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Diffusion Coefficient of Iron in ZnSe Polycrystals from Metal Phase for mid-IR Gain Medium Application

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Diffusion coefficient of Fe in polycrystalline host ZnSe as a mid-IR gain medium has been measured in the annealing temperature ranges of 850 to 950°C. The synthesis of the samples was carried out in quartz ampoule in which the Fe thin film deposited by physical vapor evaporation method on the ZnSe. One can realize that the diffusion coefficient strongly depends on the surface active surfactants through the cleaning process and the substrate temperature during the thin film deposition leading to 2.04×10^{-9} cm^2/s for Fe^{2+}:ZnSe. The Annealing temperature dependence of the Fe ions diffusion in ZnSe was used to evaluate the activation energy, E_a=1.39 eV for diffusion and the pre-exponential factor D_0 of 13.5 cm^2/s.

Keywords : Solid state laser, Diffusion coefficient, Mid-IR gain medium, Fe:ZnSe

I. Introduction

There has been a high demand for tunable middle infrared (mid-IR) lasers having radiation overlapping with 2~10 μm molecular "fingerprint" spectral range. For instance, 3 to 3.5 μm laser sources are important for various applications including gas sensing, spectral analysis, infrared illumination, countermeasures, medical diagnostics, and others [1-4]. When tuned to wavelengths between 6 and 7 μm, such lasers are promising for medical applications and removing defined volumes of the soft tissue with a very little collateral damage [5,6]. However, the current types of mid-IR lasers such as optical parameter oscillator (OPO) and quantum cascade laser (QCL) suffer from drawbacks like limited power and difficulty to operate at room temperature [7]. Whereas, lasers based on group II-VI compounds doped by the transition metals (for example Fe doped binary and ternary chalcogenides), can provide very high power levels at good beam quality and high optical density, but achieving these in reality has been a challenge. For these reasons, the study on high optical dense gain-switched laser materials has spanned over four decades. However, there have been fundamental problems of developed crystal growth methods for transitional metal (TM) ions doped II-VI semiconductor materials due to the low temperature crystal sublimation (above approximately 400°C). There have been various methods of laser active TM ions introduced into II-VI host materials such as diffusion during melting growth, physical vapor transport (PVT), pulsed laser deposition (PLD) and molecular beam expitaxy (MBE) [8]. The commonly used doping methods are based on growth

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from melt, vapor growth, or after growth thermo-diffusion doping. These methods require a high temperature (1538°C) and high pressure (75×10^2 KPa) leading to unexpected and parasitic absorptions. In this study, we focus on the most effective rout for obtaining pre-assigned Fe impurity concentration in ZnSe polycrystals from the metal phase deposited by thermal evaporation techniques (TE) since the properties of thin films are critically dependent upon the deposition methods and the experimental conditions involved.

II. Experiments and Calculations

Prior to the iron thin film deposition on a polycrystalline ZnSe substrate ($10\times10\times5$ mm), the surface cleaning treatments were performed with 2.5% of HCl, 2% of KOH, and ethanol solutions. The samples were placed at sufficient distance (10 to 15 cm) from the evaporator to guarantee uniformity in film composition and thickness. The iron pellets were evaporated by resistively heated tungsten filament with pressure below 5×10^{-7} Torr. In order to obtain a homogeneous temperature distribution across the surface area, the samples were heated by 300 W halogen projector lamps to maintain the sample temperature at 300~350°C. For the thin film thickness, the evaporation rates were monitored by INFICON XTM/2 quartz crystal sensor. The iron thin films on the surface of ZnSe (only one side) were sealed in quartz ampoules at 10^{-5} Torr and immediately annealed at 1000°C for 24 days. The diffusion of Fe^{2+} took place mainly from the metal phase. The un-deposited substrate facet was also affected by the diffusion from the gas phase. However, the influence of gas phase by deposited iron films was minute comparing to the metal phase diffusion.

Once the samples were thermally annealed, the iron concentration gradient was studied via spatially resolved measurement of Fe^{2+} IR absorption band. The transmission measurement was estimated along with the diffused directions by using a Shimadzu UV-VIS-NIR-3101PC with a step size of 200 μm for an absorption coefficient. Since the absorption coefficient $\alpha(x,y,z,t)$ of the samples can be expressed in terms of the doped Fe^{2+} concentrations $N(x,y,z,t)$ and absorption cross-section σ as follows [1].

$$\alpha(x,y,z,t) = \sigma(\lambda)\cdot N(x,y,z,t) \quad (1)$$

where x, y, z are the positions of a host crystal and t is a diffusion time. At any given wavelength, the measured absorbance ($\log(I/I_0)$) is proportional to the molar concentration of the absorbing crystals and the thickness of the sample. Due to the surface imperfections and Fresnel reflections ($\alpha_{\text{Fresnel loss}}$), the average absorption coefficient α_{ave} was determined by using

$$\alpha_{ave.} = \frac{1}{d}\ln\left(\frac{1}{T}\right) - \alpha_{Fresnel\ loss} \quad (2)$$

where d is the thickness of the crystal and T is the transmission. Using the definition of Eqs. (1) and (2), the concentration of iron was estimated as shown in Fig. 1. Since a host crystal consisted of 5 mm thick

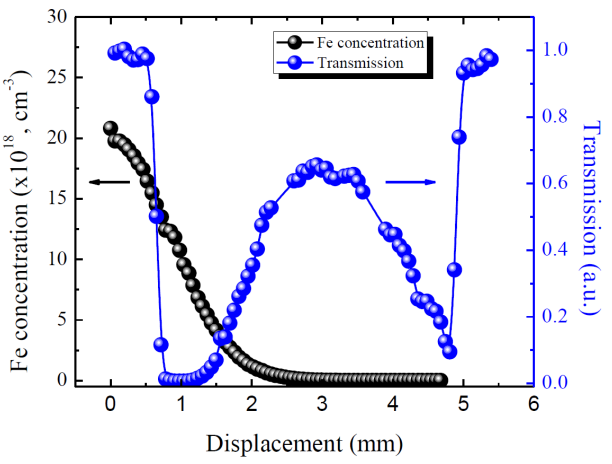

Figure 1. Transmission and Fe concentration in terms of displacement in Fe:ZnSe polycrystals.

and was maintained at ambient temperature of 1000°C for 24 days, the diffusion process of iron ions was made up to 3 mm. And the concentration of iron ions were populated in the vicinity of thin film deposited.

In data processing, the gradient of average absorption Fe:ZnSe was measured with free running 2.78 μm radiation of Cr:Er:YSGG laser (Yttrium-Scandium-Gallium Garnet crystals co-doped with chromium and erbium) as shown in Fig. 2. The Fe concentration in terms of the displacement in ZnSe was estimated for thermal diffusion parameters using Eqs. (1) and (2). The diffusion process of the transition metal ions (Fe^{2+}) in ZnSe can be described by Fick's 2nd law.

$$\frac{\partial C}{\partial t} = \nabla \cdot (D \nabla C(r,t)) \tag{3}$$

where C(r,t) is the concentration of the iron ions and D is a diffusion coefficient in ZnSe. For the estimation of the diffusion length, there were two important boundary conditions in 1-dimensional geometry in a given equation. As a host occupies the half-space which means semi-infinite media (displacement, x>0), the diffusion process has constant surface concentration, C(0). This condition is normally described in the diffusion from the gas phase as a host is annealed in the dopant vapor at constant pressure. In this case, the solution of the diffusion equation can be rewritten as

$$C(t,x) = C(0) \cdot \mathrm{erfc}\left(\frac{x}{2\sqrt{D \cdot t}}\right) \tag{4}$$

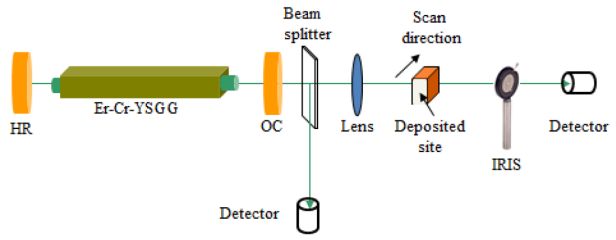

Figure 2. Cr:Er:YSGG laser setup for Fe gradient measurement.

The second condition is known as instantaneous planar source

$$C(t = 0, x) = M \cdot \delta(x) \tag{5}$$

where M denotes the number of the dopant ions per unit area. The solution of the diffusion equation from Eq. (3) can be written as

$$C(x,t) = \frac{M}{\sqrt{\pi D t}} exp\left(-\frac{x^2}{4Dt}\right) = \frac{bC_0}{\sqrt{\pi D t}} exp\left(-\frac{x^2}{4Dt}\right) \tag{6}$$

where C_0 is the concentration of iron ions in the deposited film, b is a film thickness, and t is annealing time. The diffusion length is defined by the characteristic value of $2\sqrt{Dt}$ once the diffusion coefficient D is estimated.

III. Results

Four Fe:ZnSe samples were prepared for diffusion coefficient calculations which showed Fe concentration in terms of displacement in Fig. 3. All samples were annealed in quartz ampoules at 1000°C for 24 days. The thickness of a host crystal was maintained to ~5

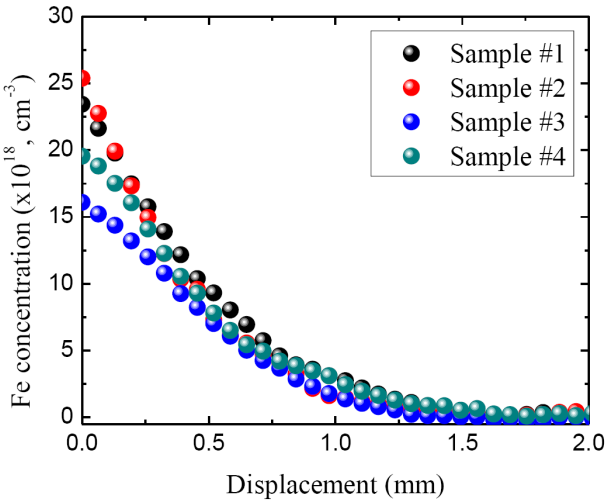

Figure 3. Four Fe:ZnSe sample for diffusion coefficient calculations.

Table 1. Estimation of the diffusion coefficients and diffusion length.

# of samples	Annealing time (hours)	Diffusion coefficient, D ($\times 10^{-9}$, cm^2/s)	Iron concentration in thin film, C_0 ($\times 10^{19}$, $atoms/cm^3$)	Diffusion length (mm)
Sample #1	576	2.12	37	1.32
Sample #2	576	2.02	37	1.29
Sample #3	576	1.96	37	1.27
Sample #4	576	2.21	37	1.35

mm and it was sufficient to avoid the influence of iron diffusion from the gas phase through the opposite crystal surface. The estimated initial concentrations of iron ions in the vicinity of thin film regions were different due to the vapor pressure during the sealing process in quartz ampoules.

Using the Eq. (6), all four samples were fitted with Mathematica and the values of D, C_0, and diffusion length were estimated as shown in Table 1. The values in Table I indicated that the surface cleaning process enhanced the diffusion of Fe ions in ZnSe and the values were consistent at the same conditions that revealed the reproducibility of high optical dense Fe:ZnSe as a mid-IR gain medium. The measured diffusion coefficient was ~2.5 times bigger than that calculated from the vapor phase diffusion experiments early reported in [1] and 100 times larger than the reports in [9] for diffusion from the gas phase.

In order to calculate the activation energy of diffusion process, the Arrhenius plots of D for four different samples as a function of annealing temperature ranges from 800 to 950°C for 7 days. Once the diffusion coefficient *D(T)* is determined, the activation energy of diffusion can be determined from the following expression,

$$D(T) = D_0 \exp\left(-\frac{E_{ac}}{K_B T}\right) \quad (7)$$

, where D_0 is diffusion coefficient for $1/T \approx 0$, E_a is the activation energy, K_B is Boltzmann constant (1.38×10^{-23} J/K≈0.695 cm^{-1}/K), and T is the annealing temperature. Using four different diffusion

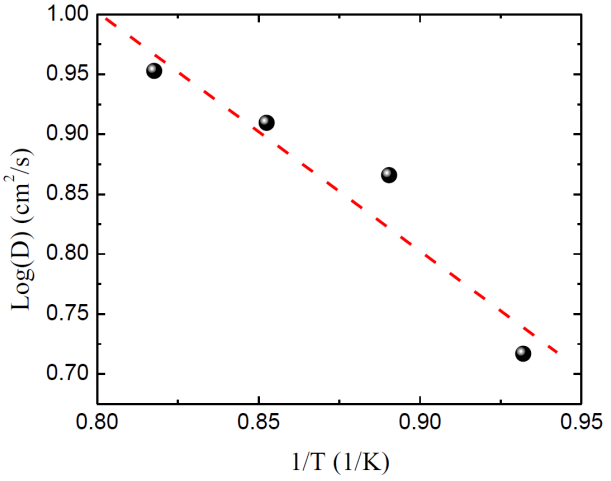

Figure 4. Arrhenius plots of D for iron in ZnSe for activation energy calculations.

coefficients (5.21 to 8.97×10^{-11} cm^2/s), the activation energy E_a for diffusion was approximately estimated as 1.39 eV for diffusion and the pre-exponential factor D_0 of 13.5 cm^2/s as shown in Fig. 4.

IV. Conclusions

We proposed new techniques of a high optical dense gain medium (Fe doped ZnSe polycrystals) diffused from metal phase by the thermal evaporation (TE) methods for the development of mid-IR laser applications. This process revealed maximum 100 times enhancement on the diffusion process in comparison to the previously reported by gas phase diffusion. One can see that the pre-cleaning of a host crystal played an important role in diffusion process. We believe that the surface pre-cleaning of ZnSe

polycrystals causes the elimination of chemical barriers and hamper Fe diffusion. In addition, the developed technology allowed us to fabricate a large highly doped laser element and homogeneous iron distribution in a host crystal.

Acknowledgements

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