Radioactive Isotopes in Photoluminescence Experiments: Identification of Defect Levels

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The characteristic lifetimes of radioactive isotopes can be used to label and identify defect levels in semiconductors which can be detected by photoluminescence (PL). This is demonstrated in GaAs doped with radioactive ^{111}In. During its decay to ^{111}Cd all those PL peaks increase for which Cd acceptors are involved. By deriving a quantitative relation between PL intensity and Cd concentration we show that this intensity increase is determined only by the nuclear lifetime of ^{111}In. Thus we gain a complete and independent identification of the Cd related PL peaks in GaAs.

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Impurities and other defects in semiconductors cause electronic states within the band gap and dominate the electric properties of semiconductors. The control of these defect states is the basis of semiconductor devices. Photoluminescence (PL) spectroscopy is a standard technique to observe the presence of these states and to determine their energy levels. However, the assignment to a particular defect is often a puzzle.

In semiconductors with residual impurities below the threshold concentration for PL detection intentional doping and its correlation to the intensity of PL transitions is used to identify the chemical nature of defect levels. In this way many defect levels in Si, Ge, and GaAs have been identified during the last decades. However, in other semiconductors, like InP or the II-VI compounds, which are of growing interest for optoelectronic applications, many defect levels are still not identified, due to the difficulty to grow high purity crystals. For example, the acceptor level A_1 is present in all InP samples and is caused by a residual impurity, which is supposed to be either Be or Mg [1]. In the II-VI compounds the problem is still unsolved, whether the difficulty to dope a p-type compound as well as an n-type is due to self-compensation by intrinsic defects [2] or to the high concentration of residual impurities [3].

In general, an unambiguous chemical identification of a defect level is provided only by the observation of any element specific property, like the isotope mass, the nuclear spin, or the isotope abundance. One possibility, e.g., is the observation of the isotope shift of no-phonon lines or local mode phonon replicas [4] in case light impurities are involved in the defect. Another possibility exists in the determination of the hyperfine interaction by electron paramagnetic resonance (EPR) or electron-nuclear double resonance (ENDOR) experiments where the defect level is determined by selective photoexcitation or photoionization of a paramagnetic level [5]. These two methods, however, need a paramagnetic level, suitable nuclear properties of the involved elements, and a control over the Fermi level for selective photoexcitation. Due to these limitations any additional method to identify defect levels is highly welcome.

In this Letter we report an identification method where another element specific property, the nuclear lifetime of a radioactive isotope undergoing a chemical transmutation, is used to identify defect levels observed by PL. If the level is due to a defect in which the parent or daughter isotope is involved, the concentration of that defect will change with the characteristic time constant of the radioactive decay. To demonstrate this, we have chosen the example of GaAs doped with radioactive ^{111}In. A similar method has been used to identify defect levels in Si observed with deep level transient spectroscopy (DLTS) [6,7].

First we show PL spectra of GaAs doped with ^{111}In that decays to ^{111}Cd. The PL intensity corresponding to the recombination of electrons into Cd acceptor states (e,Cd) increases with Cd concentration N_{Cd}. Then we derive a quantitative relation between N_{Cd} and PL intensity from samples doped with stable Cd and develop a model for the carrier recombination process in the implanted samples. With that we demonstrate that the characteristic time constant describing the time dependence of the (e,Cd) intensity in the ^{111}In doped sample is indeed the nuclear lifetime of ^{111}In. These results allow us to give an independent identification of the Cd related PL peaks in GaAs. Finally, we discuss the scope of this identification method.

Samples 3×5 mm^2 in size were cut from an undoped GaAs layer grown by molecular beam epitaxy (MBE) on GaAs and implanted with either radioactive ^{111}In or stable ^{111}Cd. A part of each sample was not implanted to serve as reference. To increase the recombination probability of excited carriers within the implanted layer a double heterostructure was used [see Fig. 2(b) for details]. Carrier-free ^{111}In [8], an ion implanter with mass separation, and a hot W surface ionization source were used to produce an isotopically pure beam of 350 keV ^{111}In$^+$. It was implanted into GaAs at 300 K to a dose of $3(1) \times 10^{11}$ cm^{-2}, resulting in a Gaussian shaped ^{111}In concentration profile centered at 100 nm depth with a width of 40 nm and a peak concentration of 3×10^{16} cm^{-3}. The implantation damage was removed by annealing the samples at 1125(25) K for 10 min in

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evacuated quartz ampoules under As atmosphere. After this treatment all In and Cd atoms are located on lattice sites with an unperturbed surrounding and the Cd atoms are electrically activated and act as acceptors [9].

^{111}In is isoelectronic to Ga and hence occupies Ga lattice sites in GaAs. It decays to ^{111}Cd with a lifetime $\tau_{^{111}\mathrm{In}} = 98$ h by electron capture [10]. Since the recoil energy of the Cd nucleus due to the emission of the neutrino is much smaller than the typical displacement energy in GaAs [11], ^{111}Cd atoms on Ga sites ($\mathrm{Cd_{Ga}}$) are created by the decay of ^{111}In on Ga sites ($^{111}\mathrm{In_{Ga}}$) and act there as shallow acceptors. This chemical transmutation was monitored by PL spectroscopy. The same was kept at 5 K and the 488 nm Ar ion laser line was used for excitation with an excitation density of 10 $\mathrm{W\,cm^{-2}}$. The emitted PL light was dispersed with a 0.25-m monochromator (0.7 nm spectral resolution) and detected with a liquid-N_2-cooled InGaAs photodiode and lock-in technique.

Figure 1 shows successively taken PL spectra from the ^{111}In doped sample. A spectrum from the undoped part is also shown. Since the intensity of PL spectra taken from the same sample varies within 25%, mainly because of the difficulty to focus reproducibly on the entrance slit of the monochromator, we normalized all spectra to the height I_{C} of the (e,C) peak. The PL spectrum of the undoped part of the sample shows the features well known for undoped MBE-grown GaAs [12]. The peaks FX and AX around 819 nm are due to the recombination of free and bound excitons. The peak (e,C) at 830 nm and its LO phonon replica (e,C)-LO at 850 nm are due to recombination of electrons from the conduction band into C acceptor states. The recombination of electrons from donor states into C acceptor states appears as a small shoulder at the right-hand sides of either of these two peaks. C is a residual impurity in GaAs present in MBE-grown material with a typical concentration between 10^{14} and 10^{15} $\mathrm{cm^{-3}}$ [12].

Since $^{111}\mathrm{In_{Ga}}$ is isoelectronic to Ga it causes no PL peaks in GaAs. Therefore, 4 h after doping with ^{111}In the only difference to the undoped part is a small increase of the low energy shoulder of the (e,C) peak. This shoulder increases steadily with time and develops into a peak after 9 days. The same happens at the lower energy side of the (e,C)-LO peak. During this time all other features in the spectra remain unchanged [the apparent increase of the (e,C)-LO peak is due to the increase of the (e,Cd)-LO peak]. Since nothing else is changing in the ^{111}In doped sample but N_{Cd}, the two growing peaks must be caused by $^{111}\mathrm{Cd_{Ga}}$ acceptors created by the decay of $^{111}\mathrm{In_{Ga}}$. The position of these two peaks differs by the energy of one LO phonon. Therefore, the peak (e,Cd)-LO at 855 nm is the LO phonon replica of the (e,Cd) peak at 834 nm, in agreement with the literature [12].

We determined the height $I_{\mathrm{Cd}}/I_{\mathrm{C}}$ of the (e,Cd) peak normalized to I_{C} as the function of time after doping.

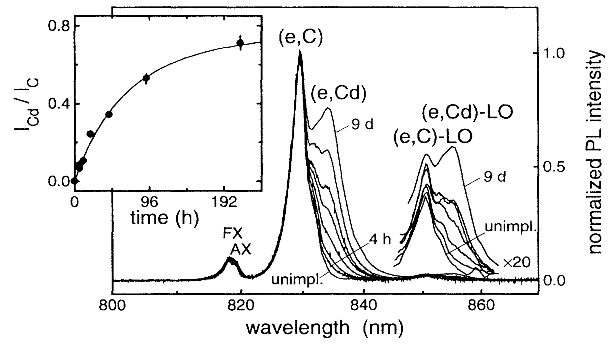

FIG. 1. PL spectra of undoped and ^{111}In doped GaAs successively taken 4 h, 7 h, 12 h, 22 h, 2 d, 4 d, and 9 d after doping. All spectra are normalized to the intensity of the (e,C) peak. In the inset, the height $I_{\mathrm{Cd}}/I_{\mathrm{C}}$ of the (e,Cd) peak in these spectra is shown as a function of time after doping with ^{111}In. The solid line is a fit to the data using Eq. (8),

This was done by subtracting the normalized spectrum of the undoped part from the normalized spectra of the ^{111}In doped part. The height $I_{\mathrm{Cd}}/I_{\mathrm{C}}$ of the (e,Cd) peak remaining in these difference spectra is displayed in the inset of Fig. 1. We fitted these data by

$$\frac{I_{\mathrm{Cd}}}{I_{\mathrm{C}}}(t) = \frac{I_{\mathrm{Cd}}}{I_{\mathrm{C}}}(t = \infty)(1 - e^{-t/\tau}) \qquad (1)$$

and obtained a time constant $\tau = 52(17)$ h, which is not the nuclear lifetime $\tau_{^{111}\mathrm{In}} = 98$ h of ^{111}In. Evidently $I_{\mathrm{Cd}}/I_{\mathrm{C}}$ is not proportional to N_{Cd}. This can also be seen in Fig. 2(a) showing I_{C} and $I_{\mathrm{Cd}}/I_{\mathrm{C}}$ obtained from samples implanted with stable Cd with dose Φ_{Cd} between 10^9 and 10^{13} $\mathrm{cm^{-2}}$. Up to $\Phi_{\mathrm{Cd}} = 10^{12}$ $\mathrm{cm^{-2}}$ $I_{\mathrm{Cd}}/I_{\mathrm{C}}$ increases with Cd dose and is practically constant for higher doses. I_{C}, which is a measure of the total PL intensity in these

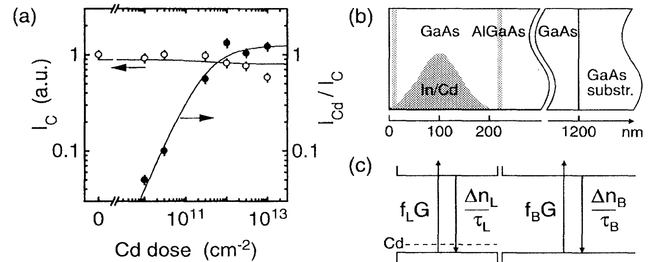

FIG. 2. (a) Height I_{C} (∘) of the (e,C) peak and height $I_{\mathrm{Cd}}/I_{\mathrm{C}}$ (•) of the (e,Cd) peak normalized to the height of the (e,C) peak in GaAs implanted with stable Cd to different doses. The solid lines are fits to the data using Eqs. (4) and (5), respectively. (b) Layer sequence of the used MBE-grown GaAs sample. On semi-insulating (100)-oriented GaAs a GaAs-$\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$ superlattice buffer layer was grown, followed by 1 μm GaAs, 10 nm $\mathrm{Al_{0.3}Ga_{0.7}As}$, 200 nm GaAs, 10 nm $\mathrm{Al_{0.3}Ga_{0.7}As}$, and 5 nm GaAs (all undoped). (c) Illustration of the model for the carrier recombination process.

samples, is practically constant within the entire dose range.

This behavior can be explained by a model describing the dynamic equilibrium between generation of excess carriers by the incoming photon flux and their recombination through the different recombination channels. In other words, we determine the quantum efficiency for (e,Cd) recombination with respect to (e,C) recombination as a function of N_{Cd}. We assume the sample to consist of two layers [Fig. 2(c)]: a homogeneously Cd-doped layer of thickness d with $N_{Cd} = \Phi_{Cd}/d$ and the undoped bulk below this layer. Assuming that no carrier diffusion occurs through the AlGaAs barriers, we neglect surface recombination and carrier diffusion between the two layers.

The PL intensity I_{Cd} is proportional to the recombination rate of excess carriers per unit area through Cd acceptors states $\Delta n_L B_{Cd} N_{Cd}$, where B_{Cd} is a recombination coefficient. The excess sheet carrier concentration in the implanted layer Δn_L can be expressed in terms of the total carrier lifetime in the implanted layer τ_L and the generation rate of excess carriers per unit area in the implanted layer $f_L G$ by using the first of the two equilibrium conditions

$$f_L G = \frac{\Delta n_L}{\tau_L} \quad \text{and} \quad f_B G = \frac{\Delta n_B}{\tau_B}. \tag{2}$$

The second one describes the balance between the generation rate $f_B G$ and the recombination rate of excess carriers $\Delta n_B/\tau_B$ in the bulk. The total generation rate G is proportional to the incident photon flux and $f_L + f_B = 1$.

To get an expression for τ_L, we assume two additional recombination processes in the implanted layer: the radiative recombination via Cd acceptors and nonradiative recombination due to residual implantation damage, and write the recombination rate in the usual small single approximation [13] as

$$\frac{\Delta n_L}{\tau_L} = \frac{\Delta n_L}{\tau_B} + \Delta n_L B_{Cd} N_{Cd} + \Delta n_L B_{nr} f_{nr} N_{Cd}. \tag{3}$$

Here $\Delta n_L B_{nr} f_{nr} N_{Cd}$ is the nonradiative recombination rate per unit area due to residual implantation damage, $f_{nr} N_{Cd}$ is the concentration of these nonradiative recombination centers, and B_{nr} is the corresponding recombination coefficient. Hence Δn_L and Δn_B can be expressed as a function of N_{Cd} and the recombination rates through all the different recombination channels and thereby the relative PL peak intensities can be deduced.

I_C is proportional to the sum of the (e,C) recombination rates per unit area in the implanted layer and the bulk and within our model we obtain

$$I_C \propto \frac{\Delta n_L + \Delta n_B}{\tau_C} = G \frac{\tau_B}{\tau_C} \left(\frac{f_L}{1 + \Phi_{Cd}/f_B b} + f_B \right). \tag{4}$$

Thereby $\tau_C = 1/B_C N_C$ is an effective lifetime describing the recombination probability through C acceptor states and b is a constant defined in Eqs. (6).

With the help of Eqs. (2) and (4) we obtain (assuming that the detection efficiencies of both peaks are equal) the following relation between I_{Cd}/I_C and Φ_{Cd}:

$$\frac{I_{Cd}}{I_C} = \frac{\Delta n_L B_{Cd} N_{Cd}}{(\Delta n_L + \Delta n_B)/\tau_C} = \frac{a}{1 + b/\Phi_{Cd}}, \tag{5}$$

with

$$a = \frac{f_L}{f_B} \frac{B_{Cd}}{(B_{nr} f_{nr} + B_{Cd})} \frac{\tau_C}{\tau_B} \quad \text{and}$$

$$b = \frac{d}{f_B (B_{nr} f_{nr} + B_{Cd}) \tau_B}, \tag{6}$$

For a better understanding of Eq. (5) we discuss two cases. (i) At low N_{Cd} $[1/\tau_B \gg (B_{Cd} + B_{nr} f_{nr}) N_{Cd}]$ the recombination via defects introduced by Cd doping can be neglected. Therefore, the effective lifetime τ_L and the excess sheet carrier concentration Δn_L are practically independent of N_{Cd}. In this regime the (e,Cd) recombination rate $\Delta n_L B_{Cd} N_{Cd}$ is proportional to N_{Cd}. (ii) At high N_{Cd} $[1/\tau_B \ll (B_{Cd} + B_{nr} f_{nr}) N_{Cd}]$ the (e,Cd) recombination and nonradiative recombination due to residual implantation damage become the main recombination pathways and determine τ_L. Then all excited electrons recombine through these two pathways and the (e,Cd) recombination rate is determined by the generation rate G, which is independent of N_{Cd}. Therefore, the (e,Cd) intensity saturates at high N_{Cd}.

By fitting Eq. (5) to I_{Cd}/I_C displayed in Fig. 2(a) we obtain $a = 1.25(8)$ and $b = 3.0(3) \times 10^{11}$ cm^{-2} as fit results. The value of b is used to determine f_B by fitting Eq. (4) to I_C displayed in Fig. 2(a) and the best fit is obtained with $f_B = 0.95(5)$. Both fits are shown as solid lines in Fig. 2(a). Writing $B_C \approx B_{Cd}$ we obtain $a/b \approx f_L/N_C d$ so that the C concentration N_C can be estimated to be about 6×10^{14} cm^{-2}, which is in the right order of magnitude for MBE-grown GaAs [12]. Although 90% of the 488-nm excitation light is absorbed in the Cd-doped layer (absorption depth $1/\alpha = 83$ nm [12]), the bulk accounts for more than 90% of the total effective carrier generation rate, which can be explained by photon recycling [13].

This model describes quantitatively the dependence of (e,Cd) intensity of N_{Cd} and we use it to describe the increase of I_{Cd}/I_C with time in the ^{111}In-doped sample. Here, in contrast to the samples doped with stable Cd, N_{Cd} is increasing with time, while the number of nonradiative centers due to residual implantation damage is constant. So we model the change of the carrier lifetime τ_L with time t in the ^{111}In doped sample as

$$\frac{1}{\tau_L} = \frac{1}{\tau_B} + B_{Cd} N_{In} (1 - e^{-t/\tau}) B_{nr} f_{nr} N_{In}, \tag{7}$$

where $N_{In} = \Phi_{In}/d$ is the initial ^{111}In concentration, $\tau = \tau_{^{111}In} = 98.0$ h is the nuclear lifetime of ^{111}In, and B_{Cd}, B_{nr}, and f_{nr} are the same constants as above. Thereby we assume that the same kinds of nonradiative recombination centers are produced by In doping as by Cd

doping and that the Cd concentration profiles are identical to the ^{111}In concentration profile. With that we obtain

$$\frac{I_{\mathrm{Cd}}}{I_{\mathrm{C}}} = \frac{a}{1 + b/\Phi_{\mathrm{In}}(1 - e^{-t/\tau}) + c/(e^{t/\tau} - 1)}, \quad (8)$$

where a and b are the same constants as above and $c = B_{\mathrm{nr}} f_{\mathrm{nr}} / (B_{\mathrm{nr}} f_{\mathrm{nr}} + B_{\mathrm{Cd}})$. The structure of Eq. (8) is similar to that of Eq. (5). In addition to a time dependent Cd dose (due to the changing Cd concentration), another summand occurs in the denominator. This c term accounts for the fact that in the ^{111}In doped sample the concentration of nonradiative recombination centers is not changing with Cd concentration. We fitted Eq. (8) to the data shown in the inset of Fig. 1, keeping $\tau = \tau_{^{111}\mathrm{In}} = 98.0$ h, $a = 1.25$, and $b = 3.0 \times 10^{11}$ cm^{-2} fixed, and obtained $\Phi_{\mathrm{In}} = 4.4(9) \times 10^{11}$ cm^{-2} and $c = 0.5(2)$. This fit is shown as a solid line and agrees perfectly with the experimental data. The fit result for Φ_{In} corresponds with the implanted ^{111}In dose and the result for c shows that in the implanted layer the nonradiative recombination rate due to residual implantation damage $\Delta n_L B_{\mathrm{nr}} f_{\mathrm{nr}} N_{\mathrm{Cd}}$ is roughly equal to the radiative recombination rate through Cd acceptor states $\Delta n_L B_{\mathrm{Cd}} N_{\mathrm{Cd}}$.

Summarizing, we have shown that a defect level can be identified with PL spectroscopy by labeling it with the nuclear lifetime of a radioactive isotope. We created Cd acceptors in GaAs by doping with ^{111}In and showed that the time dependence of the increasing (e,Cd) recombination is determined only by the nuclear lifetime of ^{111}In.

This identification technique is applicable to a large variety of defect levels since for most elements suitable radioactive isotopes exist [10]. For example, doping of InP with ^{7}Be ($\tau = 76.9$ d) or ^{28}Mg ($\tau = 30.2$ h) will unambiguously identify the respective acceptor levels and answer the question whether one of those is the A_1 acceptor. To study antisites, another class of defects in compound semiconductors, GaAs, can be doped with ^{75}Ga which decays to ^{75}As or ^{71}As which decays to ^{71}Ga.

For doping with radioactive isotopes either a conventional ion implanter or a facility like ISOLDE [14] at CERN can be used and diffusion or neutron irradiation might also work in selected cases. The isotope in mind needs a convenient lifetime (between one day and one month), the spectroscopic technique has to be sensitive enough to detect the change in defect concentration, and contamination with stable isotopes of the element studied should be avoided. If the defect studied is populated by radioactive decay, the recoil energy transferred to the daughter nucleus has to be small enough to keep the atom on its lattice site. In general, the response $I(N_D)$ of the spectroscopic technique on the defect concentration N_D has to be known for a quantitative labeling of a defect by its characteristic time dependence $I(N_D(t))$. Nevertheless, a qualitative identification is always possible because nothing else is changed in a radioactive-doped sample but the concentration of the parent and daughter isotopes.

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