



Luminescence and influence of defect concentration on excitons in $^{197}\text{Hg}/^{197}\text{Au}$ -doped CdTe

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Abstract

CdTe, implanted with ^{197}Hg ions, which decay to ^{197}Au with a half-life of 64.1 h, was investigated by photoluminescence (PL) spectroscopy. The results unambiguously verify the assignments of both, the donor–acceptor pair transition at 1.335 eV, which corresponds to an acceptor level with $E_A = 263$ meV, and the recombination of excitons bound to neutral acceptors at 1.57606 eV to single Au atoms on Cd sites. In addition, the dependence of the intensities of excitonic lines on the defect concentration was investigated quantitatively. The observed intensities are well explained, assuming that a defect can only bind an exciton if there is no additional defect within the volume of the bound exciton. The ratio between the exciton radii of the Cu- and Au-bound excitons $R_{\text{exc}}^{\text{Cu}}/R_{\text{exc}}^{\text{Au}} = 1.2 \pm 0.2$ obtained from this model is in good agreement with the ratio derived from the diamagnetic shift parameters of the two corresponding PL lines. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Photoluminescence spectroscopy (PL) provides a wealth of information on defects in semiconductors, but it is often difficult to identify the chemical identity of the defect causing a particular line in a PL spectrum. An unambiguous chemical identification becomes possible if radioactive isotopes are employed as dopants [1]. Depending on whether the parent or daughter isotope is the dopant element, the dopant concentration decreases or increases due to the radioactive decay, respectively. If the intensity of a PL line is correlated with the half-life of the radioactive decay, the parent or daughter isotope can be identified as a constituent of the defect causing the observed level.

After diffusion of stable Au into CdTe, E. Molva et al. observed a donor–acceptor pair transition (DAP) at 1.335 eV (maximum intensity at 1.27 eV), which corresponds to an acceptor level with $E_A = 263$ meV, and a recombination of excitons bound to neutral acceptors (A^0X) at 1.57606 eV. Both transitions were assigned to substitutional Au atoms on Cd sites (Au_{Cd}) [2]. Excitonic lines with nearly the same energy as the A^0X line, however, were observed after H^+ implantation [3,4] or electron irradiation [5] and were assigned to radiation damage. In order to verify the assignments of the DAP transition at 1.335 eV and of the A^0X line at 1.57606 eV to the Au_{Cd} acceptor, CdTe was implanted with ^{197}Hg ions, which decay to ^{197}Au with a half-life of 64.1 h by electron capture [6]. Hg, which is isoelectronic to Cd, is incorporated on a Cd site and does not form an electronic defect level. After the decay, the ^{197}Au atoms are still located on Cd sites because of the small recoil energy of 0.7 eV and are expected to form an acceptor level.

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It is known from the literature that the intensities of excitonic lines are reduced in semiconductors containing a high concentration of defects [7]. Intensive excitonic lines are, therefore, often used as an indicator of a good crystalline quality. Hence, additional information can be obtained from the present experiment, because the dopant concentration changes continuously due to the decay of ^{197}Hg to ^{197}Au . In this context, the fact that nothing but the elementary transmutation changes the sample, is even more important. To our knowledge, the dependence of the intensities of excitonic lines on the actual defect concentration has not yet been investigated quantitatively.

2. Experimental

The ^{197}Hg ions were implanted into Bridgman-grown, nominally undoped CdTe crystals at the ISOLDE mass-separator facility at CERN (Geneva) with a dose of 10^{13} cm^{-2} and an energy of 60 keV, resulting in an average implantation depth of 20 nm. After implantation, the crystals were annealed at 750 K for 1 h in vacuum in order to remove implantation-induced damage. The diffusion occurring during this annealing process distributes the ^{197}Hg atoms almost homogeneously within the layer of about 1 μm thickness probed by PL experiments [8,9]. The PL measurements were carried out at 1.8 K. The 351.1 nm line of an Ar laser was attenuated to 2 mW and focused to a diameter of about 200 μm . The luminescence was analysed by a 0.5 m grating monochromator and detected by a CCD camera.

3. Results and discussion

In order to observe the change of the PL spectrum due to the elementary transmutation, PL spectra were recorded at different times after annealing. Between these measurements, it was taken care that the sample temperature never exceeded 150 K in order to avoid modifications of the crystal besides those induced by the radioactive decay. A subset of the spectra is shown in Fig. 1. The intensity of each spectrum is normalised to the intensity of the DAP_{Cu} band at 1.455 eV [10]. Both Cu and effective-mass-like donors are usually present as unintentional impurities in CdTe. The data show that the intensity of the PL band around 1.27 eV increases with time. Both the energetic position and the phonon coupling constant of this band agree with the corresponding values of the DAP_{Au} band in the literature [2]. The intensity of this band was determined by integrating the intensities in the energy interval between 1.22 and 1.32 eV. The intensity $I(t)$ as a function of time t was fitted with

$$I(t) = I_0 + I_1 (1 - e^{-(\ln 2) \cdot t/t_{1/2}}). \tag{1}$$

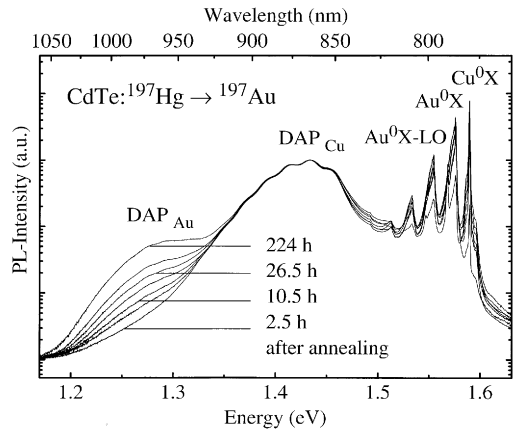


Fig. 1. PL spectra of a CdTe crystal implanted with ^{197}Hg , recorded at different times after annealing (1 h, 750 K, vacuum). The intensities of the spectra are normalised to the intensity of the DAP_{Cu} band.

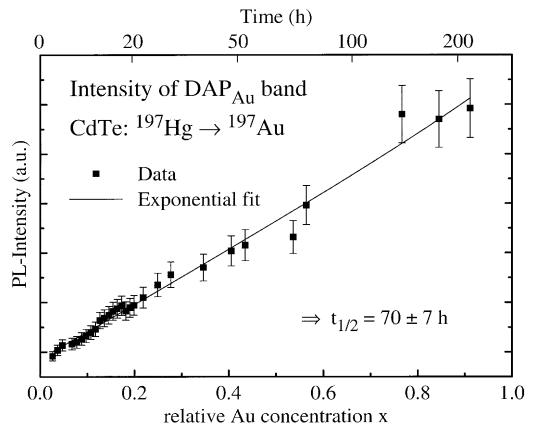


Fig. 2. Intensity of the DAP_{Au} band as a function of the relative Au concentration.

The best fit was obtained with $t_{1/2} = (70 \pm 7) \text{ h}$, which is in good agreement with the half-life of ^{197}Hg $t_{1/2} = 64.1 \text{ h}$. In Fig. 2 the data and the fit are plotted as a function of the relative Au concentration $0 \leq x \leq 1$, which is the ^{197}Au concentration normalised to the number of originally implanted ^{197}Hg atoms and is calculated from the radioactive decay $^{197}\text{Hg} \rightarrow ^{197}\text{Au}$ using $t_{1/2} = 64.1 \text{ h}$. From this linear dependence, it is obvious that the intensity of the band is proportional to the Au concentration. Therefore, it is concluded that the band is caused by a defect containing a single Au atom. Moreover, since the $^{197}\text{Hg}/^{197}\text{Au}$ atoms are incorporated on Cd sites, the acceptor level at 263 meV, which corresponds to this band, is caused by single Au atoms that reside on Cd sites.

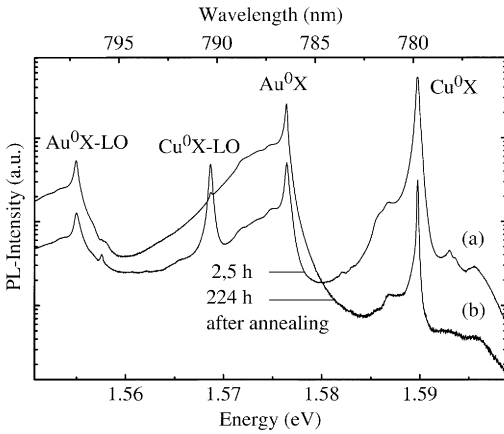


Fig. 3. Excitonic regions of the PL spectra of a CdTe crystal implanted with ^{197}Hg . The intensities of the two spectra are normalised to the intensity of the DAP_{Cu} band.

The excitonic regions of two PL spectra, which were recorded (a) 2.5 and (b) 224 h after annealing, are shown in Fig. 3. Their intensities are normalised to the intensity of the DAP_{Cu} band. At 1.5896 eV, the copper-bound exciton line (Cu^0X) [10] is observed, and at 1.5761 eV the line mentioned above is visible, which has been assigned to the Au_{Cd} defect (Au^0X) [2]. The dependence of the intensities of the excitonic lines on the Au concentration is obvious but more complex. Though the intensity of the Au^0X line increases by a factor of five, which suggests an assignment to ^{197}Au atoms, the radioactive decay $^{197}\text{Hg} \rightarrow ^{197}\text{Au}$ should effect an increase by a factor of 34. Additionally, the intensity of the Cu^0X line changes as a function of time, too. It decreases by a factor of 20, although the Cu concentration in the crystal does not change. The reduced increase of the intensity of the Au^0X line and the decrease of the intensity of the Cu^0X line cannot be explained by a competition for the charge carriers created by the laser. Though additional decay channels for the charge carriers (DAP_{Au} band and Au^0X line) are created by the radioactive decay, the intensity of the DAP_{Cu} band does not significantly change in the non-normalised PL spectra. Therefore, the competition with the created decay channels for charge carriers should be neglectable.

Obviously, the probability of binding an exciton decreases for both Cu and Au acceptors, when the Au concentration increases. The intensities of the Cu^0X and the Au^0X lines as a function of the Au concentration are plotted in Fig. 4. They are normalised to the intensities of the DAP_{Cu} and DAP_{Au} bands, and thereby normalised to the actual Cu and Au concentrations, respectively. The decrease of intensity is more pronounced for the Cu-

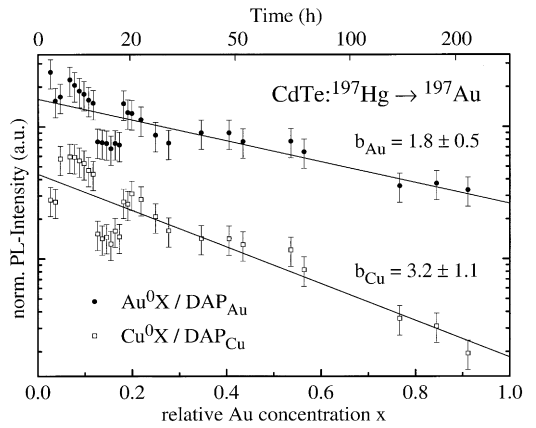


Fig. 4. Intensities of the Cu^0X line and the Au^0X line, normalised to the intensities of the DAP_{Cu} band and the DAP_{Au} band, respectively, plotted as a function of the relative Au concentration. The straight lines are fits to $p(x) = \exp(-bx)$, which yield $b_{\text{Cu}} = 3.2 \pm 1.1$ and $b_{\text{Au}} = 1.8 \pm 0.5$ (see Eq. (3)).

bound excitons than for the Au-bound excitons. This is expected because Cu-bound excitons with a binding energy of 7 meV are more extended and, therefore, more easily disturbed by an increasing defect concentration than Au-bound excitons with a binding energy of 20 meV. Since the binding energy is distributed among three particles (one hole and one electron from the exciton, one hole from the neutral acceptor), however, this argument provides an only qualitative estimate for the radius of the bound exciton.

In order to describe the intensities of the two A^0X lines quantitatively and to extract the exciton radii, we assume that a defect can only bind an exciton if there is no additional defect within the volume V_{exc} of the bound exciton. If V_{cell} denotes the volume of the unit cell and c is the defect concentration, for each unit cell the probability of containing a defect is cV_{cell} . Within the exciton volume, there are $V_{\text{exc}}/V_{\text{cell}}$ unit cells. For each Cu or Au acceptor the probability for finding no additional defect within the volume of the bound exciton is

$$\begin{aligned} p(c) &= (1 - cV_{\text{cell}})^{V_{\text{exc}}/V_{\text{cell}}} \\ &\approx \exp\left(-cV_{\text{cell}}\frac{V_{\text{exc}}}{V_{\text{cell}}}\right) \\ &= \exp\left(-\frac{4}{3}\pi R_{\text{exc}}^3 c\right), \end{aligned} \quad (2)$$

where R_{exc} is the radius of the bound exciton. The defect concentration c is the sum of two contributions: the concentration of those ^{197}Hg atoms that have already decayed to ^{197}Au ($c_{\text{impl}} \cdot x$), where c_{impl} is the concentration of originally implanted ^{197}Hg ions and x is the time-dependent relative Au concentration, and the

concentration of all other defects c_0 . This yields

$$p(x) = \exp(-\frac{4}{3}\pi R_{exc}^3 [c_{impl}x + c_0])$$

$$= \text{const} \cdot \exp(-\frac{4}{3}\pi R_{exc}^3 c_{impl}x). \quad (3)$$

In our model, $p(x)$ is proportional to the intensity of a bound-exciton line normalised to the respective dopant concentration and, therefore, proportional to the intensity ratios $\text{Cu}^0\text{X}/\text{DAP}_{\text{Cu}}$ and $\text{Au}^0\text{X}/\text{DAP}_{\text{Au}}$ in Fig. 4. In fact, the data of both ratios, $\text{Cu}^0\text{X}/\text{DAP}_{\text{Cu}}$ and $\text{Au}^0\text{X}/\text{DAP}_{\text{Au}}$, are well described by the function $p(x) = \exp(-b \cdot x)$ with $b_{\text{Cu}} = 3.2 \pm 1.1$ and $b_{\text{Au}} = 1.8 \pm 0.5$. The value of c_{impl} is estimated from the implantation dose of 10^{13} cm^{-2} and a diffusion length in the order of $1 \mu\text{m}$ for the ^{197}Hg atoms [8,9] to $c_{impl} = 10^{17} \text{ cm}^{-3}$. This yields excitonic radii of $R_{exc}^{\text{Cu}} = 20 \text{ nm}$ and $R_{exc}^{\text{Au}} = 16 \text{ nm}$. These radii, however, are uncertain by a factor of about two because the uncertainty of c_{impl} is about one order of magnitude. Therefore, it is reasonable to consider the ratio of the excitonic radii $R_{exc}^{\text{Cu}}/R_{exc}^{\text{Au}} = 1.2 \pm 0.2$, which is independent of c_{impl} .

This ratio is compared with the ratio of the Bohr radii, which are obtained from the magneto-optical parameters of the corresponding PL lines [2,12,13]. In CdTe, the radius of an A^0X complex is determined by the more weakly bound electron. This follows from a pseudo-donor model, in which the two holes are tightly bound by the short-range potential of the acceptor, producing a long-range Coulomb potential, which binds the electron, similarly to a donor [11]. It has been shown that this model is valid for Cu^0X and Au^0X complexes in CdTe [2,12,13]. In an external magnetic field \mathbf{B} , an A^0X line exhibits a diamagnetic shift [14]. Because of the strong binding of the two holes and the quadratic dependence on the radii $|r_i|$, the contributions of the two holes to the diamagnetic shift ΔE is neglected:

$$\Delta E = \sum_{i=e,h,h} \left\langle \Psi_i \left| \frac{e^2}{8m_e^*} (\mathbf{r}_i \times \mathbf{B})^2 \right| \Psi_i \right\rangle$$

$$\approx \frac{e^2}{8m_e^*} \langle \Psi_{1s} | (\mathbf{r}_e \times \mathbf{B})^2 | \Psi_{1s} \rangle$$

$$= c_{\text{diam}} B^2 \quad (4)$$

with

$$c_{\text{diam}} = \frac{e^2}{4m_e^*} a_0^2, \quad (5)$$

where e is the charge, m_e^* the effective mass, \mathbf{r}_e the position of the electron, and Ψ_{1s} is the 1s wave function of a hydrogenic donor with Bohr radius a_0 . With Eq. (5) the Bohr radius of the exciton can be estimated from the diamagnetic shift parameter c_{diam} . With $c_{\text{diam}}^{\text{Cu}} = (1.47 \pm 0.08) \times 10^{-2} \text{ meV}/T^2$ for the Cu^0X line [12] and $c_{\text{diam}}^{\text{Au}} = (1.1 \pm 0.1) \times 10^{-2} \text{ meV}/T^2$ for the Au^0X line [2,13], the Bohr radii $a_0^{\text{Cu}} = 5.7 \pm 0.2 \text{ nm}$ and $a_0^{\text{Au}} =$

$4.9 \pm 0.2 \text{ nm}$ are obtained. Their ratio is $a_0^{\text{Cu}}/a_0^{\text{Au}} = 1.16 \pm 0.09$, which is very close to the ratio $R_{exc}^{\text{Cu}}/R_{exc}^{\text{Au}} = 1.2 \pm 0.2$ obtained from the data in Fig. 4. The absolute values of the exciton radii determined from these data, $R_{exc}^{\text{Cu}} = 20 \text{ nm}$ and $R_{exc}^{\text{Au}} = 16 \text{ nm}$ (see above), are about 3.4 times the calculated Bohr radii, which is a reasonable factor since an electron described by a 1s wave function is found in a sphere with a diameter of $3.4a_0$ with a probability of 97%.

4. Summary

By doping CdTe with radioactive $^{197}\text{Hg}/^{197}\text{Au}$, it is shown that the intensity of the DAP transition at 1.335 eV is proportional to the ^{197}Au concentration in the crystal. Therefore, the acceptor level at 263 meV, corresponding to this band, is caused by a defect containing a single Au atom. As the $^{197}\text{Hg}/^{197}\text{Au}$ atoms are incorporated on Cd sites, this acceptor consists of single Au atoms that reside on Cd sites. The dependence of the intensities of both the Cu^0X and the Au^0X lines are well explained quantitatively, assuming that a defect can only bind an exciton if there is no additional defect within the volume of the bound exciton. Since the intensity of the Au^0X line at 1.57606 eV is correctly described, the defect binding this exciton also contains a single Au atom. Therefore, the assignments of both the DAP transition at 1.335 eV and the A^0X line at 1.57606 eV to the Au_{Cd} acceptor are verified.

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