Decrease of the singly ionized zinc vacancies content under high energy electron irradiation in ZnGeP2

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Zinc germanium diphosphide, $ZnGeP_2$ (ZGP) is an excellent material for frequency conversion in the 3-8 µm range, thanks to its high non-linear optical coefficient and thermal conductivity. Powerful and tunable laser sources in the mid-IR are important for various applications such as long-range detection of gases, active imaging, or surgery [1]. However, ZGP exhibits an absorption around 2 µm, which limits its use in devices pumped at 2 µm. Studies have shown that as-grown crystals exhibit large concentrations of native defects, such as the paramagnetic singly ionized zinc vacancy (V_{Zn}^-), which is known to be the major cause of the ZGP absorption near 2 µm [2]. Researches have then shown that thermal annealing (near 600°C for 400h) [3], and electron irradiation [4], reduce the optical absorption around 2 µm by decreasing the absorption of these kind of defects. Moreover, a previous preliminary study, in our team, on tin (Sn) added ZGP showed that these crystals exhibit a smaller optical absorption after both growth and annealing [5].

The present study is focused on the investigation of V^-_{Zn} content in as-grown, annealed and electron irradiated ZGP single-crystals processed with and without Sn. The 2.5 MeV electron irradiation was performed on the SIRIUS platform in LSI. The investigation of the V^-_{Zn} content in ZGP was performed by Electron Paramagnetic Resonance (EPR) spectroscopy at low temperature as the spectrum intensity is related to the defect content in the material. An experimental study on the fluence dependence of the V^-_{Zn} content under electron irradiation up to 1×10^{18} e/cm² has been carried out on all processed samples and the results are reported in Figure 1. The aim of this work is to provide an overview of the effects of the different processes and their combination on the V^-_{Zn} content reduction in ZGP. The data displayed in Figure 1 show that there are some differences between the kinetics, however, at a fluence of 2×10^{17} e/cm^2 the V^-_{Zn} content reduction is the same for all samples. Indeed, Figure 1 shows that room temperature irradiations at this fluence (6h of irradiation with flux 10^{13} e/(cm^{2}s)) can reduce the V^-_{Zn} content by a factor ~5. At higher fluences, the observed content reduction is larger than a factor 10 (~10 at 4×10^{17} e/cm^2, and >10 at 1×10^{18} e/cm^2). Due to high reductions of the signal, the correct identifications of the EPR spectra intensities are difficult. Current work is focused on on-line and in-situ optical absorption (from 650 to 1050 nm) experiments to investigate the near edge modifications.

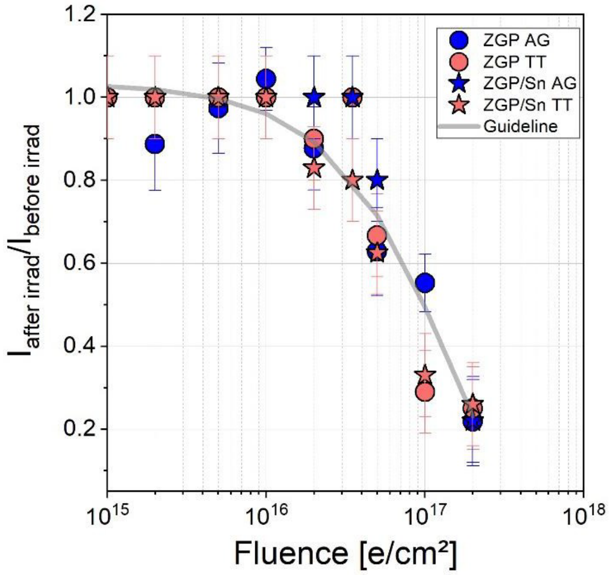

Figure 1: Ratio of experimental EPR spectra intensity of V^-_{Zn} after irradiation to prior irradiation as a function of the fluence in: as-grown (AG) and thermally treated (TT, 550°C for 600h) ZGP and ZGP/Sn. Data were compared after normalization to both samples mass and parameters of the measurement.

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