The identification and nature of bound exciton I-line PL systems in ZnO

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Abstract. The chemical identification of donor bound excitons in ZnO has been studied using radioactive ions. Implantations of ^{117}Ag – which decays to radioactive Cd and In – have enabled the identification of the I_2 optical feature as being the ionized donor counterpart of I_9, one of the most prominent optical features in the photoluminescence spectrum of ZnO. Both of these lines are consistent with In occupying a Zn site.

Keywords: Photoluminescence, ZnO, Excitons, Radioactive isotopes.

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INTRODUCTION

The donor bound exciton spectrum is a well-studied system which has been under investigation since the initial reports by Thomas over 40 years ago [1] and reviewed in some detail by Meyer [2]. The system consists of 12 sharp lines – the I_n series – and in spite of the intense work carried out on ZnO in the past 10 years, identifying the chemical origin of the features has been challenging. One of the most transparent means of chemically identifying luminescence features is through the use of radioactive isotopes. This method has been successful in identifying the I_8 and I_1 line with Ga and also in identifying a new feature related to Ge [3,4]. Here we report on studies of the I_9 line in ZnO. This is a donor bound exciton with a transition energy of 3.3567eV and which has been previously studied using radioactive isotopes and was attributed to the presence of In on a Zn site [5]. We confirm the results of Müller *et al.* and find in addition that the optical feature I_2 – with a transition energy of 3.3674 – is the ionized form of I_9; the first unambiguous identification of this optical feature.

METHOD

High quality single crystal ZnO samples were obtained from Tokyo Denpa Ltd. These were implanted at the ISOLDE facility, CERN with an implantation energy of 60kV. The typical dose was $5x10^{12}cm^{-2}$. The radioactive beams were produced following proton activation of a UC target with subsequent laser ionization and mass separation. The implanted isotope was ^{117}Ag which had a purity of >95%. This isotope decays with a half-life of 73secs. The samples were allowed to cool while the Ag decay took place and were annealed at 800C for 30 mins once equilibrium with the daughter ^{117}Cd had been reached. Following annealing, photoluminescence (PL) measurements were carried out monitoring the transition of the ^{117}Cd to ^{117}In which then decays to stable ^{117}Sn. Luminescence was generated using the 325nm line from a He-Cd laser. The sample was held at 4K in a closed cycle Janis He cryostat and the luminescence was collected using a SPEX 0.75m spectrometer equipped with a LN_2-cooled CCD camera.

RESULTS

Representative PL spectra monitoring the donor bound exciton luminescence as a function of time are shown in Figure 1(a). These lines have all been normalized to the area of the optical feature DD/DD_1 which has an energy of 3.333eV. The times of measurement are from 2.5 hours to 18.5 hours after implantation, representing the beginning of the decay of ^{117}Cd to the final production of stable Sn.

Four lines are clearly seen: the I_{10}, I_9, I_7 and I_6. It is immediately obvious that the I_9 line is decaying over time whilst none of the other lines are changing. In addition, closer inspection of the weaker optical

features I_2 and I_1 – shown in Figure 1(b) – reveal that the I_2 optical feature is also decaying over time. The time dependence for both lines is shown in Figure 2. Fits to the data allow the half-life of the resultant isotope to be extracted and in both cases is found to be 43±3minutes. This is in very good agreement with the tabulated half-life of ^{117}In which is 43.2 minutes.

As mentioned in the introduction, the identification of I_9 with In has already been made by Müller – although we have been able to improve the accuracy by more than a factor of three – but the identification of I_2 with In has not been made previously. This shows that In gives rise to a neutral and ionized donor bound spectrum. Ga and Al also give rise to such a spectrum accounting for the I_8/I_1 and I_6/I_0 systems respectively. Considering the energies of the emission features, which are in agreement with effective mass theory for substitutional impurities [2], Considering the energies of the emission features, which are in agreement with effective mass theory for substitutional impurities [2], and also PAC measurements which confirmed that In readily occupies an undisturbed Zn lattice site [5], these results are consistent with the relevant impurity occupying a substitutional Zn in the ZnO lattice.

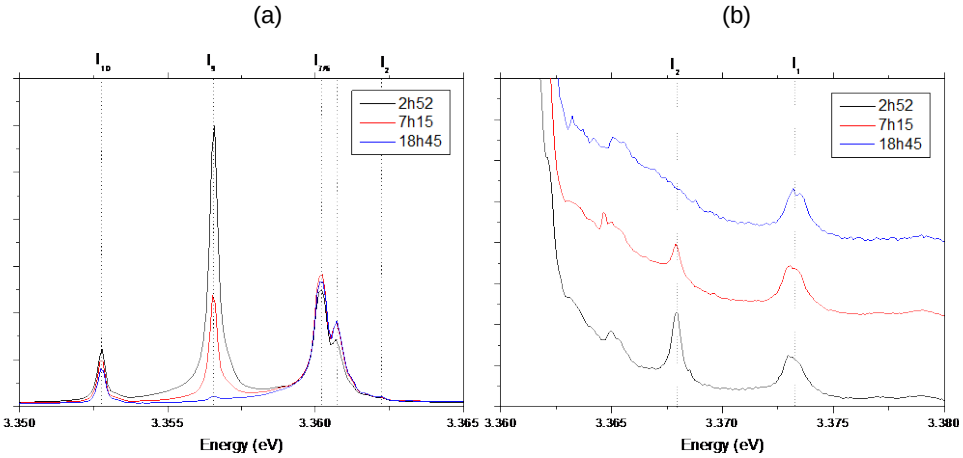

Figure 1 Representative spectra showing the behavior of the donor bound exciton features after normalizing to the DD_1 line. The three spectra show the progression of the decay of the implanted isotope over almost 19 hours. As can be clearly seen in (a) and (b) two lines are decaying as the implanted Cd decays to In and thence to Sn.

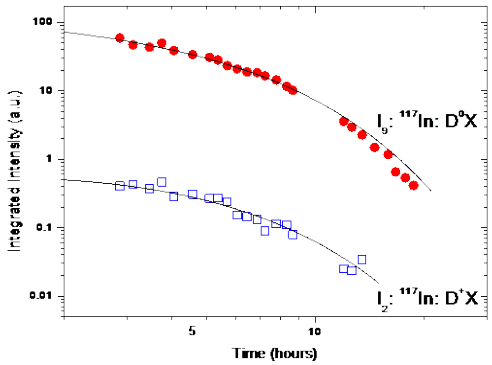

Figure 2 Fits to the data for the decay of I_9 and I_2 are shown. In both cases, the obtained half-life is consistent with the decay of ^{117}In.

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