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Structure and energy level of native defects in as-grown and electron-irradiated zinc germanium diphosphide studied by EPR and photo-EPR

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Abstract

The properties of defects in as-grown p-type zinc germanium disphosphide ($ZnGeP_2$) and the influence of electron irradiation and annealing on the defect behavior were studied by means of electron paramagnetic resonance (EPR) and photo-EPR. Besides the well-known three native defects (V_{Zn}, V_P, Ge_{Zn}), an $S = 1/2$ EPR spectrum with an isotropic $g = 2.0123$ and resolved hyperfine splitting from four equivalent $I = 1/2$ neighbors is observed in electron-irradiated $ZnGeP_2$. This spectrum is tentatively assigned to the isolated Ge vacancy. Photo-EPR and annealing treatments show that the high-energy electron irradiation-induced changes in the EPR intensities of the zinc and phosphorus vacancies are caused by the Fermi level shift towards the conduction band. Annealing of the electron-irradiated samples induces a shift of the Fermi level back to its original position, accompanied by an increase of the EPR signal associated with the V_{Zn}^- and a proportional increase of the EPR signal assigned to the V_P^0 under illumination ($\lambda < 1$ eV) as well as generation of a new defect. The results indicate that the EPR spectra originally assigned to the isolated V_{Zn}^- and V_P^0 are in fact associated defects and the new defect is probably the isolated phosphorus vacancy V_{Pi}.
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1. Introduction

The exceptional properties of zinc germanium diphosphide ($ZnGeP_2$) and the recent improvements in the growth of high quality volume crystals by the horizontal gradient freeze (HGF) technique make this semiconductor one of the most promising materials for nonlinear optical devices such as tunable mid-infrared optical parametric oscillator (OPO) laser systems [1]. The importance of the II–IV-P_2 chalcopyrite semiconductors became even more eminent with the very recent discovery of room temperature ferromagnetism in highly Mn-doped semiconducting $CdGeP_2$ [2] and $ZnGeP_2$ [3], which will enable new nonlinear magneto-optical device structures for nonlinear optics and/or spintronic applications. Electronic devices that exploit the behavior of an electronic spin rather than its charge would open up a potentially wider range of devices types and performance capabilities [4]. The unusual form of ferromagnetism observed in the II–IV-V_2 compounds might be a result of the interaction of the magnetic Mn ion with holes produced by native defects [5].

Bulk crystals grown by the HGF technique are heavily compensated and contain large concentration of defects, believed to give rise to a broad absorption band in the 1–2 μm region that increases the laser damage threshold and affects the efficiency of the frequency conversion for the aforementioned nonlinear optical devices. Both as-grown and annealed $ZnGeP_2$ samples exhibit commonly a strong EPR spectrum [6] that has been identified by ENDOR measurements as the singly negatively charged zinc vacancy (V_{Zn}^-) [7,8]. Atomistic calculations [9] have supported this conclusion. The data obtained so far appear to suggest that the disturbing absorption observed in p-type crystals is

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mainly caused by the photoionization of this deep acceptor state [10]. A large reduction of this absorption in the p-type crystals is observed after high-energy electron irradiation. This reduction is explained by recharging of the singly negatively charged zinc vacancy V_{Zn}^- to the diamagnetic charge state V_{Zn}^{2-} due to the irradiation-induced shift of the Fermi level [11]. From the photoinduced generation of the V_{Zn}^- EPR spectrum in the samples with the Fermi level above the recharging level, we conclude that the $V_{Zn}^{2-/-}$ acceptor state is located at 1.02 eV below the conduction band (CB) [12]. In addition, photoinduced EPR studies have shown two donor centers that have been attributed to the neutral phosphorus vacancy (V_P^0) [13] and the single charged Ge on zinc anti-site (Ge_{Zn}^+) [14], respectively. The recharging levels in the band gap of $ZnGeP_2$ that correlate with these native defects were recently determined by photo-EPR [12]. In this work we have studied the influence of the electron irradiation and a post-irradiation annealing of samples on the EPR spectra of the P and Zn vacancies and have investigated in detail a new defect center, tentatively identified as the Ge vacancy V_{Ge} [15]. In addition, we describe the generation and properties of a new center generated by vacuum annealing.

2. Experimental details

The $ZnGeP_2$ crystals used in this work were grown by the HGF technique and are of p-type conductivity. For the EPR studies small samples with suitable dimensions for X- or Q-band measurements were cut along the main crystallographic directions from as-grown, post-growth annealed, electron-irradiated and in different steps post-irradiation annealed samples. The electron irradiation that shifts the Fermi level towards the CB was performed with 2 MeV electrons to fluences in the range of $(5-9) \times 10^{17}$ e/cm^2 at room temperature. The EPR and photo-EPR measurements were carried out using a Bruker ESP 300 E spectrometer operating both at the X-band ($\nu \cong 9.5$ GHz) and Q-band ($\nu \cong 34$ GHz). Temperatures in the range 3.9–300 K were achieved with Oxford Instruments continuous flow cryostats. The samples could be optically excited by monochromatic or band filtered light through slits in the cavity of the X-band resonators or through a 0.4 mm optical fiber introduced into the Q-band cryostat [12].

3. Experimental results and discussion

Typical Q-band EPR spectra observed in as-grown and annealed $ZnGeP_2$ HGF samples are shown in Fig. 1(a)–(c). The spectra depict negatively charged zinc vacancy (V_{Zn}^-), together with the neutral phosphorus vacancy (V_P^0) and the positively charged anti-site center Ge_{Zn}^+. When the samples are cooled down in the dark, the spectra show only the strong EPR spectrum related to the V_{Zn}^-. From the spectral

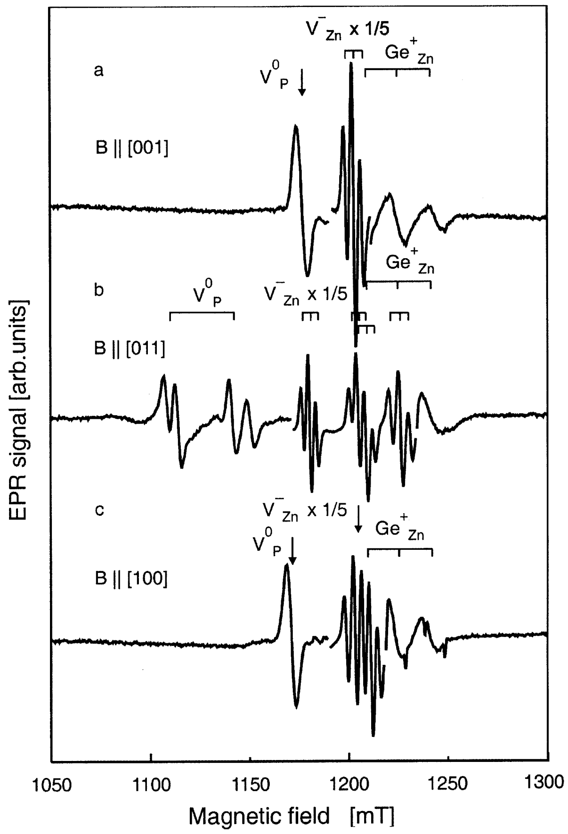

Fig. 1. EPR and photo-EPR spectra of the negatively charged zinc vacancy (V_{Zn}^-), the neutral donor (V_P^0), and the anti-site centre Ge_{Zn}^+ in as-grown and annealed HGF $ZnGeP_2$ in the Q-band ($\nu = 34.2$ GHz, $T = 10$ K) with the magnetic field B parallel to the crystallographic main directions [001], [011] and [100].

dependence of the photoinduced changes of the EPR signal intensities of the V_{Zn}^-, V_P^0 and Ge_{Zn}^+, the corresponding recharging level positions in the $ZnGeP_2$ band gap are determined [12]. For samples irradiated with high-energy (2 MeV) electrons neither the V_{Zn}^- nor the V_P^0 and Ge_{Zn}^+ EPR signals were detected before optical excitation. In samples where the Fermi level was above the recharging level $V_{Zn}^{2-/-}$ located at $E_c - 1.02$ eV, the new center mentioned in [12] is observed. Due to the weak EPR intensity and the strong overlap with residual EPR spectra caused by V_{Zn}^- centers as well as with an additional line at $g = 2.003$, this spectrum is difficult to verify in the X-band. In spite of these difficulties, the existence of the new center has been unambiguously proven [15]. The essential EPR feature of this new center, which was confirmed by Q-band measurements (Fig. 2), is a resolved hyperfine structure for B||c with a five-line spectrum with intensities in the ratio 1:4:6:4:1. This structure could be explained by the ligand hyperfine interaction with four equivalent ^{31}P neighbors [15]. For an arbitrary direction of the magnetic field, 16 transitions are possible and the overlapping of the different transitions

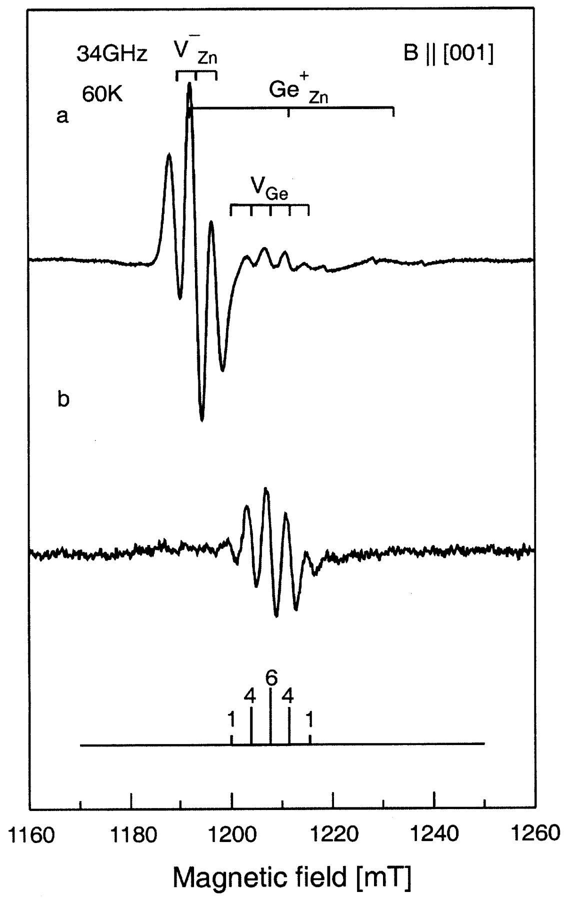

Fig. 2. Experimental EPR spectrum of an electron-irradiated $ZnGeP_2$ sample obtained for B||c in the Q-band ($\nu = 34.2$ GHz $T = 60$ K) under illumination with photon energy of 1.4 eV. The whole spectrum shows (a) the signals from the V^-_{Zn}, the new center, tentatively identified as V_{Ge}, the Ge^+_{Zn} anti-site center and residual Mn signals from the cavity; (b) demonstrates the five line spectrum of the new center with the intensity ratio 1:4:6:4:1 obtained by subtraction of spectra corresponding to illumination of the sample under study with different photon energies.

broaden the structure, which in connection with the weakness of the spectrum and a small g-anisotropy ($g_{av} = 2.0123$) prevented a complete analysis of the hyperfine structure up to now. This new EPR spectrum is not due to an existing defect that is recharged as a result of the irradiation-induced Fermi-level shift. It is caused by a new center just generated by the electron irradiation and was tentatively identified as Ge vacancy [15]. The Fermi level in the studied electron-irradiated samples is located above the optical ionization energy of this center $E_{opt} = E_C - (0.7 \pm 0.06)$ eV [15], but below the recharging level of the Ge anti-site donor level $Ge^{+/2+}_{Zn}$ at $E_{opt} = E_V + (1.7 \pm 0.03)$ eV [12]. In these crystals, the EPR signals from the center assigned to the neutral phosphorus vacancy [13] were not detected. However, the observation of the corresponding spectra under intense illumination with band-gap light shows that these centers are not removed but only recharged. Annealing of the electron-irradiated samples for a longer period of time resulted in a reverse shift of the Fermi level towards its original position and is above 150 °C accompanied by a strong increase of the EPR intensity of the V^-_{Zn} and the disappearance above 250 °C of the EPR signal of the center assigned to V_{Ge} (Fig. 3a). The small starting EPR intensity

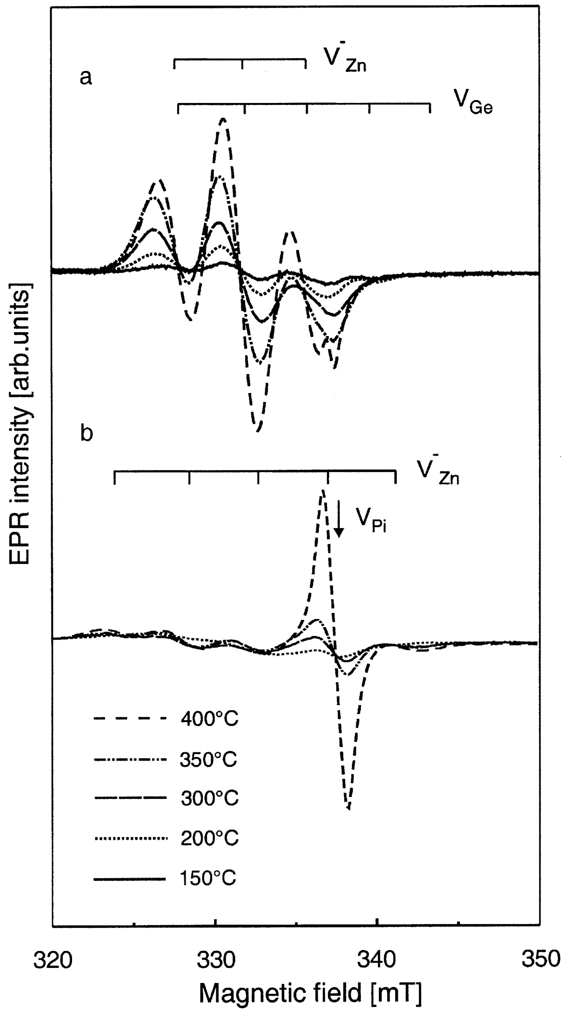

Fig. 3. Dependence of the EPR signal intensities in the X-band ($\nu = 9.45$ GHz) observed in the dark for electron-irradiated $ZnGeP_2$ annealed under vacuum for 24 h each at different temperatures (150, 200, 300, 350, 400 °C): (a) EPR spectrum observed for $B \| c$ at a measurement temperature of $T = 115$ K, demonstrating the increase of the V^-_{Zn} signal with the annealing temperature and, at low annealing temperatures, weak transitions from the V_{Ge} center, which disappeared for annealing temperature above 250 °C; (b) generation of the isotropic line at $g = 2.0026$ in dependence of the annealing temperature, measured for $B \|[557]$, the magnetic field direction with the maximum overall splitting of the V^-_{Zn} lines at $T = 8.5$ K, where the EPR spectrum of the V^-_{Zn} is partly saturated (lines for 150 °C are not shown).

of this defect makes a detailed investigation difficult, however, from the photo-EPR studies we can conclude that the center is not recharged but annealed out. Simultaneously, for annealing temperatures above 350 °C, we observed a strong generation of a single isotropic line with $g = 2.0026$ and a linewidth of 1.2 mT (Fig. 3b), which is almost identical to the weak EPR signal observed after electron irradiation [15]. While the intensity of this line is hardly affected by illumination with photon energies <1 eV, the spectrum of the assumed V_P^0 is generated under this illumination approximately proportionally to the increase of the V_{Zn}^- signal for the different annealing steps (Fig. 4). These findings and the observed 1:1 ratio in the photoinduced decrease and increase of the EPR signals of the centers assigned to V_{Zn}^- and V_P^0, respectively, in as-grown samples for excitation energies between 0.64 and 1.2 eV [12] suggest that both centers are not isolated vacancies but associated defects. The results can be explained assuming that the excitation energy of 0.64 eV is the level position of $V_{Zn}^{-/0}$ and the recharging level of the phosphorus vacancy $V_P^{-/0}$ is located between this level and the valence band. On the other hand, the assignment of the only photo-generated spectrum as V_P^0 seems to be questionable. At present, we postulate that the isotropic signal at $g = 2.0026$ generated by vacuum annealing at higher temperatures corresponds to the isolated phosphorus vacancy V_{Pi}. Further studies, in which surface investigations and EPR measurements are made after thermal annealing under different conditions and after defined etching of the samples, will aid in confirming our tentative identification and clarify the role of the formation of dangling bonds at the surface of the $ZnGeP_2$ samples.

4. Conclusions

EPR and photo-EPR studies revealed that the recently detected new center generated by electron irradiation, tentatively identified as V_{Ge}, is annealed out above 250 °C. The disappearance and recovery of the EPR spectrum of the defect assigned to the negatively charged zinc vacancy after electron irradiation and annealing at different temperatures, respectively, is in agreement with the corresponding shift of the Fermi level by both treatments of the $ZnGeP_2$ samples. The simultaneous change of the EPR intensities of the V_{Zn}^- and V_P^0 after annealing the electron-irradiated samples, together with the previously proven 1:1 ratio of the photoinduced quenching and enhancement of EPR signals, suggest that both defects are not isolated but associated centers. The missing stable EPR signal of V_P^0 in all available samples with different Fermi-level positions

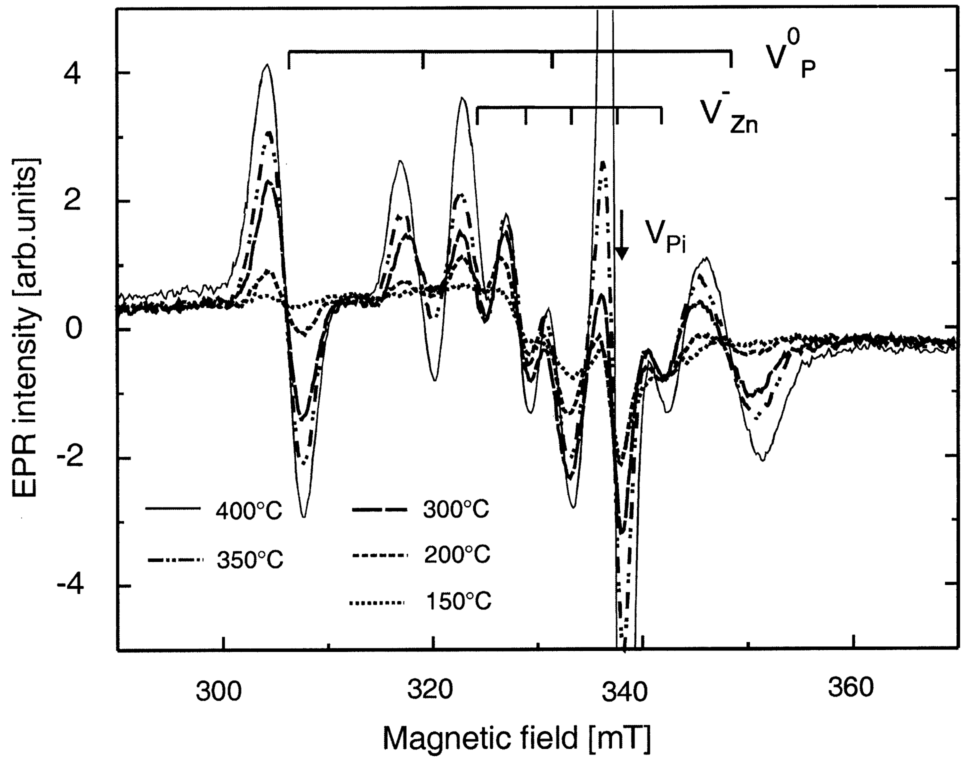

Fig. 4. Dependence of the EPR signal intensities observed under the same conditions as in Fig. 3b, but illuminated with the light of a halogen lamp cut off to $\lambda > 1.06$ μ with a silicon edge filter. The increase of the EPR signal intensities related to the V_P^0, V_{Zn}^-, and isotropic line at $g = 2.0026$ corresponds to the increase of the annealing temperature similar to Fig. 3b. The intensity of the isotropic line is not affected by the illumination.

suggests that the recharging level $V_P^{0/+}$ should be below the level of $V_{Zn}^{-/0}$ at $Ev + 0.64$ eV. The EPR studies also reveal for the first time that annealing of $ZnGeP_2$ at higher temperatures under vacuum produces a new defect, which is tentatively identified as the isolated phosphorus vacancy V_{Pi}. Such heat treatment is also used for the incorporation of high Mn concentration into the surface region of $ZnGeP_2$ for the generation of the room temperature ferromagnetism [2,3].

Acknowledgements

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