transport, dopants, Sn

1. INTRODUCTION

The electronic properties of ZnO have been extensively studied by means of low-temperature photoluminescence (PL) spectroscopy.[1-5] Bound exciton transitions associated with group III donor impurities such as Al, Ga and In were unambiguously identified with controlled intentional doping experiments.[1-7] These characteristic transitions were previously denoted as I-lines and identified as arising from neutral (D^0X) and ionized (D^+X) donor bound-exciton transitions. D^0X (I_6 , I_8 , and I_9) and D^+X (I_0 , I_1 and I_2) of the substitutional group III donors Al, Ga and In donors are now well established.[1] Shallow hydrogen and antimony related D^0X transitions have also been observed. Unlike the group III donors, these do not have D^+X transitions [1,2,4] due to their very small donor binding energies. The chemical nature of several of the I-lines in the near-band-edge region for example, I_7 , I_5 , I_3 , is still unknown.

When compared with group-III impurities, the electronic nature of the group-IV impurities (C, Si, Ge and Sn) in ZnO is not clearly understood. Group-IV impurities are potential double donors in ZnO when substituting for Zn sites.[8, 9] Cullen *et al.* have reported an unusual Ge-related donor bound exciton transition at 3324 meV in bulk ZnO crystals which binds excitons much more deeply than expected based on its shallow final state donor binding energy.[10] Recently, Mohammadbeigi *et al.* have observed carbon-related shallow donor D^0X transitions, labeled Z-lines, in carbon-doped ZnO nanowires grown by metalorganic vapor phase epitaxy.[11] Pulsed laser deposited (PLD) Si-doped ZnO thin films exhibited a two-orders-of-magnitude increase in conductivity compared with un-doped samples.[9] Sn-doped ZnO thin films exhibited increased conductivity only at low Sn concentrations (0.1 at. %) and showed a

larger resistivity at higher Sn concentrations (1-2 at %).[12] Recent PL measurements on radioactive ^{117}Ag implanted ZnO single crystals showed an appearance of the I_{10} -line at 3353 meV.[13] The center responsible for the I_{10} line was conclusively shown to contain Sn, based on the implantation of radioactive ^{117}Ag which eventually decays into stable ^{117}Sn . Meyer *et al.* have observed the I_{10} line in Li- and Na-doped ZnO single crystals [1] and previously suggested that the I_{10} center contains Li or Na, however this remains to be proven.

In this study, we performed high-resolution PL experiments on ZnO single crystals intentionally doped with Sn impurities. We show that the intentionally Sn-doped samples have a consistently higher PL intensity of the I_{10} line and the related I_{10}^+ (D^+X) transition compared with un-doped samples. We demonstrate that the I_{10} defect shares many similarities with the group III donors in terms of its bound-exciton PL properties - such as thermal activation and peak energy shift with temperature, and that this is consistent with a shallow donor impurity binding a single electron. We confirm the two electron satellite (TES) transitions and D^+X transitions associated with Sn impurities. We observe that I_{10} follows the empirical relationship between localization energy and binding energy often referred to as Hayne's rule, and that it follows the same trend as the common group III and other shallow donors, indicating a similar relatively shallow central cell potential.

2. EXPERIMENTAL

Unintentionally doped and Sn-doped ZnO single crystals were grown using the chemical vapor transport (CVT) method. The growth of single crystals of ZnO from the vapor phase is accomplished by the reduction of polycrystalline spheres of ZnO that are placed in an alumina tube (Fig. 1). The process consists of two steps: the initial step involves the reduction of ZnO with hydrogen gas to provide a concentration of zinc in the region where the bulk crystal growth

is to take place. This is achieved through the reaction: $\text{ZnO(s)} + \text{H}_2\text{(g)} \rightarrow \text{Zn(g)} + \text{H}_2\text{O(g)}$. This reaction occurs in a hot zone (1250°C) of the tube furnace. The zinc vapor is transported to a cooler growth region by a nitrogen carrier gas where the crystals grow by means of the reaction: $\text{Zn(g)} + (1/2)\text{O}_2\text{(g)} \rightarrow \text{ZnO(s)}$, which is accompanied by the reaction: $\text{H}_2\text{(g)} + (1/2)\text{O}_2\text{(g)} \rightarrow \text{H}_2\text{O(g)}$. ZnO crystals with dimensions of several centimeters can be grown by this technique. Sn-doping was achieved by mixing 0.15 mol% of SnO_2 with the starting ZnO polycrystalline material. Variations in Sn doping observed by PL are not attributed to changes in the SnO_2 precursor concentration, but rather to variations in the incorporation of Sn in different parts of the growth chamber due to variations in the temperature and other local growth conditions. The CVT process yielded needle shaped crystal ranging in diameter from ~0.2 mm to 2mm in diameter and up to 15 mm in length. The larger diameter samples were used for electrical resistivity measurements. High-resolution PL measurements were carried out at 4.2 K, in a liquid helium cryostat, by exciting the samples with the 325.031 nm line of a HeCd laser with a total power of 25 mW. The luminescence was dispersed by a double monochromator with a 0.85 m focal length and with a spectral resolution of 0.08 meV. A Hamamatsu R585 photomultiplier tube was used to count the photons. The wavelengths were corrected using the refractive index of air and converted to energy using a conversion factor of 1239841.7 eV nm. Indium was used for electrical contacts.

3. RESULTS AND DISCUSSION

Figure 1 shows the 4.2 K PL spectra of the unintentionally doped (A) and Sn doped ZnO single crystals (B,C,D,E). The PL spectrum of the unintentionally doped ZnO is mainly dominated by the D^0X transitions I_6 , I_8 and I_9 corresponding to residual Al, Ga and In donors. Following the convention of Allen *et al.* [14] their corresponding D^+X transitions are denoted as

I_6^+ (Al), I_8^+ (Ga) and I_9^+ (In), which were previously labeled I_0 (Al), I_1 (Ga) and I_2 (In) respectively.[1] The line positions of these transitions are in agreement with previous reports on bulk ZnO crystals and intentionally doped nanowires.[1, 4, 5] Unintentionally doped crystals also showed another transition with relatively weak PL intensity at 3353.2 meV, which is very close to the previously assigned I_{10} -line position (3353.1 meV).[1] These transitions are very sharp, with linewidths as low as 54 μ eV (I_{10}), 170 μ eV (I_9) and 260 μ eV (I_8) revealing the low concentrations (estimated $\leq 10^{17}$ cm⁻³) of residual shallow impurities in these crystals. The samples with significant I_{10} doping tend to have a feature at 3363.2 meV labeled I_{10}^+ in Fig. 1, which was previously attributed to the D^+X transition of I_{10} [15] however in that work the chemical origin of I_{10} was not yet known.

The PL spectra (B-E) in Fig.1 correspond to Sn-doped ZnO crystals; however the actual Sn concentration is not known but it appears to be very low based on the sharpness of the observed PL lines. The unintentionally doped ZnO crystals (e.g. A in Fig. 1) are highly transparent, with no apparent color. The doped samples exhibit varying amounts of blue color ranging from sample to sample within the same growth run. As a trend, the darker blue samples exhibit a high relative intensity of I_{10} compared with the other residual donors such as I_9 . Also, the linewidth of the I_{10} line increases from 54 μ eV for the un-doped sample to 170 μ eV for the darkest blue samples. These samples also showed strong emission at 3333.3 meV corresponding to the so-called Y-line (not shown) which has been attributed to excitons bound deeply to donor centers localized at structural defects.[1]

Meyer *et al.* have reported the I_{10} line in both Li- and Na-doped ZnO crystals [1]. Li-doped crystals showed a higher integrated PL intensity for the I_{10} line compared with Na-doped crystals.[1] However, PL measurements on systematically Li-doped ZnO samples were unable to

unambiguously assign Li to the I₁₀ line. Cullen *et al.* have also performed PL measurements on ZnO crystals implanted with the radioactive impurity ¹¹⁷Ag, which decays into radioactive ¹¹⁷In, and then to stable ¹¹⁷Sn, resulting in the appearance of the I₁₀-line, that was absent in virgin samples.[13] The time evolution of the I₁₀ emission occurred with a rate consistent with the known decay of ¹¹⁷In to ¹¹⁷Sn - thus strongly arguing that Sn is present on a Zn lattice site as the I₁₀ defect. In order to explain the observed single donor charge state they attributed the I₁₀-line to the donor complex, Sn_{Zn}-Li_{Zn}, where Li acts as a compensating acceptor.[13] Recently, Rakshit *et al.* have observed a transition at 3355 meV, which is close to the I₁₀-line in Sn-doped ZnO nanostructures grown by the vapor-solid method.[16]

PL measurements as a function of temperature indicate whether an exciton binding center has a shallow or deep nature based on the energy shift of the transitions [17] and also whether the transition is associated with a ground state or excited state - based on the thermalization behavior.[18] Fig. 2 (a) shows the energy shift of the I₈, I₉, I₁₀ and Y lines as a function of temperature in the range 4.2-45 K. The Y-lines are associated with donor bound excitons with deeply bound excitons [18] in other words, the exciton binding energy is much larger than would be predicted based on the shallow donor final state. This will be discussed in detail later in the paper. All the data are fitted using Eqn. 1 given by Viña *et al.* based on a Bose-Einstein model [19],

$$E(T) = E_0 - \frac{\alpha}{\exp\left(\frac{\Theta}{T}\right) - 1} \quad (1)$$

where, E_0 is the emission energy at $T = 0$ K, α is a parameter associated with electron-phonon coupling, and Θ is the effective phonon temperature. The solid lines represent the least squares

fits to the data points. The best fit yielded the fitting parameter $\alpha = 0.11 \pm 0.01$ eV/K for I₈, I₉ and I₁₀ and 0.31 ± 0.05 eV/K for the Y line. The other fitting parameter θ for the I₈, I₉, I₁₀ and Y-lines is 96 ± 5 K, 86 ± 8 K, 97 ± 6 K and 82 ± 7 K respectively. The amount of energy shift (ΔE) for the I₁₀ line, in the temperature range from 4.2 K to 45 K, is exactly the same as that of the group III impurities, I₈ and I₉. The energy shift of the Y-line is 5 times larger than that of the I₈, I₉ and I₁₀ lines over the same temperature range. This confirms that the impurity responsible for the I₁₀ line is a shallow donor defect with a spatial variation of the central cell potential similar to the group III donors.

The thermalization behavior of the I₁₀ line [Fig. 2(b)] is also very similar to other shallow neutral donor bound-exciton transitions. The intensity of the I₁₀ line falls steadily with increasing temperature from 4.2 K to 25 K [Fig. 2(c)] and then drops rapidly with a further increase in temperature. This is a typical characteristic of a ground-state transition and is similar to the behavior of the I₉ and other shallow lines. The activation energies of the I₁₀ and I₉ transitions are obtained by fitting [Fig. 2(c)] using a quasi-empirical relation [20],

$$I = \frac{I_0}{1 + C_1 \exp\left(\frac{-E_{a1}}{kT}\right) + C_2 \exp\left(\frac{-E_{a2}}{kT}\right)} \quad (2)$$

where E_{a1} and E_{a2} are activation energies and C_1 and C_2 are degeneracy ratios. Fitting the data points using the model in Eqn. 2 yielded activation energies E_{a2} of 19 ± 2 meV and 22 ± 2 meV for I₉ and I₁₀ respectively. These values are close to the respective spectroscopic binding energies of the I₉ and I₁₀ transitions of 18.8 and 22.4 meV. This again confirms that the I₁₀ line is associated with shallow impurity centers. In contrast, donor bound exciton transitions with deeply bound excitons such as the Y-line[1] or the Ge-related D⁰X observed by Johnston *et al.*[6]

typically thermalize very rapidly and show a large discrepancy between the activation energy and spectroscopic binding energy. This discrepancy has been attributed to the possibility that thermal dissociation involves the removal of a single particle rather than the exciton as a whole, leaving the other particle bound in a more localized state.[17]

The I_{10} line is known to be due to D^0X emission based on the observation of two-electron satellite (TES) transitions, which are D^0X transitions where the final state electron is left in an excited state. We observe a two-electron satellite transition at 3294.7 meV as shown in Fig. 3, which is close to the previously reported 2p transition of the I_{10} line. [1] Locating the 2p level allows us to estimate the energy difference between the 1s and 2p D^0X transitions. Based on these results, we determined a donor binding energy for the I_{10} donor of 71.1 meV, which compares reasonably well with the value of 72.6 meV obtained earlier.[1] It should be noted that the PL linewidths of the current samples are considerably sharper than previous reports.

It is useful to consider how the I_{10} transitions fit with trends observed in other shallow donors in ZnO. Haynes observed an empirical rule for shallow donors in various semiconductors which states that the donor exciton binding energy is linearly related to the donor binding energy.[21] This rule is well observed for the group III donors and other shallow donors including a hydrogen-related defect (I_4). Meyer et al. previously showed that I_{10} obeys Haynes rule, although the chemical origin of the transition was not known at that time. In Fig 4(a) we plot our data for the Sn-related donor on a plot of D^0X and D^+X binding energy vs. donor binding energy together with several shallow donors in ZnO - including the recently observed carbon-related D^0X transitions [Fig. 4(a)]. The I_{10} transition clearly follows the trends observed for other shallow donors including the carbon related ones. Also shown are the 2s-2p splittings

for these donors indicating a similar systematic increase in central cell correction for the 2s donor state which correlates linearly with increasing donor binding energy.

Note that In and Sn have the same core electron structure. The simplest defect model assumes that the Sn-related donor sits on a Zn site (as confirmed by Cullen *et al.*[13]) and that the excess charge of the double donor is compensated by a yet unknown single acceptor impurity for example Li or Na.[1, 13] The compensating defect is unlikely to be a Zn vacancy since this would be expected to result in a neutral defect, since the Zn vacancy is a double acceptor. Likewise, we can rule out an isolated Sn_{Zn} double donor since it is not expected to have 2s/2p excited final states due to the expected pairing of the electron spins.

While the behavior of I_{10} is very similar to the known shallow single donors, it is in strong contrast to another well studied group IV impurity Ge which has a donor bound exciton emission at 3324 meV [6]. The Ge-related defect exhibits a final state donor binding energy similar to shallow donors like I_6 , I_8 , I_9 , and I_{10} - but a much deeper exciton localization energy, as evident from Fig.4(a). Similar behavior is observed for the Y-line defect at 3333 meV, suggesting a similar possible origin. A detailed microscopic model for these transitions is not yet available.

To investigate the electrical quality of these CVT grown samples we also performed temperature-dependent resistivity measurements of samples A, B, C and E (Fig. 5). No significant correlations were observed between samples grown with different relative PL intensities of Sn impurities. Even the samples that showed the strongest I_{10} emission had room temperature resistivities much higher than those grown by PLD in Ref. 12, indicating that the Sn doping level was much lower in our case. The estimated room-temperature (295 K) resistivities are 3.92 (A), 0.86 (B), 19.7 (C) and 2.35 Ohm·cm (E). The sample E, which exhibited a

relatively strong I_{10} line, showed evidence of impurity-band conduction at low temperature. The samples A, B, and C exhibited exponential freezeout over several orders of magnitude - consistent with a very low carrier concentration and very high crystal quality. The activation energies for freezeout were observed to be 56.8 meV (A), 50.8 meV (B) and 57.2 meV (C). These values are far from the donor binding energy of Sn impurities of 71 meV determined from two-electron transitions in both this work and previous work.[1] This suggests that while the overall I_{10} defect concentration has increased, other shallow dopants dominate the electrical properties. At least for the doping levels investigated here, no significant effect on resistivity was observed that correlated with the intensity of the I_{10} emission.

4. CONCLUSIONS

We have investigated the optical and electrical properties of ZnO single crystals doped with Sn impurities. We find enhanced intensity of the I_{10} transition in intentionally Sn-doped samples. We identify neutral and ionized donor bound exciton transitions of this defect, as well as the corresponding two-electron satellite transitions. The temperature and energy level dependence of the Sn-related D^0X transitions show strong similarities with other shallow donors, including the recently observed carbon-related D^0X emission, but they are in strong contrast to the behavior of Ge-related D^0X complexes and the defect related Y-line luminescence centers in ZnO. Our results add support to a previous defect model for I_{10} consisting of substitutional Sn_{Zn} complexed with a single shallow acceptor.

ACKNOWLEDGEMENTS:

The support of the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged. Research at the Oak Ridge National Laboratory for one author (LAB) was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences,

References

- [1] B.K. Meyer, H. Alves, D. Hofmann, W. Kriegseis, D. Forster, F. Bertram, J. Christen, A. Hoffmann, M. Straßburg, M. Dworzak, U. Haboeck, and A.V. Rodina Phys. Stat. Sol. (b) 241 (2004) 231.
- [2] D.C Look, G.C. Farlow, P. Reunchan, S. Limpijumnong, S.B. Zhang, and K. Nordlund, Phys. Rev. Lett. 95 (2005) 225502.
- [3] S.P. Watkins, Z.W. Deng, D.C. Li, and H. Huang, J. Appl. Phys. 110 (2011) 083506.
- [4] E.S. Kumar, F. Mohammadbeigi, S. Alagha, Z.W. Deng, I.P. Anderson, T. Wintschel, and S.P. Watkins, Appl. Phys. Lett. 102, (2013) 132105.
- [5] E.S. Kumar, I.P. Anderson, Z. Deng, F. Mohammadbeigi, T. Wintschel, D. Huang, and S.P. Watkins, Semicond. Sci. Technol. 28,(2013) 045014.
- [6] K. Johnston, M.O. Henry, D. McCabe, E. McGlynn, M. Dietrich, E. Alves, and M. Xia, Phys. Rev. B 73 (2006) 165212.
- [7] S. Müller, D. Stichtenoth, M. Uhrmacher, H. Hofsäss, C. Ronning, and J. Röder Appl. Phys. Lett. 90 (2007) 012107.
- [8] J.L. Lyons, A. Janotti, and C.G. Van de Walle, Phys. Rev. B 80 (2009) 205113.
- [9] A.K. Das, P. Misra P, and L.M. Kukreja, J. Phys. D: Appl. Phys. 42 (2009)165405.
- [10] J. Cullen, K. Johnston, E. McGlynn, M.O. Henry, D. Dunker, D.R. Yakovlev, and M. Bayer, Phys. Rev. B 87 (2013) 165202.
- [11] F. Mohammadbeigi, E.S. Kumar, S. Alagha, I. Anderson, and S.P. Watkins, J. Appl. Phys. 116 (2014) 053516.

- [12] E. López-Ponce, J.L. Costa-Krämer, M.S. Martín-González, F. Briones, J.F. Fernández, A.C. Caballero, M. Villegas, and J. de Frutos, *Phys. Stat. Sol (a)* 203 (2006)1383.
- [13] J. Cullen, D. Byrne, K. Johnston, E. McGlynn, and M.O. Henry *Appl. Phys. Lett.* 102 (2013) 192110.
- [14] M.W. Allen, R. Heinhold, P. Miller, M.J.H. Henseler, R.J. Mendelsberg, S.M. Durbin, and R.J. Reeves, *Appl. Phys. Lett.* 103 (2013) 231109.
- [15] B. K. Meyer, J. Sann, S. Lautenschläger, M. R. Wagner, and A. Hoffmann, *Phys. Rev. B* 76 (2007) 184120.
- [16] T. Rakshit, I. Manna, and S.K. Ray, *AIP Advances* 3, (2013) 112112.
- [17] M.R. Wagner, G. Callsen, J.S. Reparaz, J.-H. Schulze, R. Kirste, M. Cobet, I.A. Ostapenko, S. Rodt, C. Nenstiel, M. Kaiser, A. Hoffmann, A.V. Rodina, M.R. Phillips, S. Lautenschläger, S. Eisermann, and B.K. Meyer, *Phys. Rev. B* 84 (2011) 035313.
- [18] B.K. Meyer, J. Sann, S. Eisermann, S. Lautenschlaeger, M.R. Wagner, M. Kaiser, G. Callsen, J.S. Reparaz, and A. Hoffmann, *Phys Rev B* 82 (2010) 115207.
- [19] L. Viña, S. Logothetidis, and M. Cardona, *Phys. Rev. B* 30 (1984) 1979.
- [20] D. Bimberg, M. Sondergeld, and E. Grobe, *Phys. Rev. B* 4 (1971) 3451.
- [21] J.R. Haynes, *Phys. Rev. Lett.* 4 (1960) 361.

Figure captions:

Figure 1: 4.2 K PL spectra of the un-doped (A) and Sn-doped (B-E) CVT-grown ZnO single crystals.

Figure 2: (a) Temperature-dependent energy positions of the I_8 , I_9 , I_{10} and Y lines for a Sn-doped sample. Solid lines are fits to the data points using equation 2. (b) PL spectra of the Sn-doped sample at different temperatures from 4.2 K to 45 K. (c) Temperature-dependent integrated PL intensity of I_9 and I_{10} lines. The degeneracy ratios C_1 and C_2 , which are assumed as independent fitting parameters in Eqn. 2 are 4 and 1403 for I_9 , and 6 and 4515 for the I_{10} line respectively.

Figure 3: Donor bound exciton and two-electron satellite spectra, corresponding to a Sn-doped sample.

Figure 4: (a) Localization energy for D^0X and D^+X versus donor binding energy for standard shallow donors (H, Al, Ga, In) as well as I_{10} and carbon-related donors (Z-lines) and "deeply bound" D^0X transitions (Ge-related and Y line). (b) 2s-2p splitting for the various donors confirming the similarity of the 2s central cell shift trend for the shallow donors, in contrast to the deeply bound D^0X transitions (Ge-related and Y-line).

Figure. 5: Resistivity vs. temperature data for the samples indicated in Fig. 1.

FIG 1

FIG 2

FIG 3

FIG 4

FIG 5

Resistivity (Ohm cm)