Gamma radiation-enhanced thermal diffusion of iron ions into II-VI semiconductor crystals

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Abstract: We investigate the effect of γ-irradiation on the rate of post-growth thermal diffusion of iron into ZnSe and ZnS. Samples had thin films of iron deposited on one facet and were annealed at 950°C for 14 days in the presence of γ-radiation and diffusion lengths were compared to those of traditional post-growth thermal diffusion in the absence of γ-irradiation. Samples of Fe:ZnSe and Fe:ZnS annealed under 44R/s γ-rays showed increases in diffusion rate of 14% and 50%, respectively.

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References and links
1. Introduction

Laser sources operating over the “molecular fingerprint” 2-14 µm spectral range are of great interest for a variety of applications including molecular spectroscopy, non-invasive medical diagnosis, industrial process control, environmental monitoring, free-space communication, and various defense related applications. Lasers based on transition metal (TM)-doped II-VI semiconductors such as ZnSe and ZnS are very promising sources for these applications [1–5]. They offer broad gain bandwidth of up to 50% of the central wavelength of emission, strong ultra-broad absorption bands in the mid-IR spectral range, and low energy optical phonon cut-off which reduces the efficiency of non-radiative decay.

These materials can be reliably produced by post-growth thermal diffusion of TM ions into bulk II-VI crystals [6–8]. This diffusion can be realized either from the metal phase from a thin film of TM deposited on a crystal facet prior to annealing or from the vapor phase by annealing crystals in the presence of TMs or TM compounds. This technique is simple, and cost effective in comparison with crystal growth [9]. This technology allows fabrication of large scale (20x20x0.5 cm) uniformly doped Cr:ZnSe crystals. Iron-doped II-VI crystals are of particular interest because as gain media they offer access to the longest spectral region among the TM dopants. They have absorption and emission over the 2.3-4.0 and 3.5-5.9 µm spectral regions, respectively, high cross-sections of emission and absorption, and negligible excited state absorption making them very effective mid-IR gain media and saturable absorbers.

The main drawbacks of post-growth thermal diffusion of iron into II-VI crystals include the limited coefficient of diffusion, non-uniform doping and large concentration gradients. These limitations effectively restrict the size of elements that may be practically produced using this technology.

The coefficient of diffusion could be increased by means of simultaneous gamma-irradiation during the thermal diffusion process. This irradiation is expected to produce a higher concentration of point lattice defects and stimulate additional diffusion channels for TM ion impurities [10, 11]. The enhancement of the diffusion process of iron ions is especially important since the diffusion length of this ion is not as big as for chromium ions [12–14]. Experiments were performed in which II-VI crystals are doped with transition metals by annealing with and without the presence of gamma radiation and the diffusion length of the metal ions for each method are measured and compared.

Laser characteristics of the irradiated and non-irradiated Cr:ZnSe and Cr:ZnS gain elements have been compared under excitation by CW Er-fiber laser [15]. Chromium concentrations in the studied samples were measured to be 2.4 x 10^{18} cm^{-3} and 5.3 x 10^{18} cm^{-3} for Cr:ZnSe and Cr:ZnS crystals, respectively. The crystals were γ-irradiated (Co^{60}) with a dose of 1.3 x 10^{8} Rad. The slope efficiency of the irradiated Cr:ZnSe gain element (44%) was very close to that of the non-irradiated crystal (45%). For Cr:ZnS the best slope efficiency was 16% for non-irradiated sample and 15% for the irradiated. So, the Cr:ZnSe and Cr:ZnS lasers based on identical γ-irradiated and non-irradiated crystals after 30 min of RT annealing featured a very similar pump thresholds, slope efficiencies and output powers. So, γ-irradiation from Co^{60} source does not result in formation of stable intrinsic defects which would reduce the lasing characteristics of transition metal doped II-VI lasers and could be used to enhance the diffusion process.

2. Sample preparation

Polycrystalline bulk ZnS and ZnSe crystals were cut to uniform sizes (7x7x3mm and 7x7x5mm, respectively), polished, and cleaned using acetone and methanol in sequence. These crystals then had thin films of thicknesses 300 nm of iron in the metal phase deposited onto a single facet by magnetron sputtering. Samples were sealed in evacuated quartz ampoules at 10^{-3} Torr and annealed for 14 days at 950°C under γ-irradiation from Co^{60}.
source. The irradiation dose rates of 44 R/s, 1.81 R/s were varied by distance between Co$^{60}$ source and furnaces. Samples annealed at the highest dose rate accumulated a total dose of 50-60 MRad and those annealed at the lower dose rate accumulated a total dose of 2-3 MRad. For comparison, identical samples were also annealed without irradiation at the same temperature for the same duration. After annealing, the crystals are removed from quartz ampoules and slightly polished on facets parallel to the direction of metal ion diffusion.

3. Experimental setup

Spectra of all samples were taken with 3101 UV-Vis and FTIR Shimadzu spectrophotometers at room temperature (RT). Characteristic absorption spectra of Fe:ZnSe crystal at $^5E \rightarrow ^5T_2$ transition measured in the direction of diffusion after 14 days 950°C annealing under $\gamma$-irradiation with a power dose of 44 R/s are depicted in Fig. 1(a) (curve i). One of the methods used to measure the iron concentration gradient was based on measurement of the dependence of the optical density versus the thickness of the crystal polished off along the diffusion direction. The samples were cut along directions parallel to the direction of diffusion of the metal film in order to avoid influence from the diffusion from other surfaces from the vapor phase. The surface through which diffusion took place was polished such that ~10-20 $\mu$m was removed, and absorption spectra measurements were repeated. This process was iterated several times to measure the change in total concentration as a function of the total material removed by polishing. The curves ii and iii in Fig. 1 demonstrate examples of subsequent absorption spectra of the Fe:ZnSe crystal after polishing-off 86 and 186 $\mu$m, respectively.

By a second method, the concentration gradient of iron ions in crystals after diffusion was measured directly by absorption of iron as a function of position within the crystal. An experimental set-up for concentration gradient measurement is depicted in Fig. 2(a). A tunable laser based on Cr:ZnS pumped by an Er:fiber was used as a source. The Cr:ZnS laser radiation was focused through a CaF lens of 150 mm (f) focal length and directed into a power meter. The laser beam diameter was measured by the knife edge method at several points in order to accurately model the location and size of the beam waist. The minimum beam diameter was measured to be approximately 109 $\mu$m with a Rayleigh length of 3 mm. For higher resolution measurements, the beam was expanded before the focusing lens to reduce the beam waist to approximately 78 $\mu$m and a Rayleigh length of 2 mm. Figure 2(b) shows dependence of the beam waist diameter as a function of the beam waist position. The estimated $M^2$ parameter of the test beam was 2.4. Cr:ZnS emission was tuned to 2637 nm and 2048 nm, in order to measure iron absorption and baseline, respectively. The crystals to be measured were then translated across the beam waist in the direction of diffusion and transmitted power was measured as a function of crystal position. Figure 1(b) demonstrates measurements of the transmitted power at 2048 nm and 2637 nm for one of the studied Fe:ZnSe samples with length 5.3 mm, curve iv and v, respectively. The sharp drop of the transmitted power of the 2048 nm radiation near the crystals edges results from shadowing of the beam by the unpolished surfaces. The slight upward trend in transmission of both wavelengths within the crystal is most likely due to non-uniform losses caused by the poor polish of the surfaces. The deviation of curve iv from curve v near crystal edges can be attributed to iron absorption. As one can see from the figure, the ratio of the measurements at two wavelengths allows us to normalize signal to Fresnel losses and polishing quality of the crystal surfaces. The gradient measurements obtained by this laser scanning method were compared to gradients measured by the polishing method in order to validate the precision and reliability of the methods. The laser scan method was then used for all further study because it offers higher resolution and the ability to measure ion distributions in samples non-destructively.
4. Results and Discussion

4.1 Fe:ZnSe samples

Figure 3(a) shows optical density (OD = \(-\ln(T)\)) at 3048 nm wavelength as a function of polished-off thickness in Fe:ZnSe crystals subjected to Fe diffusion from 300 nm thick Fe film deposited on the crystal facet during 14 days of annealing at 950 °C under \(\gamma\)-irradiation with a power dose 44 R/s (circles) and 0 R/s (triangles). As one can see from the figure the maximum concentration of iron ions near the crystal surface is approximately two times higher in the gamma radiation enhanced process. To estimate diffusion length the ion distributions were normalized to the maximum OD (see Fig. 3(b)).

According to a simple model based on Fisk’s diffusion Laws, if the diffuser is deposited initially onto the surface of a sample and spreads into one half-space, the concentration distribution \(C(x,t)\) solution is [16]:

\[
C(x,t) = \frac{M}{\sqrt{\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right).
\]
where $M$ denotes the number of diffusing ions deposited on the surface per unit area; $D$ is diffusion coefficient, and $t$ is annealing time. Using this solution the dependence of the optical density on polished-off thickness ($\delta$) could be expressed as

\[
OD(\delta) = \tilde{\sigma} C(x,t) dx = \sigma M \left[ 1 - \text{erf} \left( \frac{x}{\sqrt{4Dt}} \right) \right],
\]

(2)

where $\sigma$ is the cross-section of absorption and the error function is defined as

\[
\text{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z \exp(-\xi^2) d\xi
\]

(3)

The solid curves in the Fig. 3(b) represent fitting according to the Eq. (2). Using the parameters $L_{\text{diff}} = 2\sqrt{Dt}$ from this error function to fit measured OD data, the diffusion lengths were calculated to be $L_{\text{diff}} = 520$ $\mu$m (red curve) and $L_{\text{diff}} = 420$ $\mu$m (green curve) for radiation enhanced diffusion process and test diffusion (without $\gamma$-irradiation), respectively.

![Graph](image)

**Fig. 3.** A) Total optical density of Fe:ZnSe as a function of thickness removed by polishing comparing $\gamma$-enhanced (crossed circles) and traditional (triangles) diffusion. B) Normalized optical density as a function of thickness removed by polishing comparing $\gamma$-enhanced (crossed circles) and traditional (triangles) diffusion.

Figure 4(a) shows optical density at 2637 nm in the same samples using tunable Cr:ZnSe laser. Crystals were scanned starting from the edge of the facet on which the thin film of iron had been deposited. In addition to diffusion from the metal phase, iron sublimes in the ampoule enabling diffusion from the gas phase, accounting for the small concentration on the opposite facets of the crystals. It is noteworthy that in the case of Fe:ZnSe samples, the optical density of iron measured near the surface is $\sim$1.5 times higher in the irradiated sample. One reason for this may be that in the case of annealing under $\gamma$-irradiation, interaction between the iron metal film and crystal host is enhanced at crystal surface leading to a smaller fraction of evaporated iron with regards to thermal diffusion without $\gamma$-irradiation. These results are in agreement with data obtained from the polishing method.
Absorption coefficients at 3048 nm were calculated using experimental data and the ratio of absorption cross-sections at 2637 nm and 3048 nm [2]. Figure 4(b) shows the absorption coefficients at 3048 nm in the first millimeter of studied samples. The different symbols in curve iii represent absorption coefficients at 3048 nm measured through different sections of the same crystal. The solid curves in Fig. 4(b) show absorption coefficients calculated using parameters obtained from fitting Gaussian curves to absorption coefficients measured by the polishing method at 3048 nm. These show good agreement with the gradients measured by laser scanning method. The 1.7 times higher value of the maximum iron concentration and 1.24 times higher value in diffusion length in the γ-enhanced diffusion process resulted in twice higher initial optical density, OD = -ln(T) at 2638 nm as it shown in Fig. 4(a). Using the absorption coefficient at the maximum of the absorption band, \( \sigma_{abs} = 1 \times 10^{-18} \text{ cm}^2 \) [2], we can use the measured optical density to estimate Fe\(^{2+} \) concentration near the edge of the crystals to be \( \sim 1.6 \times 10^{19} \text{ cm}^{-3} \). The measured diffusion lengths were used to estimate the diffusion coefficient, D, using \( L_{diff} = 2\sqrt{Dt} \). This resulted in diffusion coefficient \( D = 3.7 \times 10^{-10} \text{ cm}^2/\text{s} \) for the case of Fe:ZnSe prepared by traditional post-growth thermal diffusion and \( D = 5.8 \times 10^{-10} \text{ cm}^2/\text{s} \) for radiation-enhanced diffusion. The results for traditional post-growth thermal diffusion (without gamma irradiation) are in agreement with values available in the literature [12,14].

As we mentioned in the introduction, according to reference [15] the γ-radiation dose of 1.3x10\(^8\) Rad does not result in formation of significant losses in the ZnS and ZnSe crystals. However, there is still question of whether possible formation of aggregate centers or defects could stimulate quenching of mid-IR photoluminescence of Fe\(^{2+} \) ions. In our preliminary experiments, we compared photoluminescence (PL) signals at \(^5\)T\(_2\)→\(^5\)E transition of Fe\(^{2+} \) ions at 4.1 μm in ZnSe crystal fabricated by thermal diffusion method with and without gamma irradiation under excitation by free running Er:YSGG laser operating at 2.78 μm measured under the same excitation parameters. In these experiments, the PL signals were proportional to iron absorption and were higher for Fe:ZnSe samples fabricated using radiation-enhanced diffusion. We did not find any significant influence of the gamma irradiation on quenching of mid-IR PL. However, more detailed study of the influence of the γ-irradiation on iron PL is needed.

4.2 Fe:ZnS samples

Iron-doped ZnS is of interest for several reasons. First of all, in comparison with Fe:ZnSe it shows a larger damage threshold, and stronger crystal field splitting shifts the emission of iron
in ZnS to 3.3-4.5µm spectral range. However, a smaller crystal lattice parameter, and a stronger crystal field make challenging production of a large-scale Fe:ZnS crystals using post growth thermal diffusion methods. The measurements of concentration gradients of γ-irradiated and non-irradiated samples of Fe:ZnS crystals are shown in Fig. 5(a). As one can see, the concentration near the crystal surface is nearly equal in both samples, as was not the case with Fe:ZnSe. In the samples shown, we can estimate the Fe²⁺ concentration using the measured optical density and the cross-section of absorption at 2.6µm of $\sigma_{abs} = 8 \times 10^{-19}$ cm² [2]. This gives a concentration near the edge of the crystal of approximately $9.5 \times 10^{18}$ cm⁻³. Figure 5(b) shows these optical densities normalized in order to compare the iron diffusion lengths, and one can see the diffusion length of iron in the sample which was not subjected to γ-irradiation was measured at 200 µm, whereas the irradiated sample showed a diffusion length of 300 µm. This represents a ~50% increase of the diffusion length. Using $L_{diff} = 2\sqrt{Dt}$, these diffusion lengths give a diffusion coefficient, D, of $8 \times 10^{-11}$ cm²/s for traditional post-growth thermal diffusion and $1.1 \times 10^{-10}$ cm²/s for radiation-enhanced diffusion. These results also show that diffusion length of iron in ZnS is more than a factor of 2.1 smaller than that in ZnSe for samples fabricated using post growth diffusion method.

![Graph](image)

Fig. 5. A) Optical density as a function of distance from the crystal facet for Fe:ZnS annealed with (solid) and without (dashed) γ-irradiation; B.) Normalized gradient of Fe concentration in ZnS annealed under γ-irradiation (solid) and with no irradiation (dashed).

### 5. Conclusions and future work

In conclusion, the addition of γ-irradiation during the annealing process has demonstrated a significant increase in diffusion lengths of iron in ZnSe and ZnS, 25% and 50%, respectively. This technique shows promise for production of materials doped with a more uniform dopant concentrations, larger crystal size or increase concentrations of dopants such as large rare earth ions to levels which would otherwise be difficult to achieve with this technique. Using data reported for our samples fabricated for 14 days at 950°C, we can estimate that in the case γ-radiation-enhanced thermal diffusion from two sides of a crystal, we can obtain a homogeneous distribution over 0.5mm crystals with iron concentration $1.6 \times 10^{19}$ cm⁻³ and $9.5 \times 10^{18}$ for Fe:ZnSe and Fe:ZnS respectively.

Further possible improvements of the diffusion of the TM ions into II-VI semiconductors by γ-radiation-enhanced thermal diffusion may be achieved by adjusting power dose of ionizing radiation and annealing temperature. A higher radiation dose rate or use of electron beam irradiation may increase the equilibrium concentration of point lattice defects thus further increasing the diffusion pathways, adjusting the annealing temperature may also enable enhancement of the diffusion length. Finally, further studies should be done on the effect of gamma irradiation on photoluminescence efficiency and concentration quenching.
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