# Identification of donor-related impurities in ZnO using photoluminescence and radiotracer techniques

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The results of photoluminescence measurements on ZnO implanted with stable and radioactive isotopes of Zn and Ga are presented. The donor-related exciton feature $I_8$ at 3.3600 eV is suggested to be due to bound exciton recombination at Ga donors. The $I_1$ line at 3.3718 eV is also likely to be due to Ga, and is attributed to ionized Ga donor bound exciton recombination. A feature at 3.3225 eV is observed following transmutation of radioactive Ga into stable Ge, and is attributed to Ge. Finally, a damage-related band is observed in the region of 1.8 eV when the recoil energy of the decay is capable of dislodging the host atoms from their respective lattice sites.

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## I. INTRODUCTION

ZnO is now readily available in high-quality crystalline form, which has considerably improved the prospects of the material for optoelectronic applications.[1–3] However, the chemical nature of the wide variety of donors observed in ZnO has still not been fully resolved. Progress with the production of *p*-type material has been made, but the reproducibility and control of the doping are still significant problems.[4] Therefore, there is still a real need for a deeper understanding of the impurities and defects in ZnO, including some basic information concerning impurity identification and in particular for the control of background *n* conductivity. Photoluminescence (PL), although a highly sensitive technique, does not readily provide direct chemical information. It is possible to obtain chemical identification where isotopic substitution results in line shifts, but the shifts are not always measurable, especially for large atomic mass elements where the percentage mass changes are small.[5] An alternative approach is to employ radioactive isotopes as probes and track the decay or growth over time as the implanted isotope transmutes into its daughter.[6,7] This method has already been employed with some success in the study of the isoelectronic impurity Hg in ZnO (Ref. 8), and for the identification of a variety of impurities in other semiconductors.[9,10] In this paper, we report on the luminescence properties of donor-related impurities in ZnO studied using both stable atom implantations and radiotracer techniques. New data are presented which establish the association between the $I_8$ and $I_1$ bound exciton recombination with Ga, and luminescence attributed to Ge-related deep defects in ZnO is also reported. In addition, the occurrence of secondary damage in ZnO is observed, where the recoil from the decay of the radioactive isotope is sufficient to knock host atoms off their lattice sites, generating a damage-related band in the 1.8 eV range.

## II. EXPERIMENTAL DETAILS

ZnO hydrothermal crystals, polished on the O-terminated side, were obtained from Rubicon Technology, USA. Implantations of stable isotopes were carried out at the Nuclear Physics Institute, Lisbon. Zn and Ga were implanted to a dose of $\sim 10^{13}$ cm$^{-2}$, and then annealed in an $O_2$ atmosphere of 0.5 bar at a temperature of 1073 K for 30 min. Implantation of radioactive isotopes was performed at the ISOLDE facility, CERN.[9] Radioactive beams were generated using the isotope separator on-line technique, whereby fission-induced byproducts are generated following the impact of a proton beam on a target.[11,12] The isotopes are then separated and ionized to produce a beam which is accelerated and used to implant the samples. Two different isotopes were implanted for this study: $^{72}$Zn and $^{73}$Ga. The first of these decays to stable $^{72}$Ge via $^{72}$Ga, with half-lives of 46.32 and 14.1 h, while the latter is a direct decay to stable $^{73}$Ge with a half-life of 4.87 h. Implantation doses were of the order of $10^{12}$ cm$^{-2}$ and were carried out at 260 keV. TRIM calculations give an implantation depth of approximately 100 nm in both cases. This corresponds to a concentration of the order of $10^{17}$ cm$^{-3}$. Following implantation, the samples were annealed at 1073 K in an $O_2$ atmosphere of 0.5 bar in order to repair the implantation damage. The samples were mounted in a cryostat and measurements were carried out over the course of, typically, six half-lives. While the measurements

 

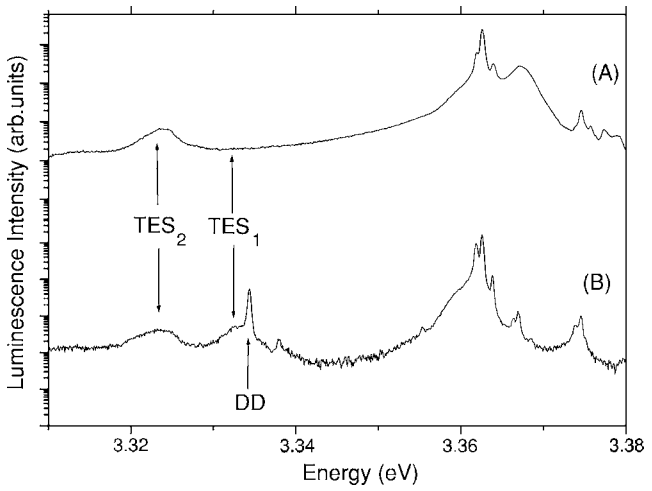


FIG. 1. Spectra of an unimplanted ZnO sample. The lower spectrum (A) is of an as-received Rubicon sample; the upper spectrum (B) is a spectrum of the sample after annealing at 1073 K for 30 min in an $O_2$ atmosphere of 0.5 bar. The "DD" line and general TES structure correspond to a donor-related feature reported by Schildkecht *et al.* (see Ref. 13).

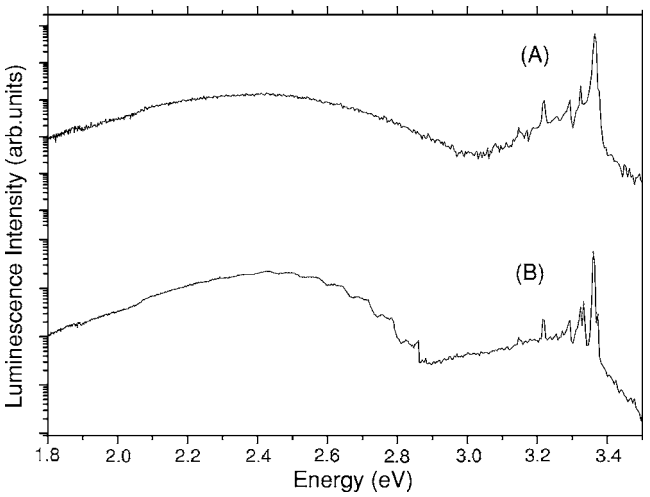


FIG. 2. Spectra of an unimplanted ZnO sample. The lower spectrum (A) is of an as-received Rubicon sample; the upper spectrum (B) is a spectrum of the sample after annealing at 1073 K for 30 min in an $O_2$ atmosphere of 0.5 bar. As can be seen, the visible band becomes structured after annealing.

were being conducted, the temperature of the system never rose above 77 K; the actual measurement temperature was 1.5 K. In all cases, PL was generated using a HeCd laser operating at 325 nm and a power of 80 mW. The luminescence was analyzed using a Bomem DA8 Fourier transform spectrometer for the stable isotope studies. For the radioactive samples, measurements were made at CERN using a 0.75 m SPEX grating spectrometer (1800 grooves $mm^{-1}$ blazed at 400 nm) equipped with a liquid-nitrogen-cooled. For the as-received and annealed samples, a 1 m grating spectrometer (SPEX 1704) was used with a photomultiplier tube (Hamamatsu model R3310-02) in photon-counting mode.

## III. RESULTS

### A. Stable isotope experiments

Control experiments were performed by annealing unimplanted samples and by implanting stable isotopes of Zn and Ga and annealing them using the standard procedure described above. Zn was chosen in order to examine whether implantation damage alone would result in distinctive PL features, and Ga was chosen because it is the main element under consideration here. Figure 1 shows the effect on the bandedge luminescence of annealing an unimplanted sample at 1073 K. The upper spectrum A shows the PL spectrum obtained before annealing, while spectrum B is of the same sample after the anneal. As can be seen, the effects of annealing on the PL spectrum in the bandedge region are quite striking with the relative intensities of features at the bandedge changing considerably. We note the disappearance of the broad feature at 3.3673(5), and also the appearance of a feature at 3.3333(5) eV which has been attributed to a deep donor (DD) by Schildkecht *et al.*[13] Figure 2 shows the effects of annealing on the luminescence over a broader energy range. Here, we see that the visible emission changes from a weak broad structureless band to a structured band that peaks in the green. PL measurements of the annealed sample, measured several days after the anneal and first measurement, show the same features with only slight changes in intensity which may be explained by slight changes in sample alignment.

Figure 3 shows spectra of ZnO implanted with stable Ga and Zn. For the case of implantation with stable Zn, we observe a peak at 3.3603(1) eV and also the DD feature described in the previous paragraph. We observe a line at 3.3600(1) eV for the Ga-implanted sample. We also see two-

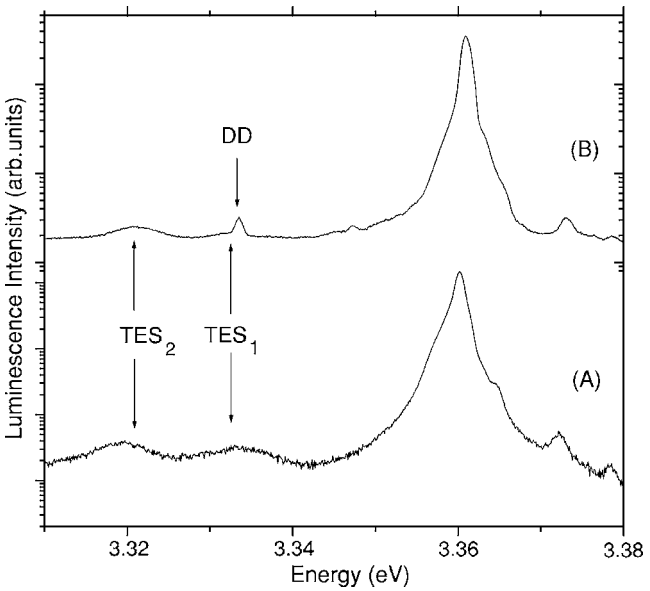


FIG. 3. Spectra of the Ga- and Zn-implanted samples measured at 6 K after annealing for 30 min at 1073 K. The lower spectrum (A) is the Ga-implanted sample; the upper spectrum (B), is the Zn-implanted sample.

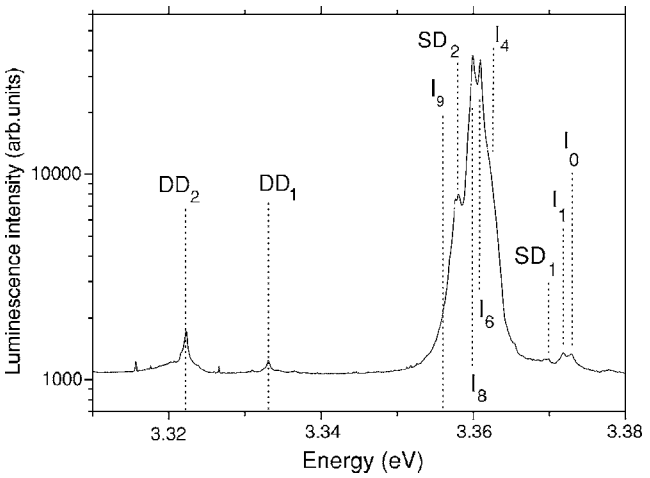


FIG. 4. Representative spectrum for the $^{73}$Ga implantations, taken at $T=2$ K. The labels are all detailed in Table I. The feature at 3.35803(3) eV is *not* the $I_9$ feature, and appears to be a new donor-related signal ($SD_2$). The donor-bound signal $I_1$ is related to Ga as is $I_8$ while the new $DD_2$ signal is attributed to the deep defect Ge.

electron satellites (TES) of the donor bound exciton (*DX*) lines in both samples. Previous reports by Kato *et al.*[14] on ZnO:Ga, based on epitaxial films grown on GaN substrates, featured an exciton peak at 3.362 eV which was assigned to $Ga_{Zn}$. In additional work by Ko *et al.*,[15] a *DX* peak observed at 3.358 eV was assigned to Ga (and labeled $I_{Ga}$). In the work carried out by Reuss *et al.*[16] on ZnO implanted with Ga, an exciton feature at 3.359 eV with an exciton localization energy of ~53 meV was reported. These line positions broadly correspond to the $I_8$ line first reported and labeled by Reynolds *et al.*[17] A recent review by Meyer *et al.*[18] associates the $I_8$ line measured at 3.3598 eV with Ga, although the attribution is still inferred primarily from doping work; a companion paper by Strassburg *et al.*[19] confirms the donor-like behavior of diffused Ga in ZnO. Schildknecht *et al.*[13] also observed a donor-bound exciton (*DX*) line at 3.36 eV with a 54 meV binding energy but did not attributed it to any particular impurity. Given the variety of line positions attributed to the Ga *DX* line in these studies, we undertook a study of ZnO:Ga using radioactive isotopes in order to provide conclusive evidence of the connection of Ga with the $I_8$ line. Such a conclusive identification, in turn, allows growers to confidently target the causes of residual *n*-type background doping in ZnO and may lead to substantial reductions in these levels, which makes the process of *p*-type conversion with good hole mobility easier to obtain.

### B. Radioactive isotope experiments

We report first the data for the $^{73}$Ga case, where there is a single stage in the decay process to Ge. A representative spectrum from the $^{73}$Ga experiment is shown in Fig. 4, and a summary of the optical features is presented in Table I. At all stages of the experiment, the PL spectrum is dominated by the (*DX*) features described in earlier work.[13,17,18] The lines $I_{0,1,4,6,8}$ are clearly visible, and the TES recombination/emission[20] of lines $I_6$ and $I_8$ is also seen. The DD line[13] observed in this sample occurs regularly in Rubicon material. For the purposes of this paper we label the line $DD_1$. Since the intensity of this feature is relatively constant (to ±10%), which may be explained by slight changes in sample alignment over the course of the measurement, and since the line is also clearly separated from the rest of the bandedge peaks, we normalize the luminescence intensity data to this line. Figure 4 also shows a new line, similar to $DD_1$ and ~11 meV lower in energy at 3.3225(3) eV, which we designate $DD_2$.

TABLE I. Summary of the features which have occurred as a result of $^{73}$Ga implantation. Labels in brackets are notated as in Schildknecht *et al.*;[a] otherwise the convention of Reynolds[b] and Meyer[c] is followed. The "new" features seen in this work (TW) are labelled SD1/2 for shallow donor 1/2 and $DD_2$.[d] The labeling takes the following form: N/A indicates an optical feature without phonon or two electron satellite features; LO indicates the presence of an optical phonon; ? indicates that the feature has not been assigned to any impurity, either in this or previous work.

| Energy (eV) | Label | Features | $E_{1s\leftrightarrow 2p}$ (meV) | Identity | Reference No. |
|---|---|---|---|---|---|
| 3.3783 | $A_L$ | N/A | N/A | ? | 18 |
| 3.3731 | $I_0$ | | | ? | 18 |
| 3.3718 | $I_1$ | | | Ga | TW,[17,18] |
| 3.3699 | $SD_1$ | | | ? | TW |
| 3.3628 | $I_4$ ($D^0_{1a}$) | | Not seen | H | 13, 17, and 18 |
| 3.3610 | $I_6$ | LO (x3) | 36.91 | Al | 17 and 18 |
| 3.3600 | $I_8$ ($D^0_{2a}$) | N/A | 41.65 | Ga | TW,[13,18] |
| 3.3580 | $SD_2$ | | N/A | ? | TW |
| 3.3333 | $DD_1$ | | | ? | TW,[13] |
| 3.3225 | $DD_2$ | | | Ge | TW |

[a]See Ref. 13.
[b]See Ref. 17.
[c]See Ref. 18.
[d]After the DD feature in Ref. 13.

PL spectra recorded at three points during the Ga to Ge decay are shown in Fig. 5. It is clearly seen that the $I_8$ feature decays in intensity as the Ga transforms to Ge; a discussion of the time dependence is presented below.

The $I_0$ and $I_1$ lines are both observed in the PL spectra of the sample implanted with $^{73}$Ga. $I_1$ has been previously reported, but no chemical identification has been put forward.[18] In our experiments, the intensity of $I_1$ decreases steadily as the Ga decays to Ge, pointing to the involvement of Ga. For $I_0$, the intensity fluctuates, but no systematic change is found.

We note the appearance of two features around 3.3600 eV in the spectra of Fig. 4, and tabulated in Table I. This is the region of the spectrum where, based on effective mass theory, one expects to find the luminescence signature of neutral shallow donors. These have been studied and classified with great effort over the decades and include the $I_i$ lines under discussion in this paper. More details about the underlying theory and previous work associating these lines with emission from excitons bound to shallow donors can be found in Refs. 18 and 21. Based on this prior work, we label these lines as SD, standing for shallow donor, to indicate

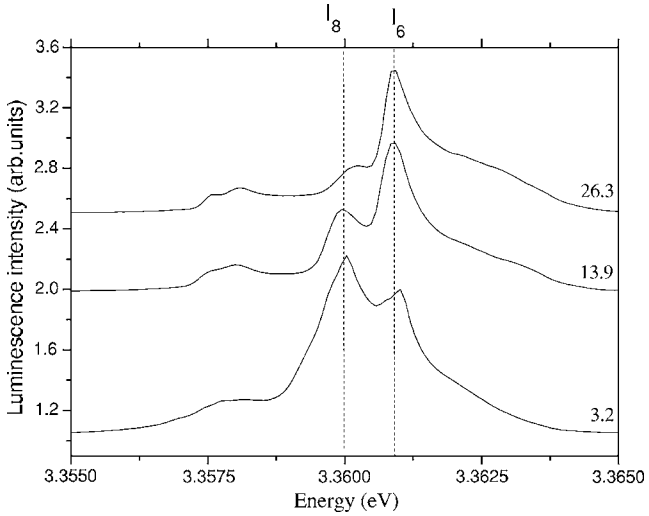


FIG. 5. Representative spectra taken of the $^{73}$Ga sample at different time intervals: 3.2, 13.9, and 26.3 h into the PL measurement. The labels $I_8$ and $I_6$ are the features listed in Table I.

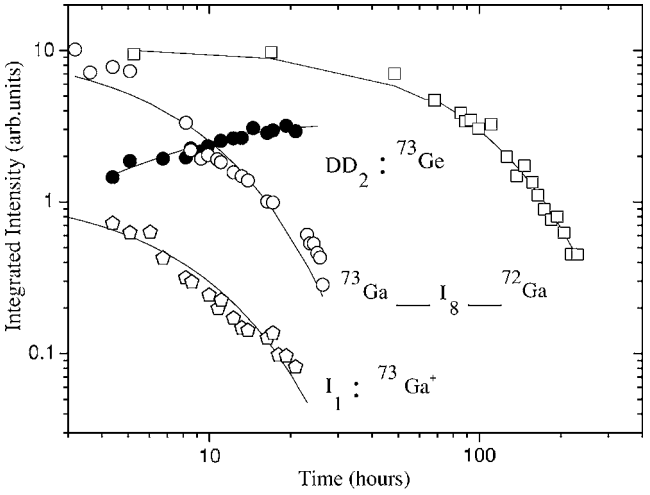


FIG. 6. The fits to the data obtained from the various experiments are modeled [using Eqs. (1)–(3)]. The values for the half-life arising from the fits are summarized in Table II. The unfilled circles and squares are the data for the $^{73}$Ga and $^{72}$Zn implantations, respectively; the filled circles are the data for the growth of the $^{72}$Ge peak. Also included on the graph are the data for the decay of the line $I_1$: this is due to the ionized Ga donor ($D^+X$).

they occur in the spectral region conventionally associated with such emission. The first of these, labeled, $SD_1$, lies at 3.3699(3) eV, but its energy does not correspond to any of the known *DX* lines. Another feature labeled $SD_2$ occurs at 3.35803(3) eV. The intensities of these lines do not change with time, and therefore they are related to neither Ge nor Ga. We do not consider them further in this study.

For the case of $^{72}$Zn$\rightarrow$ $^{72}$Ga$\rightarrow$ $^{72}$Ge, there is a two-stage process involving the growth and decay of $^{72}$Ga culminating in stable $^{72}$Ge. Yield information using $\gamma$-ray spectroscopy showed that the ion beam contained both $^{72}$Ga and $^{72}$Zn atoms, due to the mass coincidence, with the result that the ZnO sample contained $^{72}$Zn and $^{72}$Ga in the ratio 3.2:1 after implantation. This means that the population of $^{72}$Ga atoms in the sample over time is driven by two processes: (i) The decay of the directly implanted $^{72}$Ga, and (ii) the growth and subsequent decay of $^{72}$Ga formed by transmutation of implanted $^{72}$Zn. The features in the PL spectra for this case are essentially the same as those for the case of $^{73}$Ga shown in Fig. 4, with the $I_8$ line intensity decreasing over time, also.

## IV. DISCUSSION

Our full set of data for the behavior of the $I_8$ line for ZnO implanted with $^{72}$Zn$\rightarrow$ $^{72}$Ga$\rightarrow$ $^{72}$Ge and $^{73}$Ga$\rightarrow$ $^{73}$Ge are presented in Fig. 6, where normalized intensities over the duration of the radioactive decays are plotted on a log-log scale. Changes of an order of magnitude are observed in the relative intensities of the $I_8$ lines in both cases. To fit the data for $^{73}$Ga implantation, we use the simple exponential equation for the Ga concentration:

$$[\mathrm{Ga}](t) = [\mathrm{Ga}](0)e^{-\lambda_{\mathrm{Ga}}t}, \quad (1)$$

where $\lambda_{\mathrm{Ga}}$ is the decay constant. [Ga](0) is the concentration of the Ga at $t=0$, which is the time at which the annealing was completed. A fit to the data, shown by the open circles and solid line in Fig. 6, gives a value of 4.9±0.3 h for the half-life, which is very close to the known $^{73}$Ga half-life value of 4.76 h.

For the two-stage $^{72}$Zn$\rightarrow$Ga$\rightarrow$Ge case, the beam consists of both Ga and Zn atoms, and the population of $^{72}$Ga follows the relation:

$$[\mathrm{Ga}](t) = [\mathrm{Ga}](0)e^{-\lambda_{\mathrm{Ga}}t} + \frac{[\mathrm{Zn}](0)\lambda_{\mathrm{Zn}}(e^{-\lambda_{\mathrm{Zn}}t} - e^{-\lambda_{\mathrm{Ga}}t})}{\lambda_{\mathrm{Ga}} - \lambda_{\mathrm{Zn}}}. \quad (2)$$

For the fit, [Ga](0) and [Zn](0) are constrained to have the ratio 3.2:1, the value of $\lambda_{\mathrm{Zn}}$ is fixed at 0.015 h$^{-1}$, and $\lambda_{\mathrm{Ga}}$ is allowed to vary. The data and the fit are shown by the open squares and solid line in Fig. 6. A value of 12.7±1.5 h is found for the half-life of $^{72}$Ga, which compares well to the expected $^{72}$Ga half-life of 14.1 h. These two sets of data very convincingly indicate the involvement of Ga in the $I_8$ line emission and, based on these data, we attribute the $I_8$ emission to *DX* recombination at substitutional $\mathrm{Ga_{Zn}}$ impurities.

The majority of the $I_i$ lines are commonly associated with neutral donor-bound excitons (*DX*), but Zeeman measurements have shown that $I_2$ and $I_3$ originate from the recombination of excitons bound to ionized donors, which we label ($D^+X$).[17] Our results for line $I_1$ provide strong evidence to link this line with the Ga donor, also. The line appears in the spectra after implantation with $^{73}$Ga, although the intensity is low. As can be seen from Fig. 6, $I_1$ decays as the Ga isotope decays to Ge, and a fit of the data using Eq. (1), shown in Fig. 6 by the open pentagons and solid line and labeled $Ga^+$, yields a half-life value of 4.9±0.3 h which compares very favorably with the quoted half-life of 4.76 h. Accordingly, we attribute $I_1$ to the recombination of excitons bound to the $Ga^+$ ionized donor.

We now consider the stable Ge that is produced in the radioactive decay. The spectra for the $^{73}$Ga experiment, presented in Fig. 7, show that the feature $DD_2$ is obviously

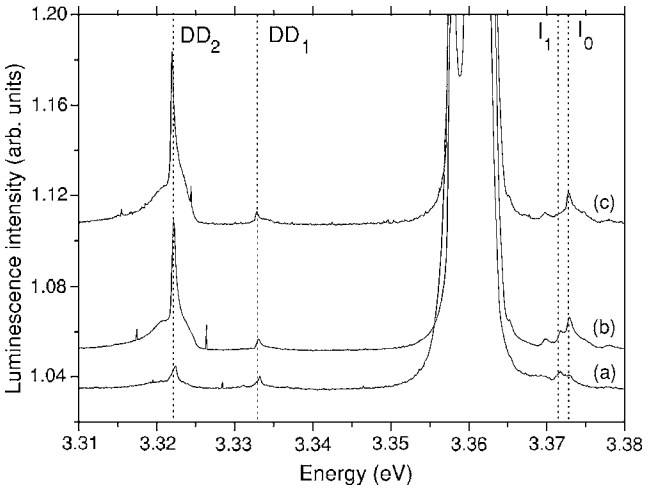


FIG. 7. The growth of the Ge-related feature, $DD_2$, and decay of the Ga-related $I_1$ feature over time: (a) 3.183 h, (b) 13.883 h, and (c) 26.67 h after annealing, following implantation of $^{73}$Ga. Note that in addition, the peak $DD_1$ is remains unchanged throughout the course of the measurement; we normalize to this peak.

growing in time as the Ga transmutes into stable Ge. All of the data were again normalized to the $DD_1$ line. In this case, the integrated luminescence intensity is expected to fit the simple equation

$$[\mathrm{Ge}](t) = [\mathrm{Ge}](0)(1 - e^{-\lambda_{\mathrm{Ge}} t}), \tag{3}$$

where λ again represents the decay constant of the mother isotope. The data and a fit using Equation (3) are shown by the solid line and filled circles in Fig. 6 (see also, Table II). The value for the half-life obtained from the fit is 4.9±0.2 h, very close to the half-life of 4.76 h for $^{73}$Ga. The line $DD_2$ is also seen in the sample implanted with $^{72}$Zn but with much lower intensity. The peculiar shape of the broader band on which it resides, which also grows, is as-yet unexplained. Although it has the appearance of a TES, there is no candidate *DX* line to which it could be associated. However, given that the $DD_2$ line appears in the two cases where Ga decays to Ge, we can confidently associate the line with Ge impurities.

TABLE II. Details of the radioactive properties of the isotopes under consideration and fits to the luminescence data. The recoil energies are calculated using the method of Vesagi.[a] $^{73}$Ge is stable: for $^{73}$Ge$^*$ the value is derived from the decay of $^{73}$Ga [using Eq. (3)].

| Isotope | $E_{\mathrm{recoil}}$ (eV) | $t_{1/2}^{\mathrm{tabulated}}$ ($h$) | $t_{1/2}^{\mathrm{fitted}}$ ($h$) | Error ($h$) |
|---|---|---|---|---|
| $^{72}$Zn | 1.58 | 46.50 | | |
| $^{73}$Ga | 16.00 | 4.76 | 4.9 | 0.3 |
| $^{73}$Ge$^*$ | | 4.76 | 4.9 | 0.2 |
| $^{72}$Ga | 118.00 | 14.10 | 12.7 | 1.5 |
| $^{73}$Ga$^+$ | | 4.76 | 4.9 | 0.3 |

[a]See Ref. 31.

It is interesting to consider the consequences of this association. The site of an impurity in a semiconductor determines its electrical effect on the material. In prototypical single-crystal material, e.g., Si, this is relatively straightforward; donors are produced by impurities from group V of the periodic table, e.g., P; acceptors are produced by substituting with elements from group III, e.g., B. The case of compound semiconductors is more complex and is dependent on electronegativties and chemical similarities. Control of doping in wide-band-gap materials is also hampered by an inherent doping asymmetry, where either *n*- or *p*-type conductivity is preferred over the other, often due to the low formation energies of native defects which hinder the nonpreferred conductivity.[22] This situation is further exacerbated by the apparent problem that the "text-book" approach to doping does not always apply to ZnO; obvious *p*-type impurities, such as P and As, are predicted from *ab initio* calculations to be more stable on the Zn rather than the O site.[23] Recent experimental work provides evidence that As does in fact occupy the Zn site and should therefore be treated as a donor, rather than an acceptor as previously thought.[24] In the context of this work, the Ge feature is observed after the implantation of $^{73}$Ga which decays to $^{73}$Ge with a recoil of ~16 eV. This is insufficient to dislodge the implanted isotope from its implanted and annealed position—see more below—therefore, the fact that the implanted Ga gives rise to the *DX* $I_8$ line indicates that it occupies a Zn site in the lattice, and that the resulting Ge will also be so incorporated giving rise to this "DD" luminescence.

The possibility of radiation damage, and other effects due to damage being the source of the effects observed in these experiments, needs to be examined. We consider three aspects—nuclear recoil, electron emission, and potential Fermi-level shifts due to changes in carrier concentration.

If the recoil energy is sufficient to displace an atom from its normal site, and the sample temperature is kept low, we can expect that simple native defects, such as interstitials, will be produced. For ZnO, the displacement energy is 45 eV for an O atom and 18 eV for Zn.[25,26] The $^{73}$Ga recoil of 16 eV is below these values, whereas the recoil energy of 118 eV for $^{72}$Ga is much greater. Accordingly, we would expect evidence of damage in the latter, but not in the former samples. The results shown in Fig. 8 corroborate this expectation. A broad luminescence band with its peak at 1.78(1) (~696 nm) and extending well into the red is found to grow only in the sample implanted with $^{72}$Zn→$^{72}$Ga→$^{72}$Ge. We note that in a study of electron irradiated ZnO, Gorelkinskii and Watkins[27] observed two main peaks, one at 900 nm (1.378 eV) and one at ~700 nm (~1.771 eV), following low-temperature irradiation. The 900 nm band almost disappears under annealing up to 100 K and a band grows in with its peak at ~680 nm, very close to the peak of 696 nm in our case. Since our sample was cycled repeatedly between liquid-helium temperatures and 77 K over the nine days duration of the study, we believe that the broad spectrum in our samples is the same as the ~680 nm band that recorded by Gorelkinskii and Watkins[27] for their annealing temperature of 140 K. The facts that the band is created in our sample while the temperatures is kept well below 100 K, and that the Zn and O vacancies are stable up to at least room

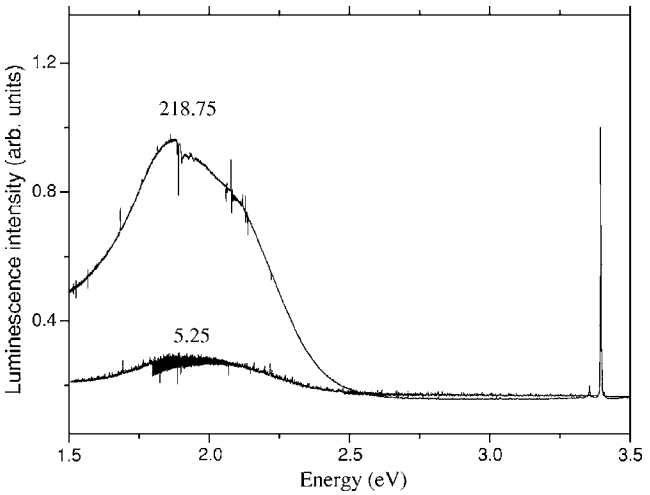


FIG. 8. The appearance of a large red band after five half-lives of $^{72}$Zn. The lower spectrum was taken after 5.25 h; the upper at 218.75 h. This feature is the same as seen by Gorelkinskii and Watkins (Ref. 27) and is believed to be due to intrinsic impurities. From the work carried out here, we believe that it may involve either Zn or O interstitials. The absorption shown in at 1.67(1) eV is either derived from Ni or Li (see Refs. 32 and 33).

temperature[28,29] indicate that the band is most likely due to a defect involving an interstitial atom. This is consistent with the behavior of other semiconductors, such as diamond, where the interstitial is known to be mobile at low temperatures.[30]

The products of the radioactive decays for $^{72}\mathrm{Zn} \rightarrow {}^{72}\mathrm{Ga} \rightarrow {}^{72}\mathrm{Ge}$ and $^{73}\mathrm{Ga} \rightarrow {}^{73}\mathrm{Ge}$ include high-energy electrons, with mean energies in the region of 448.5, 502.6, and 85.6 keV for $^{73}$Ga, $^{72}$Ga, and $^{72}$Zn, respectively. These could potentially cause the generation of defects in the crystals that might influence the PL intensities. On this point, we note that the total dose of electrons absorbed by the samples, assuming all emitted electrons are absorbed, is at most $10^{12}$ electrons. In contrast, the doses used by Gorelkinskii and Watkins[27] were in the range $10^{16}$ to $10^{17}$ electrons, so it is extremely unlikely that the much lower doses that occur in the samples studied here have any effect on the PL spectra.

Finally, we consider possible effects on PL intensities of shifts in the Fermi-level position due to changing carrier concentrations. For the two cases considered above, the donor concentrations increase as the decays occur from $\mathrm{Zn} \rightarrow \mathrm{Ga} \rightarrow \mathrm{Ge}$ or $\mathrm{Ga\ Ga} \rightarrow \mathrm{Ge}$. Since the crystals are already *n* type at the start of the experiment, these changes will cause only a small shift of the Fermi-level position toward the conduction band edge. The effects of a Fermi-level shift on the PL would be expected to take the form of a sharp change in the PL intensity due to a change of charge state as the level moves through an impurity energy level in the band gap. It is most unlikely that a moving Fermi level could induce changes in the PL intensity that exactly follow the characteristic half-life of the radioactive isotopes.

Taking all the results into account, in particular the excellent agreement between the half-life values of the isotopes and the fits obtained in our analysis, the simplest and most convincing explanation for the effects we report is that the PL intensities are proportional to the population of the mother/daughter isotopes, supporting our direct identification of the changing PL lines with particular elements.

## V. SUMMARY AND CONCLUSIONS

This paper has provided new information about the properties of donors in ZnO. Based on radioactive isotope implantations, the *DX* line $I_8$ is strongly suggestive of being unambiguously related to the neutral Ga donor; the $I_1$ line behaves similarly and we assign the line to ionized donor bound exciton recombination due to Ga, denoted $D^+X$. In addition to these Ga-related features, a new line at 3.3225(3) eV indicates that it is related to Ge; this is likely to be the first observation of luminescence associated with a Ge donor in ZnO. A damage-related band is found to occur when the recoil energy of the nuclear decay is sufficiently high to displace the Zn and O atoms. This is likely to be the same band as that reported by Gorelkinskii and Watkins[27] for electron irradiated ZnO and we attribute the band to an interstitial defect, or a related complex.

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