EFFECT OF FAST ELECTRON IRRADIATION ON ELECTRICAL AND OPTICAL PROPERTIES OF $CdGeAs_2$ AND $ZnGeP_2$

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ABSTRACT

We report on the effects of fast electron irradiation on the optical absorption (α) of $CdGeAs_2$ and $ZnGeP_2$ and on the electrical properties of $CdGeAs_2$. In p-$CdGeAs_2$ irradiation led to the reduction in α and an increase in the electrical resistivity. The lowest values of α (about 0.1 cm^{-1} at $5\mu m<\lambda<10\mu m$) were obtained on irradiated crystals of p-type with the highest degree of compensation. Further accumulation of the electron dose caused conversion to n-type and deterioration of the optical transmission. In $ZnGeP_2$ irradiation caused a decrease in α at $\lambda>0.85$ μm and increase in α at $\lambda<0.85$ μm. At $\lambda=2.05$ μm, α for the o-ray could be reduced to less than 0.08 cm^{-1}. At higher doses, saturation in α was observed. The effects of irradiation are discussed in connection with possible mechanisms of optical absorption in $CdGeAs_2$ and $ZnGeP_2$.

INTRODUCTION

High demand for lasers for the 3 to 12 μm range has stimulated a search for nonlinear optical materials operational as tunable optical parametric oscillators (OPO) and second harmonic generators (SHG) of CO_2 lasers. The remarkable optical and nonlinear optical properties $ZnGeP_2$ and $CdGeAs_2$ make them the best candidates for a variety of mid-IR NLO applications [1]. For the efficient operation of a nonlinear optical device, α in the crystal must be below 0.1cm^{-1} at the wavelengths of interest. Unfortunately, both $ZnGeP_2$ and $CdGeAs_2$ exhibit optical absorption within their fundamental transparency range. Post growth annealing is used conventionally in order to improve to some extent the optical transmission of the crystals [2-5]. However, using the annealing alone, the desired degree of transmission has been achieved neither for $CdGeAs_2$ nor for $ZnGeP_2$. This calls for exploration of alternative treatments leading to the more pronounced reduction in α. Irradiation of $ZnGeP_2$ and $CdGeAs_2$ with high energy electrons may represent such an alternative.

EXPERIMENT

Batches of $ZnGeP_2$ (150g) and $CdGeAs_2$ (350 g) were synthesized from 6N grade pure elements using the two-temperature technique [6-7]. In order to remove the residual oxygen, synthesis of $CdGeAs_2$ was combined with pre-purification of the elemental components followed by *in situ* purification of the synthesized charge. Large $ZnGeP_2$ and $CdGeAs_2$ single crystals were grown from stoichiometric melts using the technique of Horizontal Gradient Freeze (HGF). The HGF set-up was similar to that used for $CdGeAs_2$ by Borshchevsky and co-authors [8] and included a gradient furnace with a semi-transparent gold-coated Pyrex tube serving as a heat shield. Before irradiation, some of the as-grown $ZnGeP_2$ crystals were heat-treated at 500°C for 300 hours in accordance with the annealing procedure developed in the work [2].

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Irradiation of $ZnGeP_2$ and $CdGeAs_2$ with Fast Electrons

$CdGeAs_2$ and $ZnGeP_2$ samples of various shapes, including 2.5 mm thick wafers and 9 x 9 x 14 mm^3 XYZ parallelepipeds were irradiated with fast electrons at room temperature. A summary of the irradiation conditions is given in **Table I**.

Table I. Conditions of Fast Electron Irradiation of $ZnGeP_2$ and $CdGeAs_2$.

Crystal	Temperature	Electron Energy, MeV	Irradiation mode	Accumulated Dose, Mrad
$ZnGeP_2$ as-grown	20 - 25°C	1 to 4.5	Continuous, dc	1 to 4,000
$ZnGeP_2$ annealed	20 - 25°C	1 to 20	Continuous, dc	0.1 to 40,000
$CdGeAs_2$ as-grown	20 - 25°C	10	Continuous, dc	10 to 40,000

Characterization of Irradiated Crystals

$CdGeAs_2$

The crystals were characterized by the measurements of the optical transmission, conductivity type and electrical resistivity (ρ). Effect of 10MeV fast electrons on ρ of a $CdGeAs_2$ crystal measured along the <001> growth direction is presented in **Figure 1**. Irradiation at $\Phi=1\cdot10^{17}$ cm^{-2} caused an increase in ρ from 4 to 7 Ωcm to 30 to 90 Ωcm and amplification of the electrical nonuniformities. Increase in Φ to $2\cdot10^{17}$ cm^{-2} caused conversion to n-type and decrease in ρ to 1.5 to 2.5 Ωcm.

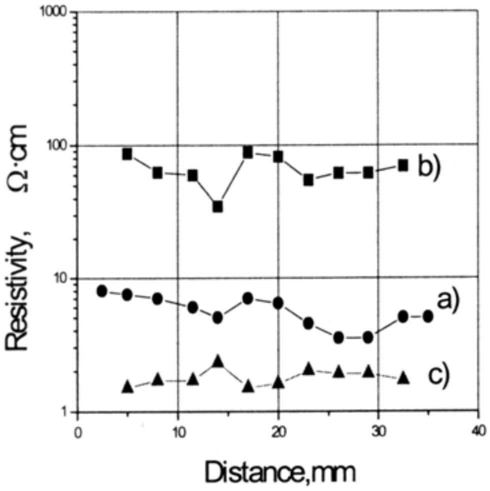


Figure 1. Resistivity distribution in $CgGeAs_2$ crystal: a) as-grown p-type; b) $\Phi=1\cdot10^{17}$ cm^{-2}; c) n-type after $\Phi=2\cdot10^{17}$ cm^{-2}.

Measurements of optical transmission were performed on polished 2.5mm thick wafers with non-polarized light using a Perkin Elmer 1600 FTIR spectrophotometer. The area of each wafer was mapped with a beam collimated to 2.5mm in diameter. An absorption spectrum measured for an as-grown wafer is presented in **Figure 2**, curve **a**. The spectrum shows a decrease in α with an increase in λ from 3 to 11 μm, a broad peak near 5 μm, and the peaks of the multi-phonon absorption between 12 and 14 μm.

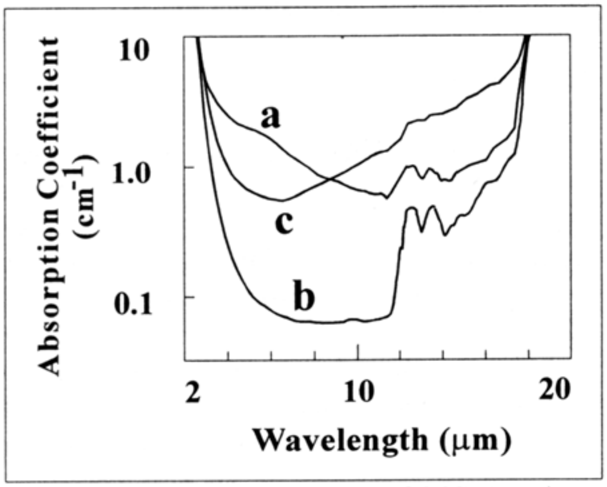


Figure 2. Absorption spectra of $CdGeAs_2$: a) p-type; b) highly compensated after $\Phi=1\cdot10^{17}$cm^{-2}; c) converted to n-type after $\Phi=2\cdot10^{17}$cm^{-2}.

Curves **b** and **c** in **Figure 2** show the effect of fast electron irradiation on the optical absorption of $CdGeAs_2$. Irradiation with $\Phi=1\cdot10^{17}$cm^{-2} caused reduction in α to 0.1 to 2.6 cm^{-1} at λ=5.3 μm and to 0.07 to 1.1 cm^{-1} at λ=10.6 μm, and disappearance of the structure near 5 μm (see curve **b**). In several spots, our

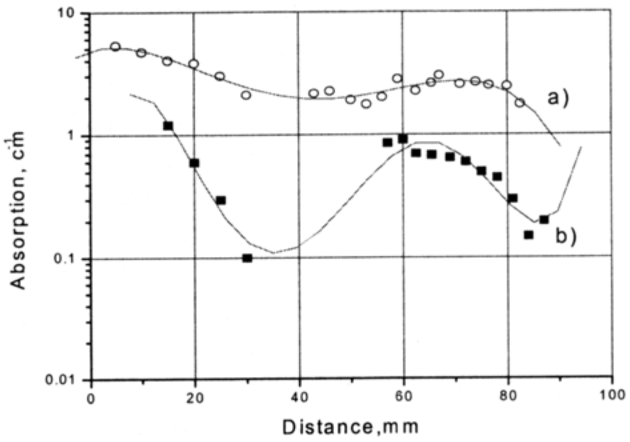


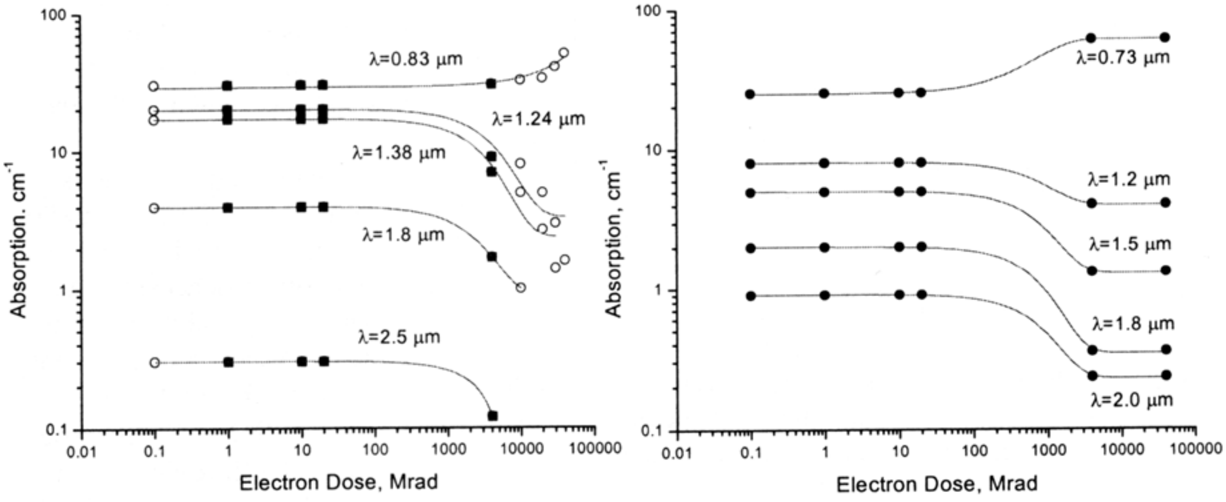
Figure 3. Distribution of optical absorption at λ=5.3 μm in $CdGeAs_2$ along <001> growth direction: a) as-grown, b) after irradiation. Solid lines represent polynomial fit.

measurements registered the lowest absorption ever reported for $CdGeAs_2$: $\alpha \approx 0.1\pm0.1$ cm^{-1} at λ=5.3 μm and $\alpha \approx 0.07\pm0.1$ cm^{-1} at λ=10.6 μm. Curve **c** in **Figure 2** shows the absorption of a crystal converted to n-type after irradiation with $\Phi=2\cdot10^{17}$cm^{-2}. Overall increase in the absorption and a change in the slope of the curve are noticeable.

Our measurements revealed considerable scattering in α, which, for the as-grown samples, varied from 2 to 7 cm^{-1} at λ=5.3 μm and from 0.7 to 4 cm^{-1} at λ=10.6 μm. Distribution of the optical absorption in a $CdGeAs_2$ single crystal measured along the <001> growth direction is presented in **Figure 3**. One can see that electron irradiation caused amplification of optical nonuniformities.

$ZnGeP_2$

$ZnGeP_2$ crystals were characterized by measurements of their optical transmission, photoluminescence (PL) and EPR. Irradiation with fast electrons caused significant changes in the optical transmission of $ZnGeP_2$. Effect of the electron dose (for 4.5 MeV fast electrons) on the absorption of as-grown and annealed wafers is presented in **Figure 4a,b**. A comparison between our experimental points obtained after irradiation of as-grown $ZnGeP_2$ and those of the work [9] is shown in **Figure 4a.** After recalculation of the fluence (cm^{-2}) into the dose (Mrad), an agreement between these two sets of data obtained for 2MeV and 4.5MeV electrons, respectively, became evident. The data in **Figure 4** show that electron irradiation causes increase in the optical absorption at shorter wavelengths and reduction in the absorption at longer



a

b

Figure 4. Effect of 4.5 MeV electron dose on the optical absorption of 2.5 mm thick $ZnGeP_2$ wafers: **a** - as-grown; **b** - annealed. Open circles - data from Brudnyi et al. [9].

wavelengths. According to our measurements, the wavelength, at which neither increase nor reduction occurs, is at ≈0.85μm. The curves in **Figure 4b** produced for an annealed sample show saturation of the optical absorption with the dose.

Optical absorption (o-ray) vs wavelength measured for a 14mm thick $ZnGeP_2$ crystal, which was annealed and then irradiated with fast electrons, is presented in **Figure 5.** One can see that for λ between 1.4 and 2 μm the effect of irradiation exceeds the effect of annealing. Due to the large optical extinction of a thick crystal, the plot $\alpha(\lambda)$ shows significant scattering for $\lambda<1.4$ μm. The inset in **Figure 5** demonstrates that a very low optical absorption (0.08 cm^{-1} or lower) can be achieved in $ZnGeP_2$ by irradiation with fast electrons.

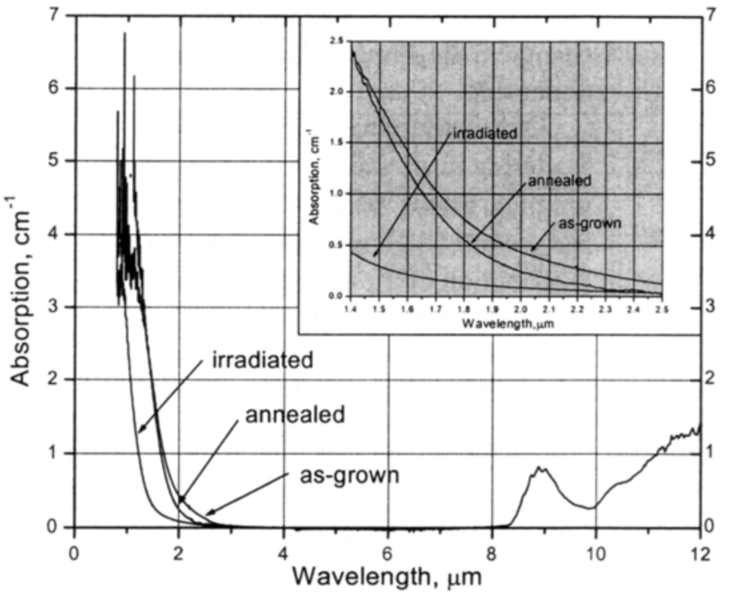


Figure 5. Effects of annealing and fast electron irradiation on optical absorption of $ZnGeP_2$ (o-ray, 14 mm thick crystal).

Irradiated samples of $ZnGeP_2$ were characterized using time-resolved photoluminescence (PL) and EPR measurements. The measurements were conducted in the 4 to 29K temperature range. More details on the PL and EPR experimental conditions can be found elsewhere [10-14]. A dominant feature in the PL spectra of $ZnGeP_2$ is a strong peak positioned near 1.2 eV. The intensity of the peak correlated with the optical absorption of the material and increased with the increase in α, as shown in **Figure 6**.

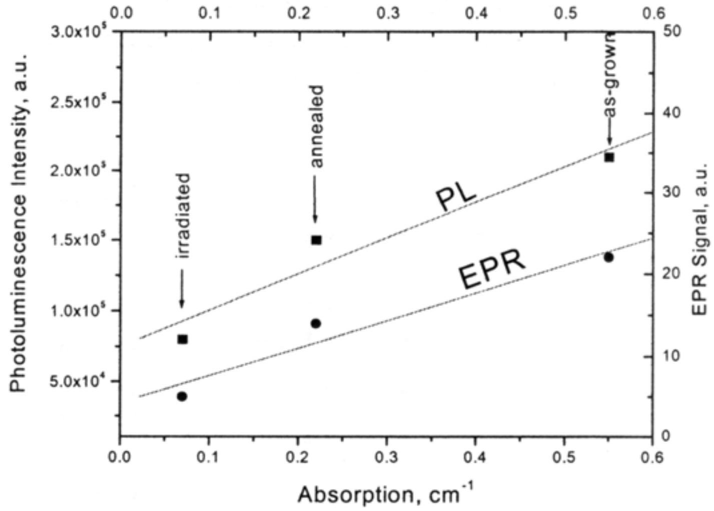


Figure 6. Intensity of PL peak at 1.2 and amplitude of EPR signal from A1 center versus optical absorption (for o-ray, 2.05 μm) for as-grown, annealed and irradiated samples.

Three paramagnetic centers known from the earlier EPR studies [12-14] were identified. They included a dominant acceptor A1 (presumably, V_{Zn}) and two donors (presumably, V_P and Ge_{Zn}). V_P and Ge_{Zn} became visible under illumination with λ=632 nm. The amplitude of the EPR signal was also in correlation with α, being the largest in the as-grown samples and the smallest in the irradiated samples (see **Figure 6**). In the irradiated samples, illumination with λ=632 nm led to the increase in the intensity of the EPR signal from A1 by nearly an order of magnitude.

DISCUSSION

Effects of nuclear irradiation (fast electrons, neutrons and gamma) on electrical properties of $ZnGeP_2$, $CdGeAs_2$, $ZnSnAs_2$ and $CdSnAs_2$ had been studied [9,16-18]. Irradiation of p-type crystals caused migration of the Fermi Level (FL) from the valence band (VB) toward the conductance band (CB). This had been assigned to the compensation of the p-type semiconductor as a result of the introduction of shallow donors and acceptors.

Effect of Irradiation on Optical Absorption in $CdGeAs_2$

The valence band of $CdGeAs_2$ contains the main upper band V_1 and two lower split-off bands V_2 and V_3 formed by the tetragonal lattice compression and spin-orbit interaction. Analysis carried out in the works [20-21] showed that the optical absorption in p-$CdGeAs_2$ is due to the intraband transitions. A comparison between the experimentally measured optical absorption in p-$CdGeAs_2$ and a model based on the intraband transitions is presented in **Figure 7** [21] showing that transitions from V_2 to V_1 bands may be responsible for the absorption maximum near 5 μm and the tail stretching to 14 μm, while transitions from V_3 to V_1 bands contribute to the 3.5 to 5 μm absorption shoulder.

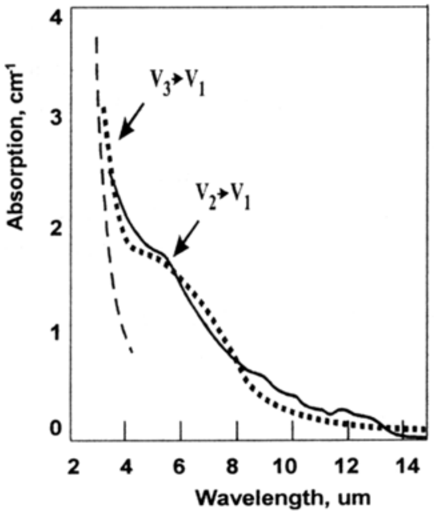


Figure 7. Optical absorption in p-$CdGeAs_2$ solid line – experiment, dashed – fundamental cut-off, dotted – model.

Thus, the effect of fast electron irradiation on α in the case of p-$CdGeAs_2$ is clearly due to the changes in the compensation level. Irradiation of an initially p-type crystal increases the degree of compensation, causes shift in the position of FL from VB toward CB, which reduces the number of holes in the valence band. As a result, it reduces the probability of the intraband transitions.

Effect of Irradiation on Optical Absorption in $ZnGeP_2$

The mechanism of optical absorption in $ZnGeP_2$ is a subject of controversy. Similarly to $CdGeAs_2$, the valence band of $ZnGeP_2$ is split into three sub-bands. However, the hole concentration in $ZnGeP_2$ is very small ($\approx 10^{10}$-$10^{12}cm^{-3}$), which make the intraband transitions unlikely. $ZnGeP_2$ is a compensated semiconductor containing native acceptors and donors in high concentrations (in the order of $10^{19}cm^{-3}$). Due to the high degree of compensation, the acceptors should be mainly ionized with only a small fraction ($\approx 10^{17}cm^{-3}$, according to [9]) remaining neutral.

Two different mechanisms of optical absorption have been suggested for $ZnGeP_2$: 1) electron transitions form VB to a deep neutral acceptor [9]; 2) transitions from an ionized deep acceptor to CB or to a donor [2,10]. Neither of the above models fits the experiment. If the first mechanism is responsible for the absorption, then α should be proportional to the concentration of the neutral acceptors. Accordingly, in compensated by irradiation $ZnGeP_2$ the number of the neutral acceptors should be reduced while the number of ionized increased. However, the EPR studies show an opposite: not the neutral acceptors, but single-ionized disappear upon annealing and irradiation (see **Figure 6**). If the second mechanism is responsible for the absorption, then α should be proportional to the concentration of the ionized acceptors. In this case one would expect higher absorption in irradiated crystals as a result of compensation, which is in total conflict with the experiment.

A double ionized zinc vacancy (V_{Zn}^{--}) had been suggested in the work [14]. If such a state is possible, then the number of V_{Zn}^{--} should increase with the degree of compensation. V_{Zn}^{--} should be non-paramagnetic, and this may explain the reduced EPR signal from V_{Zn}^{-} in the irradiated crystals. This concept may be fruitful and deserves further thoughts.

There is one more aspect of irradiation that should be taken into account, namely chemical compensation. The simplest radiation damage defect is a Frenkel pair – a pair of a free interstitial atom and a vacancy. In diamond-like crystal lattices the free self-interstituals are very mobile, tend to migrate and react with other defects. They may form complexes with the defects pre-existing in the lattice and convert them from electrically/optically active defects into inactive ones [19]. Thus, the effect of irradiation may be based on the removal of the optically active point defects pre-existing in the lattice.

Annealing of the irradiated crystals showed that the defects induced by irradiation are different from those pre-existing in the $ZnGeP_2$ crystals. Particularly, radiation defects anneal at relatively low temperatures whereas pre-existing defects are stable. It is quite possible that the vacancies identified by the EPR studies reside in clusters, while the defects introduced by irradiation are individual vacancies [19].

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