Optically dense Fe:ZnSe crystals for energy scaled gain switched lasing

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ABSTRACT

This work is focused on study and optimization of diffusion of Fe in ZnSe from the metal phase, comparative spectroscopic characterization of kinetic properties of Fe:ZnSe crystals with a wide range of concentrations, and energy scaling of the Fe:ZnSe gain-switched laser. Iron doping of ZnSe polycrystals was performed by thermal diffusion from the iron film made by thermal evaporation process. Special cleaning of the ZnSe surfaces and optimization of the ZnSe substrate temperature and the rate of Fe evaporation resulted in significant enhancement of the diffusion process and enabled fabrication of high optical density crystals with Fe concentration up to $2x10^{20}$ cm^{-3}. The diffusion coefficient and diffusion length of iron in ZnSe at $1000^{\circ}C$ were estimated as $2.1x10^{-9}$ cm^{2}/s and 1.3 mm, respectively. We report a detailed absorption, emission, and kinetics of fluorescence of Fe:ZnSe spectroscopy performed over a broad range of Fe concentrations ($5x10^{18}$ - $2x10^{20}$ cm^{-3}) and temperatures (14-300K) under direct 2.78μm excitation.

Keywords: Mid-IR lasers, solid state lasers, Mid-IR laser gain media; Fe:ZnSe

1. INTRODUCTION

For more than two decades, a significant effort has been made in the development of novel mid-IR lasers promising for a wide range of applications such as free space optical communication, remote sensing, material diagnostics etc. Although various mid-IR lasers have been developed, the majority of them have not been commercialized due to a limited output power and difficulty to operate and maintain performance at room temperature.

There are several approaches to develop laser sources for mid-IR spectral region such as molecular gas lasers, optical parametric oscillators (OPO), semiconductor quantum cascade lasers [1,2], etc. One of the most promising approaches is based on direct lasing of transition metal (TM) doped II-VI wide band semiconductors [3,4]. For example, Cr^{2+} doped chalcogenide lasers have been studied as an attractive source of tunable laser radiation in the 2-3μm spectral region [5,6,7,8]. Recently a progress has been also demonstrated with Fe^{2+} doped II-VI crystals [9] promising for room temperature tunable mid-IR lasing over 3 to 6 μm spectral range.

Cr and Fe doped II-VI crystals can be directly grown from melt using vertical Bridgman technique [10,11]. However, due to sublimation of II-VI material at temperatures much smaller than melting temperature, this technology requires simultaneous application of high temperature and pressure and, hence, is not commercially available.

High vacuum pulsed laser deposition (PLD), molecular beam expitaxy (MBE), and chemical vapor deposition (CVD) are used to grow thin film structures [12]. However, these methods are not appropriate for fabrication of bulk uniformly doped crystals with sufficiently high concentration of Fe ions. Notable technologies used to fabricate mid-IR bulk gain elements are mainly based on post-growth thermal diffusion of active impurities (e.g. Cr and Fe) in II-VI crystals grown by physical or chemical vapor transport (PVT, CVT) methods [13]. On the contrast to effective Cr post-growth diffusion from metal Cr film deposited by plasma sputtering, plasma sputtering of iron films is not trivial and requires special magnetrons enabling high magnetic field. Therefore it is desirable to review alternative technological methods for cost-effective fabrication of high quality Fe doped gain materials. Optimization of deposition parameters and study of post-growth thermal diffusion of Fe ions in II-VI materials was one of the major objectives of this work.

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2. SYSNTHESIS BY POST-GROWTH THERMAL DIFFUSION OF Fe:ZnSe

The post-growth thermal diffusion of iron in ZnSe was carried out from the iron thin films deposited on the crystal surfaces via thermal evaporation using resistively heated tungsten filament sources. Before deposition of Fe on ZnSe, all host crystals were pre-cleaned with 2.5% HCl, 5% NaOH, Acetone and Methanol solutions. The technique of thermal evaporation has been used for the deposition of ZnSe (polycrystalline substrates) in sufficient distance to guarantee uniformity in film composition and thickness. Iron metal pieces (pellets) were evaporated from resistively heated tungsten filament sources.

Each deposition rate was monitored by Quartz crystal thin film sensor. The major features of a conventional thermal deposition system are depicted Fig. 1.

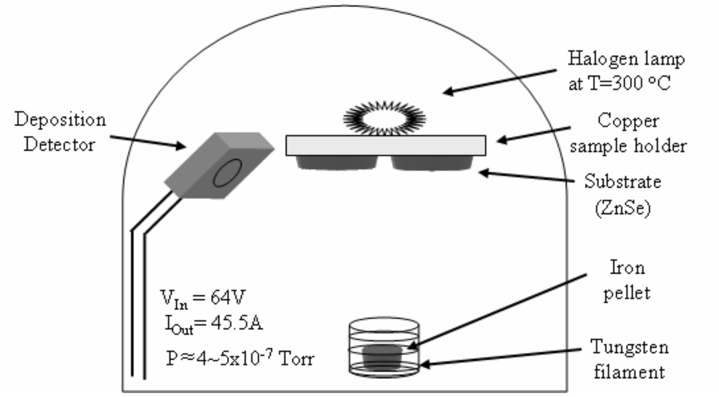

Fig. 1 Schematics of thermal evaporation

The metal species were evaporated on the surface of II-VI semiconductors in high vacuum. Normally, the chamber is pumped to 5 x 10^{-7} Torr using diffusion pump. During the deposition, ballistic propagation of the vapor requires a residual gas background with pressure below 10^{-5} Torr.

Evaporation source materials for our experiments were mostly Fe (99.95% purity) available in various forms such as pellets, rods or powders. The distance between the source and substrate was experimentally optimized (approximately in the range of 10 to 15cm) to provide a high uniformity of the deposited film.

Once the substrate has been deposited with Fe thin film in a high vacuum, the samples were sealed in a silica ampoule under high vacuum ($P < 10^{-4}$ Torr), placed in a furnace, heated up within about 2 hours to ~ 1000°C, and finally annealed at 1000°C for a few days.

3. OPTICAL CHARACTERIZATION OF Fe:ZnSe

Optimization of thermal diffusion parameters has been performed by measurement of gradient of Fe distribution over the crystal volume as a function of temperature and annealing time. The diffusion process of iron in the host can be describe using *Fick's 2nd low*:

$$\frac{\partial C}{\partial t} = \nabla \cdot \left(D \nabla C \right) \tag{1}$$

where $C(r,t)$ -concentration of the dopant ions and *D*- is a diffusion coefficient. There are two important boundary-initial conditions for practical applications in the case of one-dimensional geometry. First is diffusion with constant surface concentration *C(0)* when host occupies the half-space (semi-infinite media, $x>0$). This condition is usually realized in the diffusion from the gas phase when host is annealed in the dopant vapor at constant pressure. In this case solution of the diffusion equation can be written as:

$$C(t,x) = C(0) \cdot erfc\left(\frac{x}{2\sqrt{Dt}} \right) \tag{2}$$

where the abbreviation is

$$erfc(z) \equiv 1 - \frac{2}{\sqrt{\pi}} \int_0^z \exp\left(-\eta^2\right) d\eta \tag{3}$$

Second commonly encountered initial condition is so-called instantaneous planar source:

$$C(t=0,x) = M\delta(x) \tag{4}$$

It describes experiments with initial condition when thin-film layer of the dopant is deposited on the host surface before annealing. M denotes the number of the dopant ions per unit area. The solution of the diffusion equation in this case can be written as :

$$C(x,t) = \frac{M}{\sqrt{\pi Dt}} \exp\left(-\frac{x^2}{4Dt} \right) = \frac{bC_0}{\sqrt{\pi Dt}} \exp\left(-\frac{x^2}{4Dt} \right) \tag{5}$$

where, C_0 is concentration of atoms in the deposited film, *b* is a film thickness, and t is annealing time. The characteristic value of $2\sqrt{Dt}$ is usually defined as a diffusion length.

Three identical samples of group A having Fe film of thickness 1020 nm deposited only on one surface of ZnSe crystal were annealed at 1000 ºC during 564 hours and were used to estimate the diffusion parameters of Fe in ZnSe, such as diffusion coefficient and diffusion length. To verify the correctness of diffusion parameters estimation from the group A experimental data, the diffusion parameters of iron in ZnSe were also estimated using another Fe:ZnSe sample (group B) identical to samples of group A, but annealed at 1000 ºC during 420 hours. The samples thickness was equal to ~5mm and it was sufficient to avoid the influence of iron diffusion from the gas phase through the opposite crystal surface.

The room temperature absorption measurement (by Shimadzu UV-VIS-NIR-3101PC and Bruker "Tensor-27" FTIR spectrophotometers) of the annealed samples (see Figure 2) was carried out to confirm the corresponding $^5E \rightarrow {}^5T_2$ vibronic transition of Fe^{2+} ions as well as an average Fe concentration in ZnSe. Iron distribution in the annealed crystal was measured using 2.78μm radiation of a pulsed Cr:Er:YSGG operating in free running regime. Laser radiation was focused into a spot with ~130μm beam diameter. To avoid absorption saturation, the pulse energy was reduced to the level below the saturation energy of Fe optical centers.

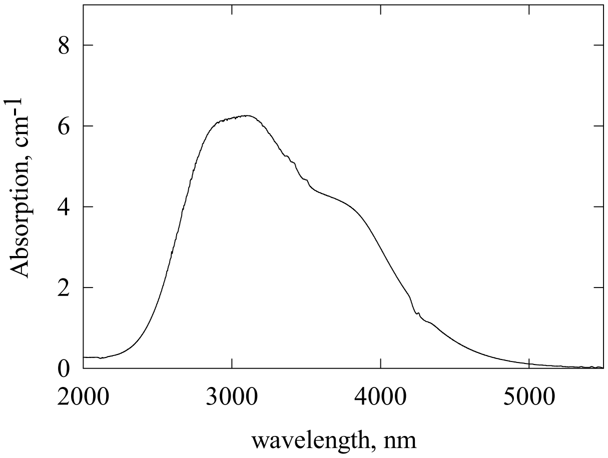

Fig.2 Room temperature absorption spectra of Fe:ZnSe sample.

Figure 3 A and B depicts experimental data (squares B, and dots A) for gradient of iron concentration in ZnSe measured via transmission of 2.78 μm radiation at different displacement of the beam from the crystal surface. Solid lines represent theoretical fit of experimental data using Eq. (5) for the thin film geometry case.

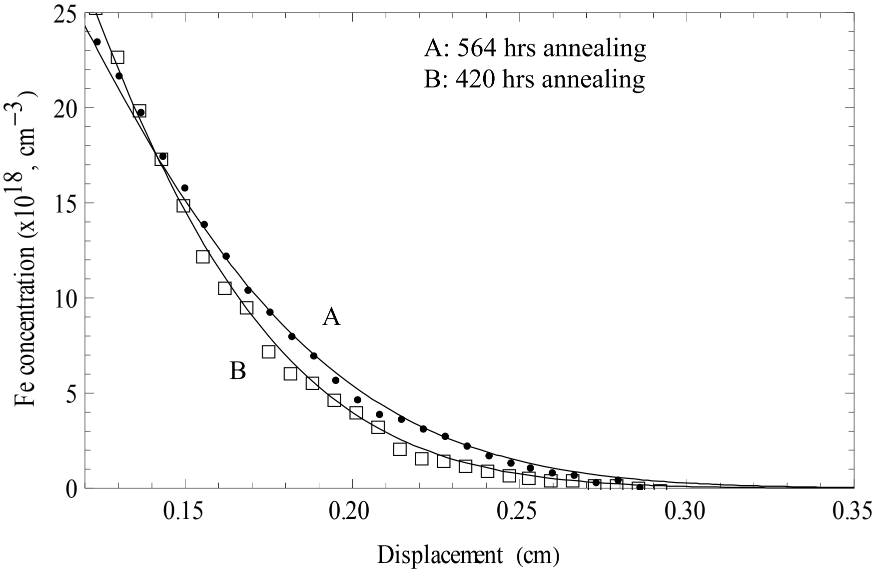

Fig. 3 Diffusion coefficient calculations by Mathematica for experimental (*dots*) and fitted (*solid*) data.

Sample of Fig. 2A was annealed for 564 hrs at 1000 °C and fitting of experimental data results in diffusion coefficient $D = 2.1\text{x}10^{-9}$ cm^2/s, and diffusion length of 1.3mm. The diffusion parameters for three different samples with identical Fe films and annealed at the same conditions were very close to each other and varied over the range 1.97-2.1x10^{-9} cm^2/s. Sample of Fig.2B was annealed for 420 hrs at T=1000 ºC and fitting of experimental data resulted in D=2.24x10^{-9} cm^2/s and diffusion length of 1.16mm as shown in Table 1. The measured diffusion coefficient was ~2.5 times bigger than that calculated from the vapor phase diffusion experiments early reported in [14] for diffusion from the gas phase. We believe that this difference is due to ZnSe surface pre-cleaning and elimination of chemical barriers hampering Fe diffusion in

[14]. It is noteworthy that in our initial experiments of iron thermal diffusion from the metal phase without careful cleaning of the sample surfaces the iron diffusion length was more than 3 times smaller than what was obtained from Fig. 3.

Table 1. Annealing conditions and diffusion parameters for Fe:ZnSe

Sample	Annealing Time (hrs)	Annealing Temperature (ºC)	Diffusion Coefficient ($x10^{-9}$, cm^2/s)	Diffusion Length (mm)
1	564	1000	2.1	1.3
2	564	1000	2.01	1.28
3	564	1000	1.97	1.27
4	420	1000	2.24	1.16

To estimate the threshold of Fe:ZnSe concentration quenching we studied the luminescence kinetics of low and highly doped Fe:ZnSe crystals over the 14-300K temperature range. For spectroscopic experiments, we used 1.3mm thick Fe:ZnSe samples annealed at 1000ºC. As one can see from the previous experiments this thickness is close to the measured diffusion length. In addition, for these experiments the iron films were deposited on both sides of the samples to provide a uniform distribution of iron ions through the sample.

Actively Q-Switched Er:Cr:YSGG laser operating at 2.78μm with 80ns pulse duration was used for optical excitation of studied samples. A closed-cycle refrigerator system (Janis Research Co., Inc., Model CCS-450) was utilized for spectroscopic measurements at low temperatures. The photoluminescence spectra were measured using an Acton Research ARC-300i spectrometer.

Figure 4 shows temperature dependence of Fe:ZnSe luminescence spectra. As one can see, Fe:ZnSe features a broad (3500-5500 nm) luminescence band.

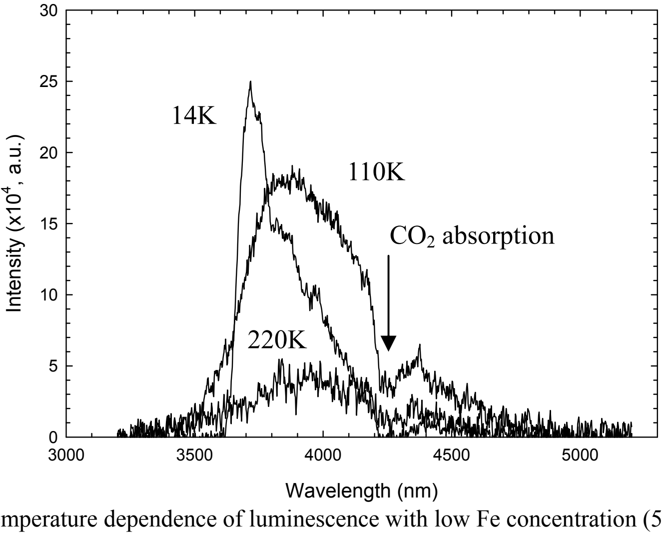

Fig. 4 Temperature dependence of luminescence with low Fe concentration ($5.8x10^{18}$ /cm^3).

The nonselective PL kinetics were measured using 3-5.5μm bandpass filter in front of optical detector. The luminescence kinetics measured at different temperatures for Fe^{2+} ions concentration varied from $5.82x10^{18}$ to $85x10^{18}$

ions/cm^3 are shown in the Fig 5. The PL decays of the low concentrated sample samples can be fit within the experimental error using a single exponential decay with a lifetime at 14K equal to 53μs.

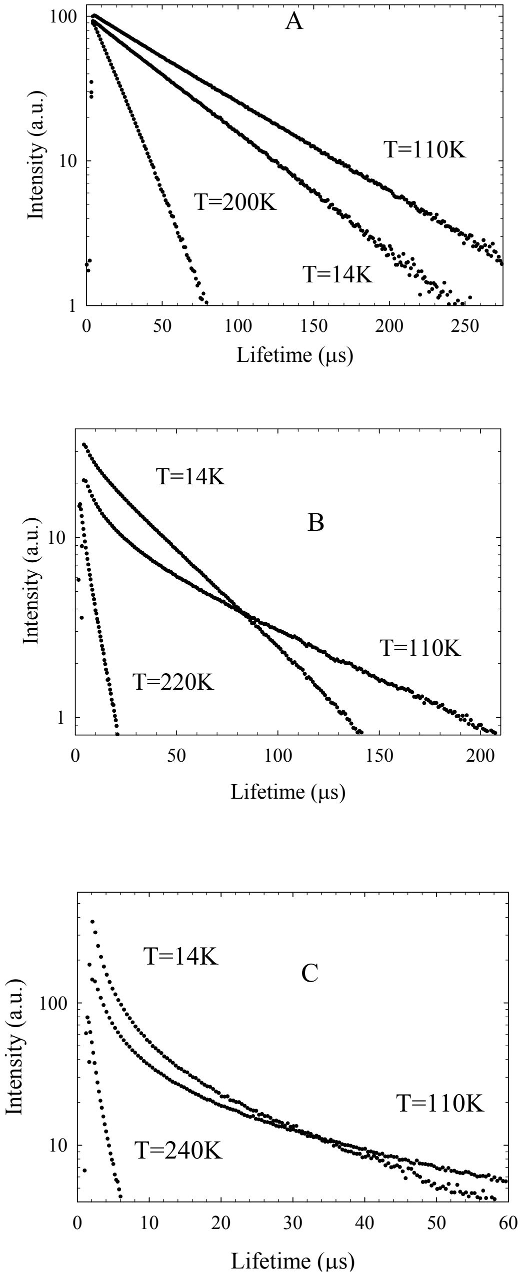

Fig. 5 Temperature dependence of luminescence lifetime with A: 4.6x10^{18} /cm^3, B: 37.64x10^{18} and C: 85.8x10^{18} /cm^3 Fe concentration

The measured Fe^{2+} lifetime increases in the 14-120K temperature range (see Fig 6) and this increase could be a result of different radiative lifetimes of the components of the $^5E \leftrightarrow {}^5T_2$ transition, or luminescence re-absorption due to overlapping of the Fe^{2+} absorption and emission bands at higher temperatures. The re-absorption of the photoluminescence could also explain why lifetime increase in the low concentrated sample C=5.8x10^{18} /cm^3 (from τ=53 µs at T=14K to τ=69 µs at T=110K) is smaller than for samples with iron concentration C=13x10^{18} /cm^{3} (from τ=52 µs at T=14K to τ=81 µs at T=110K).

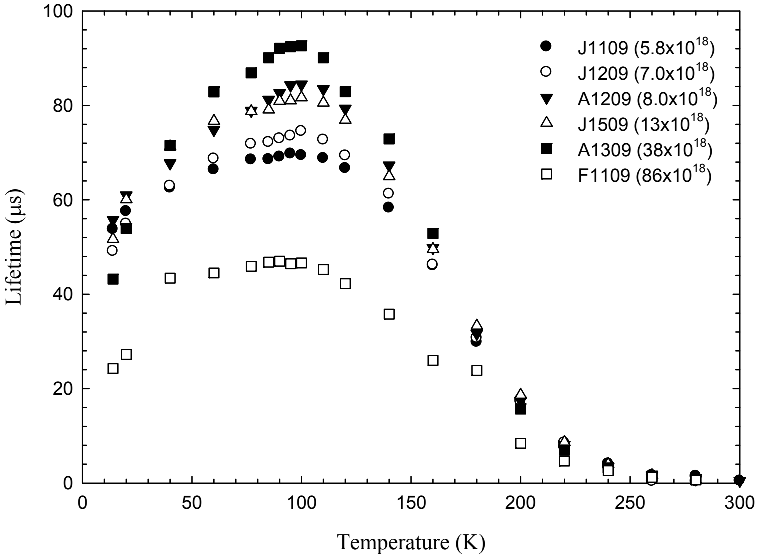

Fig. 6 Temperature dependence of luminescence lifetime for Fe:ZnSe crystals

The decreasing of luminescence lifetime at temperatures higher than 120 K is mainly due to thermally activated nonradiative decay. For highly concentrated sample the PL kinetics are not described by single exponential decay (Fig.5 B and C). As one can see from the Fig. 6, the lifetime drops ~2 times when iron concentration increases from 3.8x10^{19} to 8.5x10^{19} ions/cm^{3} (90 and 45 µs at 110K, respectively).

4. CONCLUSION

Fabrication of high optical density Fe:ZnSe was realized by post-growth thermal diffusion of iron in ZnSe crystals from thermally evaporated Fe metal film. The measured diffusion coefficient of iron in ZnSe was 2.5 times bigger than that calculated from the vapor phase diffusion experiments early reported for diffusion from the gas phase. The temperature dependence of luminescence kinetics was studied for Fe^{2+} ions concentration varied over 5.82x10^{18} to 85x10^{18} ions/cm^{3} range. It was shown that Fe:ZnSe concentration quenching occurs for iron concentration between 38 and 85x10^{18} /cm^{3} . Within this range of concentrations the lifetime of Fe^{2+} optical centers drops by a factor of 2.

5. ACKNOWLEDGEMENT

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