

Optical properties of the isoelectronic trap Hg in ZnO

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Nominally undoped ZnO crystals were doped with Hg by implanting radioactive $^{197}\text{Hg}/^{197}\text{Au}$ atoms. After annealing at 1073 K, the photoluminescence (PL) spectra recorded at 1.6 K exhibit a Hg related band in the region between 3.28 and 2.85 eV. The sharp no-phonon line, which is observed at 3.276 51 eV, is assigned to a bound exciton. At lower energies, a phonon sideband is visible, which is caused by the strong coupling with acoustical and optical phonons. It is shown that these PL signals are caused by an exciton bound to a Hg atom that resides on a cation site. © 2003 American Institute of Physics. [DOI: 10.1063/1.1576912]

There is a renewed interest in the wide band gap semiconductor ZnO because of its application as piezoelectric transducer, varistor, phosphor, and transparent film. Due to its band gap, ZnO is a potential material for optoelectronic devices in the blue and UV range like UV light emitting diodes (LEDs) or UV laser diodes. For the fabrication of optoelectronic devices, knowledge about the properties of impurities, like donors, acceptors, and isoelectronic impurities, is of essential interest. Thus, it is known that isoelectronic traps can enhance the efficiency of the radiative recombination of electrons and holes, as has been shown for LEDs based on GaP.¹

An isoelectronic impurity is generated by substituting a host atom by an atom of the same column of the periodic table. In 1965, the observation of an exciton bound to an isoelectronic nitrogen atom in GaP was reported.² According to Hopfield *et al.*, the difference in electronegativity between nitrogen and phosphor was suggested to be responsible for the binding of the exciton to the nitrogen center.³ Alternatively, the binding mechanism can be described as a consequence of the lattice deformation due to the atomic size difference between impurity and host atom. A recent overview of theoretical models describing the binding of excitons to isoelectronic impurities has been given by Zhang.⁴ Besides GaP:N some more isoelectronic traps have been discovered, which, however, were incorporated always on the anion sites of III–V or II–VI semiconductors.^{1,5} Only in the case of the II–VI semiconductor ZnTe doped with the isoelectronic alkaline earths elements Ca, Sr, and Ba, the occurrence of the corresponding states on the cation site was reported.⁶

In this letter, about photoluminescence (PL) spectra of Hg doped ZnO is reported and a characteristic band is assigned to an exciton bound to the isoelectronic Hg impurity on a cation site by applying PL spectroscopy in combination with radioactive impurity atoms.^{7,8} This is a case of an isoelectronic trap caused by a group IIb element.

Nominally undoped ZnO crystals were implanted with radioactive ^{197}Hg ions at the ISOLDE mass-separator at CERN (Geneva). Since the isotope ^{197}Hg decays with the

lifetime⁹ $\tau_1 = 92.53$ h to stable ^{197}Au , the concentrations of ^{197}Hg and ^{197}Au atoms in the crystals change with time in a predictable way, and a change with time of the intensities of all PL lines that are related to defects containing Hg or Au atoms is expected to occur, accordingly.

For the PL investigations state-of-the-art ZnO single crystals (Eagle Picher, USA) were used, which were grown by seeded chemical vapor transport. Before implantation, the ZnO crystals were etched in a solution of 37% HCl for 60 s and subsequently rinsed in an ultrasonic bath in bidistilled water and in acetone. After implantation of the ^{197}Hg ions with a dose of 10^{13} cm⁻² and an energy of 60 keV, the crystals were annealed at 1073 K for 30 min in oxygen atmosphere in order to remove the implantation-induced radiation damage. Recording the γ -ray spectrum of the implanted samples using a germanium detector revealed that radioactive isotopes other than the isotopes ^{197}Hg and $^{197\text{m}}\text{Hg}$ were not implanted. The fractions of metastable $^{197\text{m}}\text{Hg}$ decaying to ^{197}Au (7%) and ^{197}Hg (93%) with the lifetime⁹ $\tau_2 = 34.34$ h were estimated to about 20% at the time of implantation. Therefore, the time dependence of the concentration of ^{197}Hg atoms $c_{\text{Hg}}(t)$ normalized to the time of implantation is described by

$$c_{\text{Hg}}(t) = 1.2958 \exp(-t/\tau_1) - 0.2958 \exp(-t/\tau_2). \quad (1)$$

During 20 days, a sequence of PL spectra was recorded at the sample position yielding the highest intensity of the PL lines under investigation. This position could be reproduced with an accuracy of less than 100 μm in all measurements. In order to avoid additional modifications of the crystal during the time between the different PL measurements, in particular by aging processes, the sample temperature was always kept below 120 K. The PL spectra were recorded at 1.6 K, using the 325 nm line of a HeCd laser for the excitation of the ZnO crystals. The luminescence was analyzed by a 0.5 m grating monochromator and detected by a LN₂-cooled charge coupled device camera.

Figure 1 shows two PL spectra that were recorded (a) 2 and (b) 458 h after annealing of the implantation-induced damage in ZnO. Like in Fig. 2, the spectra are normalized to

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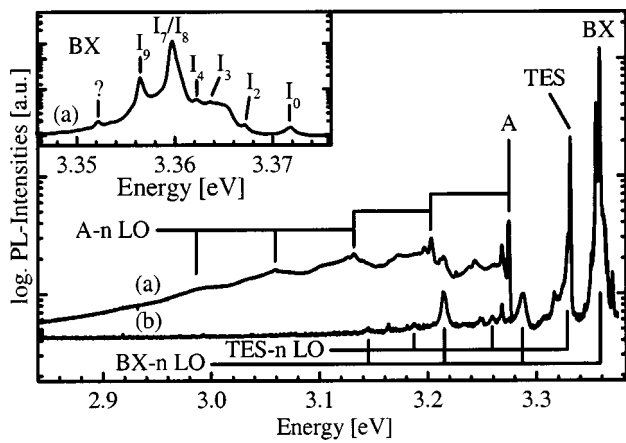


FIG. 1. PL spectra measured at 1.6 K, (a) 2 and (b) 458 h after annealing of the radiation damage in ¹⁹⁷Hg implanted ZnO along with an expanded overview of the bound exciton region, labeled according Ref. 10.

the intensity of the first LO phonon replica of the bound excitons (BX) at 3.289 eV (BX-ILO). At the time of recording the second spectrum, the ¹⁹⁷Hg atoms almost completely decayed to ¹⁹⁷Au atoms due to the lifetimes of 92.53 and 34.34 h of the radioactive isotopes ¹⁹⁷Hg and ^{197m}Hg. Both spectra show signals of bound excitons¹⁰ and two-electron satellites (TES) of the neutral donor-bound exciton¹¹ along with their phonon replica. The expanded view of the bound excitons, shown in the inset and labeled according Ref. 10, documents the crystalline quality of the sample after annealing. Only spectrum (a) shows a pronounced new band with a no-phonon line A at 3.27651 eV and several phonon replicas at its low energy side. The fact that the intensities of these lines decrease as a function of the elapsed time along with the transmutation of the radioactive ¹⁹⁷Hg into ¹⁹⁷Au (see also Fig. 2) shows the involvement of the element Hg. Contrary, there was no line with an increasing intensity observable, which can be related to Au atoms.

Figure 2 shows a blow-up of the energy region 3.200–3.295 eV of 5 PL spectra that were recorded at different times. Obviously, the intensity of the no-phonon line A, like the whole band, monotonously decreases with time. In Fig. 3, the intensity of the no-phonon line A is plotted as a func-

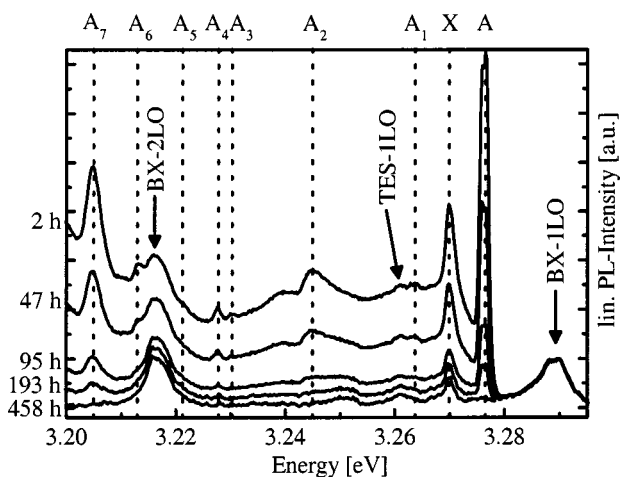


FIG. 2. PL spectra of the Hg band (blow-up of the PL spectra in Fig. 1) recorded at different times at 1.6 K. Like in Fig. 1, the spectra are normalized to the LO replica of the bound exciton (BX-ILO).

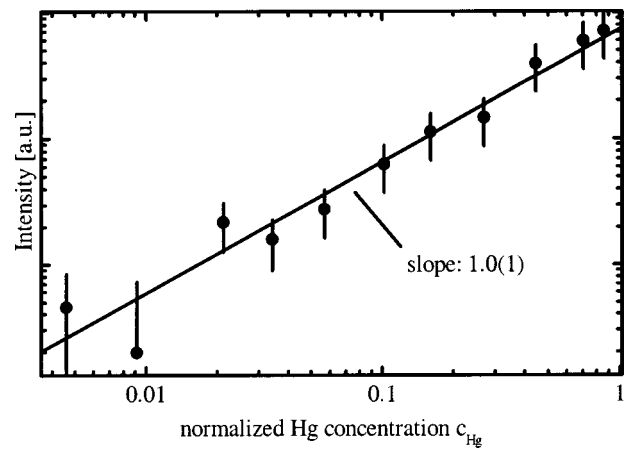


FIG. 3. Intensity of the no-phonon line A as function of the normalized Hg concentration c_{Hg} .

tion of normalized Hg concentration c_{Hg} , which was extracted from 11 PL spectra using Eq. (1). The intensity of this line was determined by integrating the PL spectra between 3.2746 and 3.2776 eV, whereby the background was determined using the PL spectrum recorded after 458 h.

The data in Fig. 3 show that the intensity of the no-phonon line A is proportional to the Hg concentration. Therefore, the no-phonon line A has to correspond to a defect containing a single Hg atom. Based on its chemical properties, Hg is expected to be incorporated on Zn sites of the ZnO lattice after implantation and annealing. The incorporation of Hg on Zn sites is corroborated by recent emission channeling experiments using the β^+ radiation of ¹⁹⁷Hg.¹² The preliminary analysis of this data confirms our assumptions. Therefore, it is concluded that the observed luminescence of line A corresponds to an isolated isoelectronic Hg atom incorporated on a cation site of ZnO. The sharpness of the no-phonon line A, exhibiting a linewidth of 0.82 meV, indicates that the Hg line is caused by an excitonic recombination process. This assignment is supported by measuring the intensity of the no-phonon line I_A as a function of the intensity of the exciting laser power I_L , yielding $I_A = I_L^{1.13(4)}$, what is expected in case of an excitonic recombination process.¹³ Also the PL investigations, performed as a function of temperature and yielding a thermal activation energy of 134(7) meV, are consistent with the assignment of line A to a bound exciton.

Figure 2 shows that different PL lines occur in the Hg band between the no-phonon line A and its first LO replica. Beside the no-phonon line A, the spectrum includes different lines that have the general characteristics of replicas caused by phonon-assisted transitions. The energy differences ΔE of the most significant lines (A_1 – A_7 , X) to the no-phonon line A are listed in Table I. By comparing the ΔE values with phonon energies of different branches at the Γ point of the Brillouin zone,¹⁴ the lines A_1 – A_7 can be identified as the phonon replicas of the optical modes at the Γ point (see Table I). The continuous part of the phonon sideband is assigned to the interaction of Hg bound exciton with different optical and acoustical phonons. It should be noted that similarly strong phonon sidebands were observed for other isoelectronic traps, like for nitrogen in GaP.^{3,4} At present, no unique assignment of the X line can be made. Its intensity is

TABLE I. Lines observed in the Hg band along with their energy differences ΔE to the no-phonon line A extracted from the PL spectra ("Exp.") and the proposed assignments. The energies of the ZnO host phonons at the Γ point of the Brillouin zone ("Raman," "Theory") are taken from Ref. 14 (LO: longitudinal optical, TO: transversal optical).

Line	ΔE (meV)			Assignment
	Exp.	Raman	Theory	
X	6.25	?
A ₁	12.3	12.2	11.4	E_2^{low}
A ₂	32.4	...	32.2	B_1^{low}
A ₃	46.7	47.3	49.2	A ₁ (TO)
A ₄	49.1	51.3	52.8	E ₁ (TO)
A ₅	55.0	54.4	55.7	E_2^{high}
A ₆	64.1	...	66.9	B_1^{high}
A ₇	72.9	71.2	69.3	A ₁ (LO)
		71.9	71.5	E ₁ (LO)

also proportional to the Hg concentration and, therefore, this line seems to be connected with a defect containing a single Hg atom. But, at the same position an other defect related line is present, which is still visible after the decay of all ^{197}Hg atoms (see Fig. 2).

The investigation of the no-phonon line A using a higher-resolution grating shows that this line actually splits into two lines, A and B, with an energy difference of 0.86 meV (see Fig. 4). The intensity of the no-phonon line B decreases with increasing temperature and disappears at about 15 K. A similar behavior was observed by Hopfield

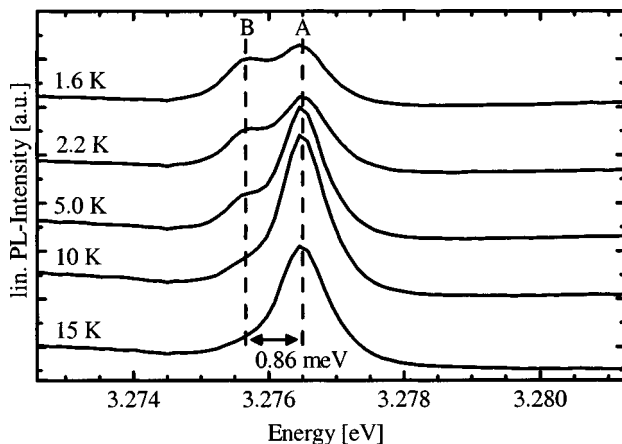


FIG. 4. High-resolution PL spectra of the no-phonon line A at 3.27651 eV (see Figs. 1 and 2) recorded at different temperatures and showing the splitting in two different lines A and B.

et al. in the case of ZnTe:O and GaP:Bi.³ The authors explained both no-phonon lines by the coupling of the angular momenta of the electron ($j=1/2$) and the hole ($j=3/2$) to the total angular momenta $J=1$ or $J=2$, and assigned the lower energetic line to the dipole-forbidden transition with the total angular momenta $J=2$. Thus, lines A and B in the case of ZnO:Hg are tentatively assigned to the two no-phonon lines caused by bound excitons with the total angular momenta $J=1$ and $J=2$. But, this assignment has yet to be verified by PL measurements in an applied magnetic field.

In order to explain the binding of the exciton to the isoelectronic Hg atom in ZnO, the model of Hopfield *et al.*³ might be suited: The Pauling electronegativities of Zn and Hg are 1.65 and 2.00, respectively. Thus, within this model, Hg tends to bind an electron more strongly. Via the Coulomb interaction the electron binds a hole and, thereby, forms an exciton. In addition, the covalent radii of Zn and Hg are 0.131 and 0.148 nm, respectively, yielding a 13% larger covalent radius of Hg as compared to Zn. Due to the induced lattice deformation about the Hg atoms a strain field should develop. Both mechanisms can explain the formation of an isoelectronic trap at Hg in ZnO in a qualitative way.

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