



# Energy levels of native defects in zinc germanium diphosphide

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## Abstract

Electron paramagnetic resonance (EPR) and photo-EPR investigations of as-grown, post-growth annealed and electron irradiated zinc germanium diphosphide ( $\text{ZnGeP}_2$ ) crystals allowed the determination of native acceptor- and donor-related defect levels in the  $\text{ZnGeP}_2$  bandgap. From the photoinduced generation of the  $V_{\text{Zn}}^-$  EPR spectrum for electron-irradiated samples with the Fermi-level above the recharging level it is inferred that the  $V_{\text{Zn}}^{-/-}$  acceptor state is located at  $1.02 \pm 0.03$  eV below the conduction band. Observation of the recharging process in as-grown and post-growth annealed samples yields the localization of the Ge anti-site donor level  $\text{Ge}_{\text{Zn}}^{+/++}$  at  $E_{\text{opt}} = E_V + 1.70 \pm 0.03$  eV. Moreover, photoinduced processes involving the quenching and generation of the  $V_{\text{Zn}}^-$  and  $V_{\text{P}}^0$  EPR spectra, respectively, are observed with an energy of  $E_{\text{opt}} = 0.64 \pm 0.03$  eV. A model that can explain the complementary changes of the  $V_{\text{Zn}}^-$  and  $V_{\text{P}}^0$  EPR intensities is briefly discussed. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:**  $\text{ZnGeP}_2$ ; Photo-EPR; Native defects; Energy levels

## 1. Introduction

Zinc germanium diphosphide ( $\text{ZnGeP}_2$ ) is one of the most technologically important materials among the ternary II–IV– $V_2$  compounds due to its promising applications for non-linear optical devices such as tunable mid-infrared optical parametric oscillator (OPO) laser systems. However, up to now the performances of such OPOs are affected by a broad absorption band extending from the fundamental edge near 625 nm up to 2.5  $\mu\text{m}$ , which overlaps with the desirable OPO pump wavelengths. This unwanted absorption with a pronounced plateau near 1  $\mu\text{m}$  is mainly attributed to the photoionization of a deep acceptor center associated with the negatively charged state of the zinc vacancy ( $V_{\text{Zn}}^-$ ) [1]. A large reduction of this unwanted absorption could be obtained by high-energy electron irradiation of the crystals. Electron

paramagnetic resonance (EPR) and photo-EPR investigations of as-grown, electron-irradiated and annealed  $\text{ZnGeP}_2$  samples have shown strong differences in the  $V_{\text{Zn}}^-$ -related EPR signal intensity, which are mainly caused by a meta-stable recharging of the  $V_{\text{Zn}}^-$  centers owing to the preparation induced shift of the Fermi-level [2]. Photoinduced EPR studies of such highly compensated bulk  $\text{ZnGeP}_2$  crystals have identified two donor centers, that have been attributed to the neutral P vacancy ( $V_{\text{P}}^0$ ) [3] and the singly charged  $\text{Ge}_{\text{Zn}}$  anti-site ( $\text{Ge}_{\text{Zn}}^+$ ) [4] centers, respectively. No clear defect assignments have been made for the usually broad photoluminescence bands in the range from 1.2 to 1.6 eV. However, a correlation with the concentration of the phosphorus vacancies was observed [5] and some parts of the broad infrared emission exhibit features of classical donor–acceptor recombination in dependence of the excitation density and time-decay character [2,6]. An assignment of the three identified native defects described above to energy levels in the  $\text{ZnGeP}_2$  bandgap determined by electrical measurements [7] does not exist to date. In the present article, we report for the first time the wavelength dependence of the photoinduced changes in the EPR signal intensities associated with the acceptor

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center  $V_{Zn}^-$  as well as the donors  $V_P^0$  and  $Ge_{Zn}^+$  in  $ZnGeP_2$ .

## 2. Experimental details

The  $ZnGeP_2$  bulk crystals used in this work were grown by the gradient freezing Bridgman method. For the EPR studies, small samples with dimension  $1 \times 1 \times 5 \text{ mm}^3$  were cut along the main crystallographic directions from as-grown, post-growth annealed and electron-irradiated samples. The EPR and photo-EPR measurements were performed at the Q-band ( $\nu \cong 34 \text{ GHz}$ ) in the temperature region 4–50 K using a Bruker ESP 300E spectrometer. The samples could be irradiated with monochromatic light via a 0.4 mm optical fiber in the rod inserted into the helium cryostat, which had the sample mounted on the other end. Light from a 100 W Xenon or Halogen lamp was dispersed by a grating monochromator and coupled, after passing additional glass filters, into another 0.4 mm optical fiber at the end of which the spectral dependence of the photon flux was measured. When illuminating the samples, the two fibers were connected.

## 3. Experimental results and discussion

In the dark, both the as-grown and annealed  $ZnGeP_2$  samples studied exhibit only the strong EPR spectrum described in Ref. [8], which has been identified as the single negatively charged zinc vacancy ( $V_{Zn}^-$ ) by ENDOR measurements [9,10].  $ZnGeP_2$  has a tetragonal chalcopyrite crystal structure where the  $c$  direction is denoted as [001] and the two equivalent  $a$  directions are labeled [100] and [010]. The line positions of the electron spin transitions are given by the linear Zeeman interaction for  $S = 1/2$  and the principal  $g$ -values  $g_1 = 2.002$ ,  $g_2 = 2.021$  and  $g_3 = 2.074$  in the main directions [011],  $[\bar{1}00]$ ,  $[0\bar{1}1]$ , respectively [3]. In the tetragonal crystal structure, there are four crystallographic equivalent center orientations. Every electron spin transition is split into a triplet with the intensity ratio 1:2:1 by the hyperfine interaction with two equivalent phosphorus nuclei ( $I = 1/2$ , 100% abundant) varying from 3.5 to 5.5 mT in magnitude. For an arbitrary direction of the magnetic field, an overlapping of the triplets belonging to the four center orientations is observed in the X-band, but a complete resolution of the hyperfine interaction of the different center positions can be obtained at least for some directions in the Q-band owing to the 3.5 times higher Zeeman splitting. Fig. 1(a)–(c) show typical Q-band EPR spectra for the negative charged zinc vacancy ( $V_{Zn}^-$ ), together with the photoinduced spectra

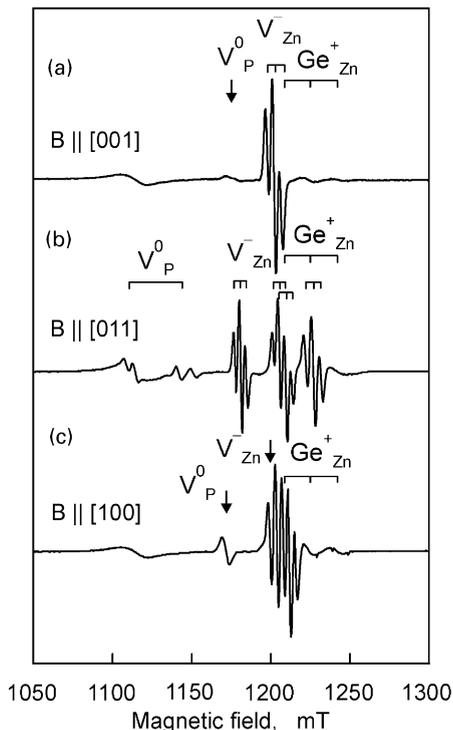


Fig. 1. EPR and photoinduced EPR spectra of the negatively charged zinc vacancy ( $V_{Zn}^-$ ), the neutral donor ( $V_P^0$ ), and the anti-site center  $Ge_{Zn}^+$  in as-grown and annealed  $ZnGeP_2$  in the Q-band (34.2 GHz) at 15 K with the magnetic field  $B$  parallel to the directions (a) [001], (b) [011] and (c) [100]. (By a small misorientation of the sample the degeneracy of the inner  $V_{Zn}^-$  lines and of the  $V_P^0$  lines is removed, see Fig. 1(b)).

related to the neutral phosphorus vacancy ( $V_P^0$ ) and the anti-site center  $Ge_{Zn}^+$  for the three directions of the external magnetic field  $B$  parallel to [001], [011] and [100]. The illumination of as-grown and annealed samples with monochromatic light changes the EPR signal intensity of the  $V_{Zn}^-$  centers and generates only the EPR spectrum of the neutral donor  $V_P^0$  for photon energies from 0.6 to 1.5 eV. For photon energies between about 1.55 and 2.5 eV, the spectrum of the anti-site center  $Ge_{Zn}^+$  is produced and a photoinduced enhancement of EPR signal intensities both of the  $V_{Zn}^-$  and neutral donor  $V_P^0$  centers is observed. By avoiding saturation effects by corresponding choice of temperature and microwave power, we have determined the dependence of the EPR signal intensity on the photoexcitation energy normalized for a constant photon flux for the three centers (Fig. 2). The presentation establishes that the observed photoinduced quenching of the  $V_{Zn}^-$  signal in the low-energy region (0.6–1.5 eV) is always stronger than the photoinduced generation of the  $V_P^0$  signal. For the higher energy

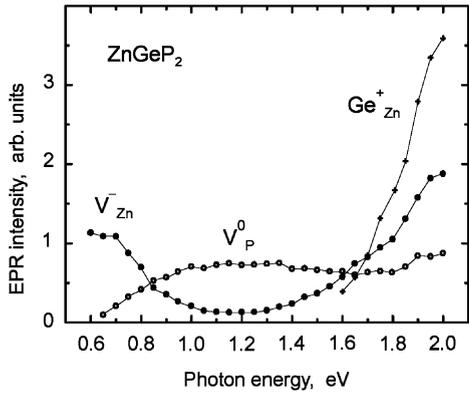


Fig. 2. Spectral dependence of the photoinduced changes of the EPR signal intensities at 15K. The points ( $\bullet$ ,  $\circ$ ,  $+$ ) represent the experimental values for the negatively charged zinc vacancy ( $V_{Zn}^-$ ), the neutral donor ( $V_P^0$ ) and the anti-site center  $Ge_{Zn}^+$ , respectively. The corresponding lines are provided as a guide to the eye.

region (1.55–2.5 eV), the increase of the  $Ge_{Zn}^+$  signal is always stronger than the sum of the increase of the intensities from the  $V_{Zn}^-$  and  $V_P^0$  signals. Since all three centers are systems with spin  $S = 1/2$  and both the anisotropy and differences between the  $g$ -values are small, the changes of the signal intensity are directly proportional to the number of recharged centers.

In order to monitor further the kinetics and the wavelength dependence of this photoinduced effect in detail, we fixed the external magnetic field  $\mathbf{B}$  at the position of maximum intensity of the first derivative of one of the non-overlapping EPR lines belonging to each one of the three centers and monitored the time dependence of the EPR signal intensity ( $I_{EPR}$ ) upon an illumination sequence of increasing photon energies. As an example, the photoinduced changes of the intensity of the  $V_{Zn}^-$  EPR signal are shown for different photoexcitation energies  $h\nu$  in Fig. 3. By fitting the time dependence of  $I_{EPR}$  by exponential decay functions, we have estimated the saturation value  $\Delta I_{EPR}$  of the difference between the photoinduced EPR signal intensity and  $I_{EPR}$  measured prior to illumination for the different photoexcitations. The  $Ge_{Zn}^+$  related spectral dependence of  $\Delta I_{EPR}$  normalized to a constant photon flux is presented in Fig. 4(b). In this energy region (1.55–2.5 eV) identical spectral dependencies are observed for the  $V_{Zn}^-$ ,  $Ge_{Zn}^+$  and  $V_P^0$ -related EPR spectra. This pointed to the fact that the photoionization process responsible for the enhancement of the EPR signals occurs on the same localized states in the  $ZnGeP_2$  gap to the conduction (valence) band. In the low-energy region (0.6–1.5 eV) the same spectral dependence for the decrease of the  $V_{Zn}^-$  and the generation of the  $V_P^0$  signal is observed. In the context of all the

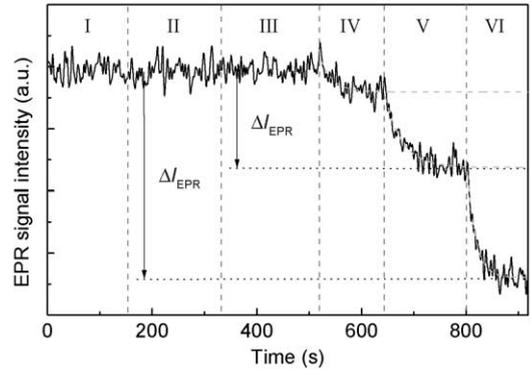


Fig. 3. Time dependence of the EPR signal intensity  $I_{EPR}$  of the negatively charged zinc vacancy ( $V_{Zn}^-$ ) at  $T = 15$  K for different excitation photon energies  $h\nu$ (eV)=0.52 (I), 0.57 (II), 0.6 (III), 0.65 (IV), 0.70 (V), 0.75 (VI). The solid lines are experimental data and dashed curves are exponential fits. The horizontal lines represent the saturation values obtained from the fits. The vertical bars give the  $\Delta I_{EPR}$  values used for the determination of the optical cross sections.

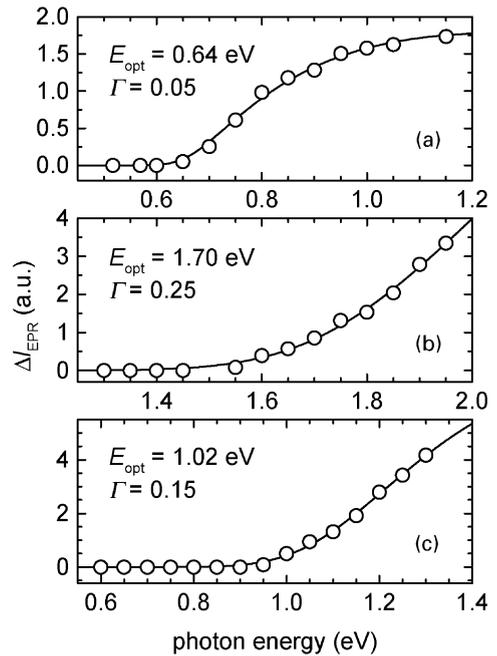


Fig. 4. Dependence of the enhancement of the EPR signal ( $\Delta I_{EPR}$  as defined in Fig. 3) vs. the photon energy for (a) the  $V_P^0$  center, (b) for the  $Ge_{Zn}^+$  center, (c) photoinduced generation of the  $V_{Zn}^-$  EPR signal in an electron irradiated sample. The circles are experimental values and the solid lines are fits to the data by the extended Lucovsky formula, Eq. (1).

observed photoinduced recharging processes, it is unlikely that this process involved the valence band. Therefore, we infer that an electron from the  $V_{Zn}^-$  center is directly transferred to the positively charged

phosphorus vacancy ( $V_P^0$ ), leaving behind the  $V_{Zn}$  center in the non-paramagnetic state  $V_{Zn}^0$ .

The ionization energy  $E_{opt}$  of a defect involved in such PT is determined by the spectral dependence of the optical cross section, which must be determined from the photo-EPR data. The different methods for the determination of the optical cross section are discussed in Ref. [11]. How the relation between the  $\Delta I_{EPR}$  values and the optical cross section can be obtained within the framework of the saturation value method is described in detail in Ref. [12]. This method has the advantage that different initial starting populations of the center under study prior to each subsequent photoexcitation can be considered. The  $\Delta I_{EPR}(v)$  dependence of the optical cross section for a given PT is described by a system of kinetic equations that includes all excitation, recombination and captures processes in the sample. However, specific shifts of the Fermi-level in the initial samples can be very helpful in verifying the different dominant processes, and restricting the latter to only a few. Also, the complexity can be reduced using the fact that the light intensity  $I$  and the optical cross section  $\sigma$  always appear together in the form of  $\alpha = I \times \sigma$  in the kinetic equations that describe the photoionization process. Using only values from the linear regime  $\Delta I_{EPR}(v) \sim \alpha$  and assuming that only one dominant photoionization process is responsible for the decrease or enhancement of the studied EPR signal, we see that  $\Delta I_{EPR}(v)$  is directly proportional to the corresponding optical cross section [12]. Fitting the spectral dependence  $\sigma(v)$  of the considered photoexcitation by the modified Lucovsky formula extended to account for the electron-phonon interaction [11]

$$\sigma(v) \propto \int_{-\beta}^{\infty} dz e^{-z^2} \frac{(hv - E_{opt} + \Gamma z)^{3/2}}{(hv + \Gamma z)^3} \left(1 + \frac{\Gamma z}{hv}\right)^{-1}, \quad (1)$$

where  $\Gamma$  describes the effect of broadening on the PT absorption band with the temperature, the ionization energy  $E_{opt}$  can be determined, see Fig. 4. For the recharging of the  $V_{Zn}^-$ ,  $Ge_{Zn}^+$  and  $V_P^0$  centers we determine  $E_{opt} = 1.70 \pm 0.03$  eV and for the decrease of the  $V_{Zn}^-$  and generation of the  $V_P^0$  signal  $E_{opt} = 0.64 \pm 0.03$  eV.

In agreement with [2], for samples irradiated with high-energy (2 MeV) electrons neither the  $V_{Zn}$  EPR signal nor the  $V_P^0$  signal could be detected before optical excitation, if the samples are cooled down in the dark and infrared irradiation by black body emission from the resonator walls is avoided. However, illumination with infrared light simultaneously generates the  $V_{Zn}^-$  and the  $Ge_{Zn}^+$ -related EPR signals. While, whether in the dark nor upon illumination the signal from the  $V_P^0$  could be detected, a new center [13] could be observed with increasing signal intensity upon irradiation. The photo-induced generation of the  $V_{Zn}^-$  signal was recorded

for different excitation wavelengths. The determined spectral dependence  $\Delta I_{EPR}$  normalized to a constant photon flux is presented in Fig. 4c. From the fitting procedure described above the photoionization energy  $E_{opt} = 1.02 \pm 0.03$  eV is obtained. The observed process is interpreted as direct electron excitation from the doubly negative charged zinc vacancy ( $V_{Zn}^{--}$ ) to the conduction band, connected with a partial capture of the photoinduced electrons by the  $Ge_{Zn}$  centers recharging these to the paramagnetic state  $Ge_{Zn}^+$ .

#### 4. Conclusions

The present photo-EPR study reveals three photo-induced recharging levels connected with native defects in the bandgap of  $ZnGeP_2$ . The zinc vacancy acceptor level  $V_{Zn}^{--/-}$  is established at  $E_{opt} = E_C - 1.02 \pm 0.03$  eV and the Ge anti-site donor level  $Ge_{Zn}^{+/++}$  at  $E_{opt} = E_V + 1.70 \pm 0.03$  eV. The excitation energy  $0.64 \pm 0.03$  eV connected with the photoinduced decrease and increase of the EPR signals from the  $V_{Zn}^-$  and  $V_P^0$ , respectively, seems to be caused by a direct recharging of weakly associated defects  $V_{Zn}^-V_P^+$  to  $V_{Zn}^0V_P^0$ , which can be realized only for Fermi levels below the  $V_{Zn}^{--/-}$  level at  $E_C - 1.02 \pm 0.03$  eV. Above this level position a new center could be detected.

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