Photoluminescence due to Group IV impurities in ZnO

J. Cullen[1], K. Johnston[2, 3], M. O. Henry[1], E. McGlynn[1], and the ISOLDE Collaboration[2]
[1]School of Physical Sciences, Dublin City University, Collins Avenue, Dublin 9, Ireland
[2]CERN, CH-1211 Geneva 23, Switzerland
[3]Technische Physik, Universitat des Saarlandes, D66041 Saarbrucken, Germany

ABSTRACT

We report the results of photoluminescence measurements on ZnO bulk crystals implanted with both stable and radioactive species involving the group IV impurities Ge, Si and Sn. We previously confirmed the identity of a line emerging at 3.3225 eV as being related to Ge and present here uniaxial stress data which show that the defect responsible has trigonal symmetry. Experiments with Si provide circumstantial evidence of a connection with the well-known line at 3.333 eV. Our measurements indicate that for the case of Sn on the Zn site luminescence is not observed. We also confirm that the I_9 and I_2 lines are due to substitutional In impurities.

INTRODUCTION

Steady progress has been made in recent years in unambiguously identifying the principal band edge bound exciton (I_n) lines in the photoluminescence (PL) spectra of ZnO, and several of these lines have now been assigned to bound exciton recombination at either neutral or ionised group III donor impurities on the Zn site. Nevertheless, several of the dominant I_n lines remain to be positively identified, in addition to some new lines recently reported [1, 2] in the PL spectra below the usual bound exciton region. These new lines are sharp, with full width at half maximum values similar to those of the I_n lines. In contrast to the I_n lines, however, their thermal binding energy is much lower than their spectral binding energy [2].

Ion implantation allows for controlled doping of impurities and for unparalleled control over the depth of these impurities after doping. However, the implantation process can induce defects not native to the semiconductor which may survive annealing procedures, making spectral features that appear after ion implantation difficult to assign unambiguously to the implanted impurity. Radioisotopes have been used in conjunction with traditional spectroscopic techniques for decades [3] and their use removes some of the ambiguity by correlating the decaying (increasing) intensity of a feature to the mother (daughter) isotope in the sample. Radioisotopes have already been combined with PL to accurately study the behaviour of specific dopants in a variety of semiconductors, including ZnO [3,4].

In this paper we expand on earlier work [2] that used radioisotopes to identify a sharp PL line at 3.3225 eV with Ge impurities. We provide more detail on the properties of this Ge-related line, and we also examine samples implanted with Si and with radioactive Ag that decays through In to stable Sn. We also note results obtained by other workers for the case of the group IV impurity Pb [5].

EXPERIMENT

For radiotracer ion implantation high quality single crystal ZnO obtained from Tokyo Denpa Ltd. (Tokyo, Japan) and Rubicon Technology, Inc. (Illinois, USA) was used. Radioactive ion implantation was performed at the ISOLDE facility at CERN using an energy of 60 keV and typical doses of 5×10^{12} atoms cm^{-2}. Details of the radiotracer implantation procedure are given elsewhere [2]. For stable isotope implantation an energy of 100 keV and typical doses of 1×10^{13} atoms cm^{-2} were used. The use of different implantation conditions is due to instrument constraints. However, the range/straggle for the radioactive and stable implantations are 32/14 nm and 49/20 nm, respectively [6], resulting in approximately the same peak concentrations sufficiently close to the sample surfaces. Following implantation, samples were annealed in O_2 gas or in air at 750°C for 30 minutes. We have found over many ZnO PL studies that the use of air or O_2 as annealing ambient has no significant effect on the band edge PL.

For uniaxial stress measurements, hydrothermally grown single crystal samples (supplied by Tokyo Denpa Ltd.) with planes cut perpendicular to the (11-20), (10-10) and (0001) axes were used in order to investigate the lines under stresses parallel and perpendicular to the c-axis (0001). Details of the stress apparatus are given elsewhere [7].

Luminescence was generated by the 325-nm line of a HeCd laser operating in the range 80 - 200 mW. The spectra were recorded at temperatures in the range 2.7 - 10 K using Janis closed cycle helium cryostats. The luminescence was analysed by a SPEX 0.75 m grating spectrometer equipped with a LN_2-cooled Jobin-Yvon CCD detector for the radiotracer implanted samples, and a Jobin-Yvon iHR320 grating spectrometer fitted with an Andor Newton EM-CCD detector cooled to -25°C for the uniaxial stress and normal PL measurements.

RESULTS AND DISCUSSION

A typical PL spectrum of as-received Tokyo Denpa ZnO is shown in figure 1 (a) below.

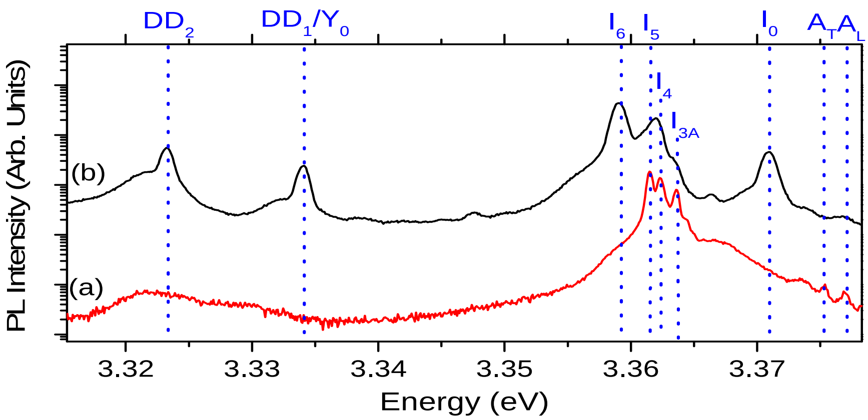

Figure 1. (a) A medium resolution PL spectrum for c-plane as-received ZnO. Shown in (b) is the same sample after ion implantation with Ge impurities and subsequent annealing. Spectra are vertically shifted for clarity and were recorded at 10 K.

The spectrum is composed of the free A-exciton (transverse and longitudinal) just below 3.38 eV, the ionised and neutral donor bound exciton lines around 3.36 – 3.37 eV and the lower energy two-electron satellites around 3.31 to 3.33 eV. Not shown here are the longitudinal optical phonon replicas which occur at ~73 meV intervals extending down to lower energies. The recently investigated 'Y-Lines' [1] that occur in the vicinity of 3.333 eV are not observed in any of our as-received hydrothermally grown material supplied by Tokyo Denpa.

ZnO:Ge

The PL spectrum of a sample implanted with stable Ge and subsequently annealed at 750°C in O_2 for 30 minutes is shown in figure 1 (b) above. Two sharp lines, at 3.3225 eV and 3.333 eV, appear in the spectrum well below the normal I_n line region; the relative intensities of the I lines are also changed from those in the as-received material. The 3.333 eV line (variously labelled as Y_0 or DD_1) which also occurs in un-implanted but annealed samples, has been reported previously [1,2,8] and in an earlier work we reported on the main properties of the 3.3225 eV line, including a positive identification of the line with Ge impurities on the Zn site [2]. We now present the results of uniaxial stress and polarisation measurements on this line, which we label DD_2 hereafter. Regarding the polarisation properties, our results show that the line is not significantly polarised, with a difference of ~19% between the intensities for polarisation parallel and perpendicular to the c-axis. This compares to a difference of 55% for the I lines.

Representative PL spectra under uniaxial stress are presented in figure 2. For stress parallel to the c-axis all lines shift to higher energy, with similar (but unequal) shift rates, while they all shift to lower energies for stress perpendicular to the c-axis (data not shown), also with similar but unequal shift rates.

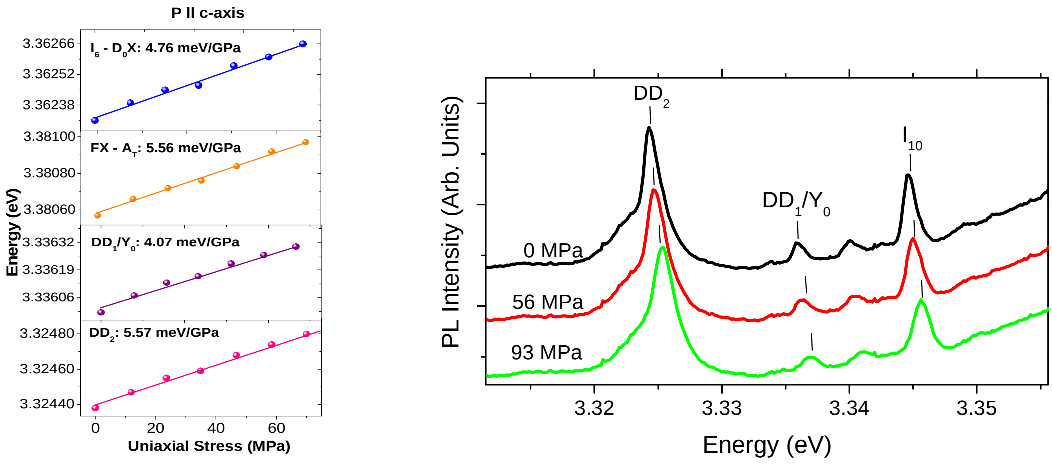

Figure 2. Spectra and shift rates for the DD_2 and nearby lines under uniaxial stress parallel to the c-axis. All lines shift to higher energy for stress parallel to the c-axis, with similar shift rate.

It is noteworthy that the DD_2 line does not split for any stress, and up to the largest stress value used, the line shape remains essentially the same. The absence of any splitting of this line for the two stresses means that the line originates at a centre of trigonal symmetry [9] further supporting the assignment of the line to isolated Ge atoms, and therefore corroborating a previous identification of the line with Ge on Zn sites [2]. The observed shift rate for the free exciton under stress parallel to the c-axis of + 5.56 meV/GPa is in reasonable agreement with the value of + 4.71 meV/GPa reported by Wagner *et al* [1] in a recent study of the Y_0 line.

The contrast between the large spectral binding energy relative to the free exciton position (~57 meV) and the observed weak thermal binding energy (~15 meV) was noted in previous work [2], and the tentative identification of the line with exciton recombination at Ge double donors in that work remains to be proven.

ZnO:Sn

We explored the case of ZnO:Sn by means of a sample implanted with a radioactive pre-cursor that transforms to stable Sn as its final decay product. Radioactive ^{117}Ag is available at ISOLDE at high purity thanks to a highly selective laser ionisation process. The decay sequence of this isotope is Ag(73 s)/Cd(2.5 hrs)/In(43 mins)/Sn(stable). The short half life of ^{117}Ag rules out the possibility of detecting Ag-related signals in PL, but the populations of Cd, In and Sn over a 24-hour period allow for the examination of In-related D_0X and D_+X lines in addition to the possibility of observing Cd- or Sn-related PL.

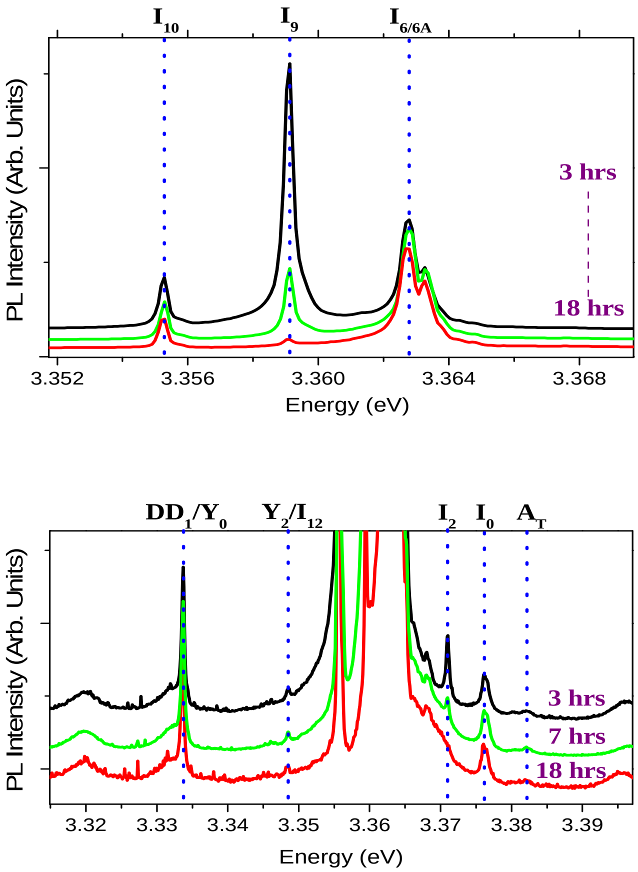

Figure 3. Representative spectra showing the disappearance of the I_9 and I_2 features due to substitutional In on a Zn site (In_{Zn}) as the In decays to Sn (with a half life 43.2 mins). Spectra are vertically shifted for clarity and shown on a linear y-axis.

The PL data over five half-lives of ^{117}In are shown in figure 3 above, and fits to the time dependence of the line intensities are shown in figure 4 below. It is immediately clear that both the I_9 and I_2 lines are due to In: the calculated half life of 43±2 minutes is in very good agreement with the tabulated half life of 43.2 minutes. The association of I_9 with In had been confirmed earlier using ^{111}In [10], but this is the first proof of I_2 being the D_+X line for In donors. There is no evidence of Sn-related (or Cd-related) PL in the data we recorded during this experiment.

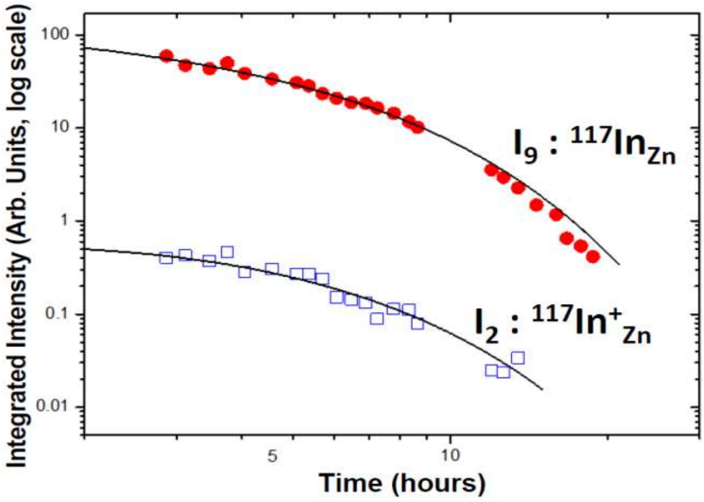

Figure 4. The intensity values over time represented by the red circles and blue squares for I_9 and I_2, respectively, and the accompanying fits to the decay of the lines.

ZnO:Si

We examined samples implanted with stable Si, but did not observe any PL lines unique to the case of ZnO:Si samples. However, we found some indications that the line at 3.333 eV (Y_0 or DD_1) may be related to Si, as its intensity was slightly enhanced in ZnO:Si compared to as-received samples. We note that Si is one of the principal impurities in the Tokyo Denpa material we used. Nevertheless, at this stage we cannot make a positive association of the 3.333 eV line with Si.

SUMMARY AND CONCLUSIONS

We have undertaken a PL study of several of the group IV impurities in ZnO, and of these, we find clear evidence with considerable spectral detail only for the case of ZnO:Ge. The uniaxial stress data in particular show that the DD_2 line at 3.3225 eV originates at a centre with trigonal symmetry, adding to the evidence that this line is due to a simple single-atom impurity in the ZnO crystal. Overall, the data we present here corroborate the evidence from earlier work linking the line to Ge_{Zn} impurities. It remains to be proven, however, that the source of the luminescence is bound exciton recombination at Ge double donor centres.

For the case of ZnO:Si we have circumstantial evidence only of a link between Si and the 3.333 eV (Y_0) line. So, although Si in ZnO has been predicted to act in a similar fashion to Ge [11], the data we have obtained to date do not provide proof of this. It should be noted, however, that Si is a major impurity in the ZnO crystals we have used, and future work will be carried out on starting material with lower Si contamination.

We now consider the cases of ZnO:Sn and ZnO:Pb. We find that samples with Sn impurities on Zn sites, formed by the decay of radioactive In, do not produce any Sn-related PL. Other workers, in a study of nanostructured ZnO likely to include significant Pb contamination, suspected a correlation of I_7 with Pb, but examination of Pb-implanted bulk material in the same study did not corroborate the result [5]. However, subsequent work by the same group indicates that there may be a Pb-related PL line at 3.3637 eV [12].

It is clear from the foregoing discussion that there remain several questions regarding the properties of group IV impurities in ZnO. To date, the only cases to present evidence of band edge recombination are Ge and Pb. Whether any of the other group IV impurities also act as binding centres for exciton recombination remains to be established.

ACKNOWLEDGEMENTS

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