NATIVE DEFECT CHARACTERIZATION IN $ZnGeP_2$

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Abstract

Electron paramagnetic resonance (EPR) as well as time-resolved and time-integrated photoluminescence (PL) are used to characterize the defect centers in $ZnGeP_2$ bulk crystals. The samples, as-grown, electron-irradiated and annealed, reveal a strong intensity dependence of the V_{Zn}-correlated EPR-transitions. Photo-EPR experiments show that this intensity behavior is mainly caused by a recharging of the V_{Zn} centers owing to the preparation induced shift of the Fermi-level. The luminescence spectra show a broad infrared emission with peak position at 1.23 eV that exhibits features of classical donor-acceptor recombination. The hyperbolic decay characteristics, investigated in energy range from 1.2 eV up to 1.5eV, suggest that this broad emission band is related to one energetic recombination center. This recombination is interpreted to be between donor-acceptor states related to residual disorder on the cation sublattice that is retained in metastable equilibrium during the formation of the chalcopyrite structure. The emission decay behavior in the energy range from 1.2 eV up to 1.6 eV is characterized by two hyperbolic time constants, and explained as the super-composition of the decays from the broad emission center peaked at 1.2 eV and an additional donor-acceptor recombination centers at 1.4 eV.

I. Introduction

Zinc germanium diphosphide ($ZnGeP_2$) with a pseudo bandgap of ~ 2.1 eV at room temperature [1] has an attractive transparency range [2] from 0.67 μm to 13 μm and a relatively large second order susceptibility tensor component (d_{36} = 75 pm/V). Steady state photoluminescence (PL) studies revealed abroad peak maxima around 1.2 eV [3]. Time resolved measurements in the energy range between 1.2 and 1.6 eV show hyperbolic behavior which has been interpreted as donor-acceptor pair (DAP) recombination [4]. Higher energetic luminescence structures at 1.6 eV and 1.7 eV were revealed after annealing of $ZnGeP_2$ crystals. $ZnGeP_2$ grown under Ge-deficient condition by horizontal high pressure physical vapor transport (HPVT) show an additional emission structure at 1.8 eV and a sharp donor-acceptor emission at 1.778 eV associated with the presence of additional donor states. Electron paramagnetic resonance (EPR) measurements support the strong relation of the EPR signal with an acceptor band and restricted the possible nature of the defect related acceptor band to be either Zn_{Ge} sites or V_{Zn} vacancies [5]. ENDOR-measurements

Mat. Res. Soc. Symp. Proc. Vol. 607 © 2000 Materials Research Society

reveal this centers as V_{Zn} vacancies [6]. From photo-induced EPR results on as-grown $ZnGeP_2$ crystals the deep luminescence emission is attributed to DAP transitions associated with V_P-V_{Zn} pairs [7]. Most of the $ZnGeP_2$ crystals discussed in the literature are highly compensated and have a high concentration of donors and acceptors (10^{19} to $10^{20}cm^{-3}$). One possibility to reduce compensating defects is to anneal and irradiate the samples with electrons followed by re-annealing. In this paper, we describe the characterization of defect centers for variously treated $ZnGeP_2$ crystals using electron paramagnetic resonance (EPR), time-integrated and time-resolved photoluminescence (PL) and Raman spectroscopy.

II. Experimental

The $ZnGeP_2$ crystals were grown by the gradient freezing Bridgman method. In this paper we compared the results of an as-grown sample with three special post-growth treated samples. The three post-growth treatments are (1) additional annealing, (2) additional annealing followed by electron irradiation, (3) additional annealing plus electron irradiation and annealing. The energy resolved steady-state PL data in the energy range from 0.75 eV to 1.6 eV were obtained using a combination of two liquid-N_2 cooled Ge-diodes in conjunction with a 0.35 m single-grating / double-grating monochromator. The excitation was accomplished by a frequency doubled Nd:YAG laser with an excitation energy of 2.3 eV (λ= 532 nm). The output of the laser was controlled by neutral-filters with an incident power between 20 mW and 2Watt and a repetition rate 76 MHz. The pulse width is of the order of 100 ps. The resulting luminescence was collected and focused in a double monochromator and detected with slow Ge-detector. (time constant 10 ms). A single monochromator and a fast Ge-detector (time constant 0.1 ms) were used to perform the time-resolved experiments. The transients were recorded with a boxcar-averager. Micro-Raman measurements were carried out with a triple-grating Dilor spectrometer and the 623.8 nm line of an HeNe laser for excitation. The spatial resolution was better than 1μm. We were able to detect Raman shifts smaller than 0.1 cm^{-1}. The four samples from the same boule but annealed and irradiated with 2MeV electron beam in different way were investigated also by EPR to study the influence of the thermal treatment and the electron irradiation on the native defects. The EPR measurements were performed at the X- and Q-band in the temperature region 4-30K using a Bruker ESP 300E spectrometer equipped with an Oxford ESR 900 helium gas-flow cryostat. The samples could be illuminated with light from a halogen lamp with filters through the sample holder or an opening in the resonator wall. For these EPR studies small samples with dimension $2.5x2.5x10mm^3$ in high symmetry directions were cut for X-band (9.5GHz) measurements. For the Q-band the sample dimensions were reduced by a factor 3.

III. Results

Figures 1a and 1b show PL spectra as function of the excitation density for $ZnGeP_2$ crystals cut from a bulk single crystal grown by the gradient freezing (GF) method, with different post-growth treatment steps as described above. For high excitation densities a high energy shoulder at 1.4 eV is observed for all samples. This shoulders is strongly reduced in intensity – or not observed - if the excitation power is reduced. This observation is typical for donor-acceptor-pair (DAP) transitions developed in [4]. With increasing excitation densities the DAP centers leading to the 1.23 eV luminescence saturate, while DAPs having higher transition energies occur. These results indicate that an energy transfer channel opens up either due to saturation (inversion) of defect centers or as a nonlinear electron - band interaction effect.

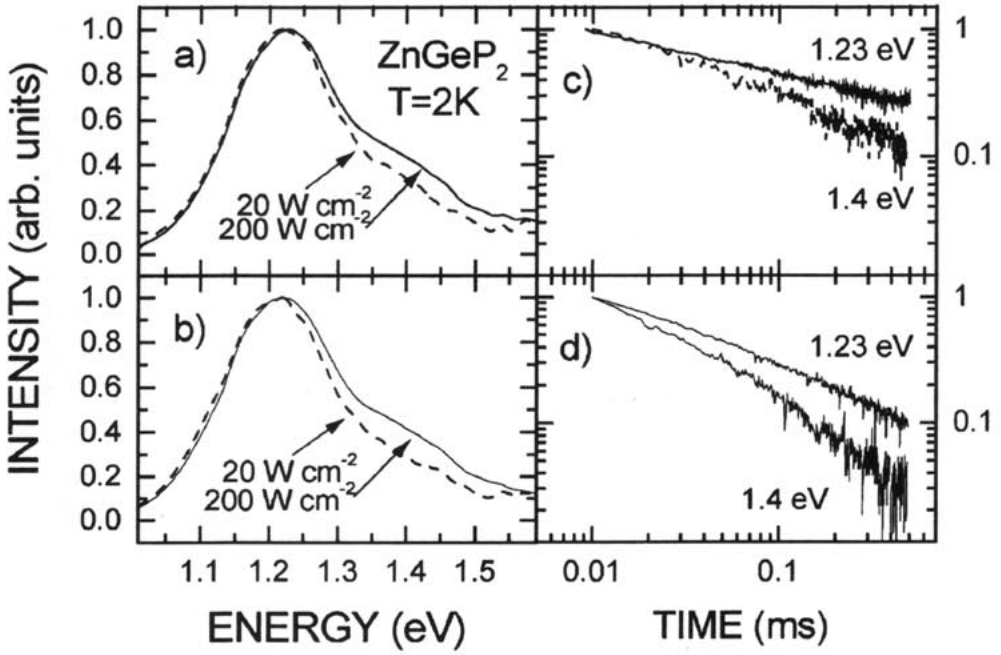

Figure 1 Photoluminescence (PL) spectra and time-resolved transients of bulk ZnGeP2 crystals. (a) PL spectra of an as-grown ZnGeP2 sample as a function of excitation density; (b) PL spectra of a post-growth electron irradiated ZnGeP2 crystal as function of excitation density; (c) transients of the luminescence at 1.23 eV and 1.4 eV for the as-grown sample; and (d) transients of the luminescence at 1.23 eV and 1.4 eV for a post-growth irradiated ZnGeP2 crystal.

In the next step we performed time-resolved PL investigations in order to clarify whether the time-response has changed as a result of the different post-treatment steps. In Figure 1c the transients of the 1.23 eV and 1.4 eV bands are shown for the as-grown sample. As already reported in earlier investigations, the decay character for all the samples investigated here can be split in two components: the first, very fast decay process is exponential and the second one is a slower decay, which is linear in a double logarithmic scale. The linear behavior is interpreted as related to DAP transitions, while the exponential decay indicates a band-acceptor or donor-band

transition. The decay process at 1.4 eV band is faster than the 1.23 eV luminescence decay. In Figure 1d the corresponding transients of a post-growth sample which was irradiated with high-energy (2MeV) electrons and later annealed are shown.

All investigated post-growth samples show a faster decay compared to the as-grown sample. This behavior suggest the incorporation of additional/modified defects after the different post-growth steps which leads to a dominating non-radiative decay. This argument is supported through our Raman studies on post-growth treated $ZnGeP_2$ samples. The post-growth treated samples show a softening of the Zn-P phonon modes while for the Ge-P modes a hardening is observed [8].

The EPR spectra for all samples studied show a dominating acceptor band in $ZnGeP_2$ [5], which has been identified as a single ionized zinc vacancy (V_{Zn}^-) by ENDOR-measurements [6]. $ZnGeP_2$ 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 [0 1 1], [$\bar{1}$ 0 0], [0 $\bar{1}$ 1], respectively. In the tetragonal crystal structure there are four crystallographic equivalent center orientations. By rotation of the magnetic field B around the a axis the resulting line positions for these four center orientations are shown in Figure 2. Since two lines are degenerated due to exact orientation of the rotation axis, only three lines are observed. In addition every electron spin transition is split in 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 mT to 5.5 mT in magnitude. With the magnetic field along the c-axis, all four center orientations are magnetically equivalent (see Figure 2) and only one hyperfine triplet is observed (Figure 3).

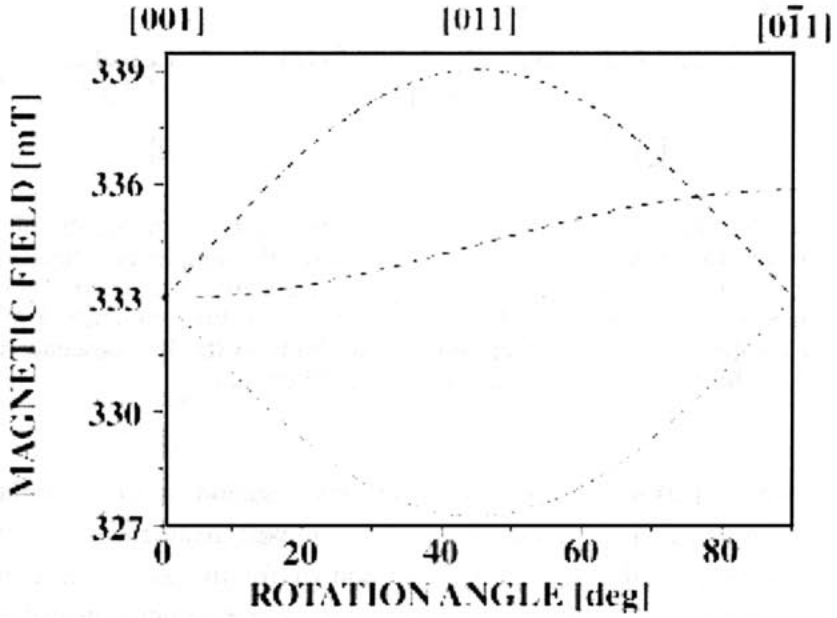

Figure 2 Angular dependence of the electron spin transitions of the V_{Zn}^- center in $ZnGeP_2$ by rotation of the magnetic field B around the a axis in the X-band (9.5 GHz). The degenerate lines (---) is split by a misorientation of the rotation axis.

For 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 direction in the Q-band owing to the 3.5 times higher Zeeman splitting.

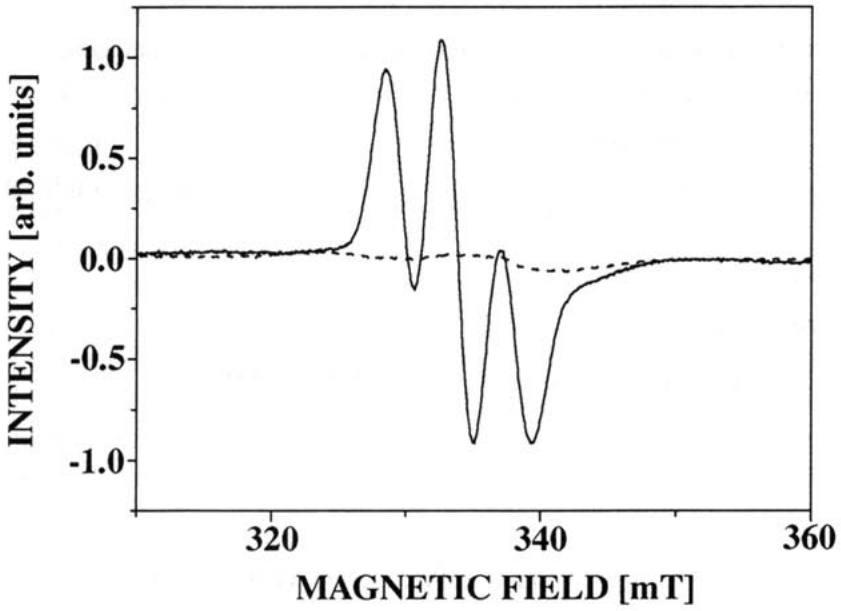

Figure 3 Comparison of the EPR intensity of the V_{Zn}^{-} center in $ZnGeP_2$ for samples after high-energy (2MeV) electron irradiation with (——) and without (----) in-situ illumination of the sample with white light. Magnetic field B || [001], X-band, T=20K.

The influence of the thermal treatment and the electron irradiation on the intensity of the EPR spectra caused by the singly ionized zinc vacancies (V_{Zn}^{-}) were investigated by measuring the complete angular dependence of the EPR spectra. At this point, only the main feature the change of the intensity is discussed, while smaller changes in the line shape and the detection of additional defects need further investigations. The relative EPR intensities of the observed main defect were shown to correlate with the observed optical absorption in the wavelength region from 0.7 to 2.5 μm in $ZnGeP_2$ [9]. For as-grown samples and for samples with an additional annealing step, strong EPR signals from the (V_{Zn}^{-}) centers are observed. After electron-irradiation with high-energy (2MeV) the EPR intensity is strongly reduced. However, our initial investigations showed that after illumination of the sample with white light, the EPR spectra related to the (V_{Zn}^{-}) centers appear again with an intensity comparable to the annealed samples without electron irradiation. This effect of illumination of the electron irradiated samples on the intensity of the EPR spectra of the (V_{Zn}^{-}) is demonstrated in Figure 3 for the magnetic field parallel to the c axis. The reappearance of the spectrum related to the (V_{Zn}^{-}) centers by in-situ illumination very strongly suggests that the main effect of the electron irradiation caused changes in the absorption behavior is above all produced by a recharging of (V_{Zn}^{-}) centers and had not led to changes in the defect structure. This

is in agreement with the results of Brunyi et al. [10], which showed that bombardment of $ZnGeP_2$ with 2-MeV electrons increases the resistivity and suggested that this increase implies a shift of the Fermi level toward the middle of the band gap due to the introduction of radiation-induced donor defects. This is further supported by the observed increase of the intensity of the EPR spectra due to the V_{Zn}^{-} centers in the negative charge state after post-annealing of the electron irradiated samples. Such post annealing causes an annealing out of donor centers generated by the beam damage through which the Fermi level is shifted in direction of the valence band.

The analyses of these data and the correlation to associated defect configuration will require extensive model simulations and the complementary measurements using a combination of optical, magnetically and electrical techniques.

IV. Acknowledgment

This work has been supported by the NSF Grant **DMI-9461802**.

V. References

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