

Cr²⁺ Diffusion Doping in ZnSe

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Abstract

Chromium doped zinc selenides crystals have recently been demonstrated to be a promising material for near-IR room temperature tunable lasers which has an emission range of 2-3 μm . In this study, a new diffusion doping process has been developed for incorporation of Cr²⁺ ion into ZnSe wafers. This process has been successfully performed under isothermal conditions, at temperatures above 800 degrees Celsius. Concentrations in excess of 10^{19} Cr²⁺ ions/cm³, an order of magnitude larger than previously reported in melt grown ZnSe material, have been obtained. The diffusivity was estimated to be about 10^{-8} cm²/sec using a classical diffusion model. Resistivity was derived from current-voltage measurements and in the 10^7 - 10^{16} $\Omega\text{-cm}$ and increased as function of Cr concentration.

Introduction

Recently a new class of transition metal-doped (Cr, Ni, Co) Zn chalcogenides (Se, S, Te) materials have been investigated as potential candidates as tunable solid state lasers with a spectral emission range of 1-4 μm [1,2]. Such lasers can be employed by NASA as source for Light Detection and Ranging (LIDAR) systems. The LIDAR instrument transmits light out to a target, interacts with it and changed by the target. Some of the light is reflected/scattered back to the instrument where it is analyzed. LIDAR can be used as range finders, for remote sensing of chemical species (such as ozone, water vapor and pollutants) in the atmosphere and for remote measurement of the wind velocity. The absorption and emission spectroscopic properties have been measured to evaluate their potential for room temperature operation. Notably, the emission cross section and temperature-dependent lifetimes have been measured and they indicated that chromium ion has a potentially high gain cross section and low non-radioactive decay losses resulting in a high emission quantum yield. The quantum yield efficiencies are generally approaching 100% for chromium, in contrast to nearly 20% for cobalt, while nickel exhibited no room temperature luminescence. A pump volume of 10 x 6 x 3 mm and a Cr²⁺ concentration of 1.5×10^{20} ion/cm³ are needed for a 1.63 μm (40 W, InGaAsP diode laser) pump light to be absorbed within about 100-200 μm from surface [1,2]. ZnSe has been previously doped with Cu, Ag, Ga, In, and Li for the achievement of suitable electrical properties. It has been reported that precipitation was observed for Ga[3], In[4], and Li[5] doped ZnSe. ZnSe has been doped with Cr²⁺ ion to investigate optical properties [6,7]. Based on the analysis of superhyperfine interactions with neighbors it has been reported that the chromium ion incorporated substitutionally into Zn lattice sites [8,9]. Up to date, there is little information about the usage of Cr doped ZnSe as solid state laser material and the doping process which can achieve Cr concentration as high as 10^{20} ion/cm. The motivation and scope of this work encompass the

innovative ideology of producing a high optical quality of ZnSe:Cr with Cr concentrations up to 10^{20} ion/cm³ or as needed. It is the purpose of this paper to report our efforts at Fisk University with collaboration of the laser group at LLNL in the development of this process and evaluation of its usefulness in fabrication of a **mid-IR** solid-state laser.

Theory

Many of the thermally activated processes that occur in **solids** are **diffusion** controlled, and the rate of the process is determined by the **diffusion** rate of **individual** atoms from one atomic site to another. The driving force for atomic **diffusion** is the *concentration gradient* that exists between one point and another. In practice there are two particular cases of **diffusion**, steady state and **nonsteady** state **diffusion**, and the **interdiffusion** of ZnSe and chromium is a case of **nonsteady** state **diffusion**.

Consider the **diffusion** of solute atoms along the x direction between two parallel atomic planes perpendicular to the plane of the paper and separated by a distance *a*. Suppose that the planes are of unit area and that there are N_1 solute atoms on plane (1) and N_2 solute atoms on plane (2), where $N_1 > N_2$. Here N has the units number/area. The atomic concentration of solute atoms in **number/volume** on plane (1) is $c_1 = N_1/a$ and on plane (2) is $c_2 = N_2/a$. Thus, a concentration gradient $dc/dx = (c_2 - c_1)/a$ exists along the x direction. The *net flux* of diffusing solute atoms, **J**, from plane (1) to plane (2) is

$$J = -1/2a^2r(dc/dx) = -D(dc/dx) \quad (\text{Eq. 1})$$

where the **diffusion coefficient** $D = 1/2a^2r$ and has units **cm²/sec**. This equation is known as *Fick's first law of diffusion*. The minus sign indicates that atom flow occurs in the direction of negative concentration gradient.

Now we can relate the rate of accumulation of atoms to the change in concentration with time as

$$dc/dt = J_1 - J_2/\Delta x \quad (\text{atoms/cnf-see}) \quad (\text{Eq. 2})$$

As Δx becomes **vanishingly** small, it then reduces to

$$dc/dt = D(d^2c/dx^2) \quad (\text{Eq. 3})$$

which is known as *Fick's second law of diffusion*. In physical terms this law states that the *rate of compositional change* is proportional to **the rate of change of** the concentration gradient rather than to the concentration gradient itself. The solution of **this latter** equation depends on the boundary conditions imposed by the particular problem of interest. As an example, a semi-infinite slab (dimensions large compared with the **diffusion** distance) of initial composition c_0 has, for all $t > 0$, the concentration at the $x = 0$ **interface** maintained at a value c_1 . This surface concentration is greater than the uniform initial composition of the **slab**, and consequently **diffusion** occurs into the slab (*in* the x direction) from the surface. The solution of the last equation mentioned and for the conditions described above is

$$c(x,t) - c_0/c_1 - c_0 = 1 - \text{erf}(x/2\sqrt{Dt}) \quad (\text{Eq. 4})$$

where $c(x, t)$ is the concentration at some point x in the slab at $t > 0$ and erf is the *Gaussian error function*, as tabulated in mathematical tables. Examples of the type of concentration curve predicted by this equation are shown in Fig.B. A particularly interesting aspect of this equation, and equivalently of the solutions to numerous other diffusion problems, is that $c(x, t)$ is completely described at all x and t by the error function of $(x/2\sqrt{Dt})$. This has two important consequences. First, if we are interested in a given composition, c' , then

$$c' - c_0/c_j - CO = 1 - \text{erf}(x/2\sqrt{Dt}) \quad (\text{Eq. 5})$$

is constant, and therefore

$$x/\sqrt{Dt} = \text{constant} \quad (\text{Eq. 6})$$

We solve for x and t so that the concentration of the diffusing species is equal to one-half the value at the interface $x = 0$. For these conditions

$$\text{erf}(x/2\sqrt{Dt}) = 0.5$$

And from mathematical tables

$$x/2\sqrt{Dt} = 0.5$$

or

$$x = \sqrt{Dt} \quad (\text{Eq. 7})$$

Thus, as mentioned above, this simple relationship can be used as a rough estimate of time and temperature needed to achieve appreciable diffusion or redistribution of solute atoms over a distance x . And since many other solutions to Eq. (3) also indicate that Eq. (7) can be used to predict the time required for diffusion to occur over a given distance, it is not only a very simple but also a very useful relationship.

Experimental

The diffusion doping ampoules were made from fused quartz. The cleaning processes of ampoules includes two steps: (a) the ampoules were cleaned with aqua regia (25% HNO₃ + 75% HCl) and rinsed with deionized water, (b) the ampoules were then heated at 100 °C above the diffusion temperature under 10⁻⁶ Torr vacuum. The Bridgman or seeded physical vapor transport (SPVT) grown ZnSe wafer, which were purchased from Eagle-Pitcher company, were loaded into pre-cleaned ampoule along with CrSe powder (4N grade from Alfa company). The loaded ampoule was then sealed under higher range of 10⁻⁷ Torr vacuum. The sealed ampoule (typical length of 10 cm and 1.2 cm ID) was inserted into the middle section of a 12 inches long heat pipe which provided a isotherm environment in the middle 10 inches region between 400 and 1100 °C. and the heat pipe was then placed in art one zone furnace. A schematic drawing of the experimental arrangement is shown in figure 1. Several diffusion experiments have been performed under this doping process with temperatures ranging from 800 to 1000 °C for durations of either 2 or 5 day annealing periods.

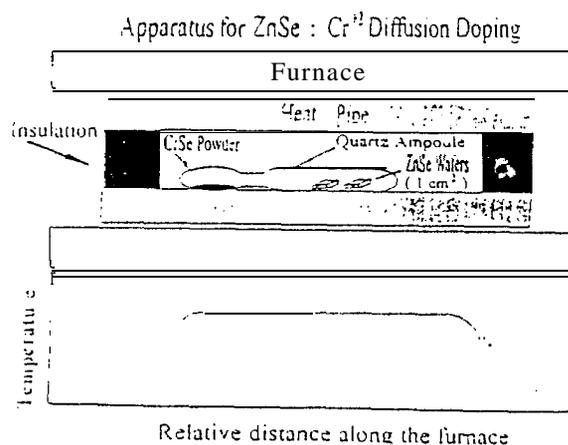


Figure 1, Experimental arrangement of diffusion doping process.

After annealing, the temperature was lowered by 5 °C/min to 400 °C, and then the furnace was shutdown and cooled to room temperature. The Cr²⁺ concentration, laser lifetime, and other optical properties were measured using optical absorption, inductively coupled plasma-mass spectroscopy, and a solid state laser testing by a solid state laser group in Lawrence Livermore National Laboratory [1,2]. Current-voltage measurement was performed at Fisk. Silver conducting paint and copper wire were used as metal contact and lead wire for connection to the I-V electronic system. A typical increment of 1 V and 1 min waiting time was used.

Results and Discussion

The following table lists the doping conditions, Cr²⁺ concentration, laser lifetime, and resistivity. The first column indicates the crystal growth method and its structural format. The first seven samples were grown by the Bridgman method and they are in the form of a polycrystalline (Poly.) and single crystalline structures with twin (Twinned).

ZnSe:Cr²⁺ Diffusion Experiment Results

Sample	Annealing Temperature (°C)	Annealing Time (days)	Concentration Cr ²⁺ (cm ⁻²)×10 ¹⁹	Lifetime (µsec)	Abs. Coeff. Cr ²⁺ (cm ⁻¹)	Abs. Coeff. Background (cm ⁻¹)	Resistivity (Ω-cm)
#12413: Bridg. Poly.	800	2	0.05	6	4.55	0.12	
#12413A: Bridg. Poly.	850	5	0.24	5	19.91	1.1	
#12429: Bridg. "twinned-top"	900	5	0.19	5	16.41	2.84	
#12429A: Bridg. Twinned-bot.	900	5	0.25		17.47	3.98	2.5×10 ⁷
#12428: Bridg. Poly.	900	5	0.18	3	11.24	6.95	6.0×10 ¹⁴
#12427: Bridg. Poly-top	950	2	0.38	2.5	26.64	4.72	2.0×10 ¹³
#12426: Bridg. Poly- bot.	950	2	0.33	3.1	20.44	2.69	8.2×10 ¹³
#12430: SPVT Single	950	1	0.17	6			9.9×10 ¹⁰
SPVT, Single	1000	5.5	1.02				1.9×10 ¹⁰

*All wafers were cut from ZnSe crystals, and purchased from Eagle-Pitcher Co.

The last two samples were **single** crystalline grown from seeded physical vapor transport method. The annealing temperature and Cr^{2+} concentration have been plotted in figure 2. For both the 2 and 5 day annealed samples, the Cr^{2+} concentration increases with annealing temperatures. This trend indicates that for 1000 °C and 5 days annealing conditions we have not reached saturation that would arise from the existence of a Cr^{2+} solubility limit in **ZnSe**. The linear least square fit lines (dashed line-2 days, solid line-5 days) seem to be fairly parallel to each other. The result proposed that the same Cr^{2+} concentration can be obtained by annealing at lower temperature for longer time as annealing at higher temperature for a shorter period of time.

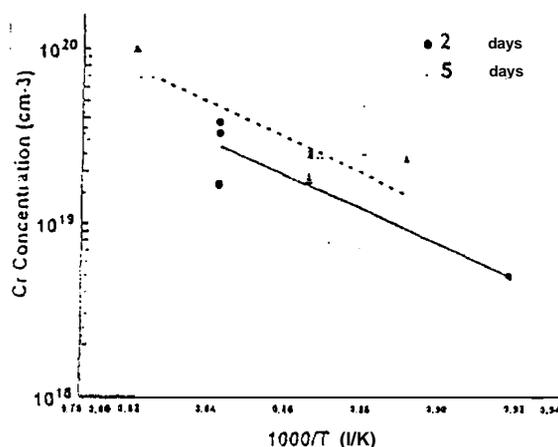


Figure 2. Plot of Cr^{2+} concentration under various annealing temperatures and times.

The possible disadvantages of high temperature annealing are the increase of the concentration of defects, such as vacancies and dislocations, and the deviation from **stoichiometry** of **ZnSe**. All samples have been polished **after** the **diffusion** doping process, and the color ranges from light reddish to darker reddish as the Cr^{2+} concentration increases. Due to the fact that the crystal growth temperature of **SPVT** grown **ZnSe** is around 1100 °C, it is a reasonable assumption that 1000 °C is very near the **limit** of annealing temperature for **SPVT** grown **ZnSe** wafer. The lifetime of single and **polycrystalline** wafer does not show a clear trend. This result maybe a good sign for industrial manufacture since that **polycrystalline ZnSe** has a much more lower production cost than single crystalline material. Figure 3 shows a **typical** I-V measurement result on the sample annealed at 1000 °C and 5 days.

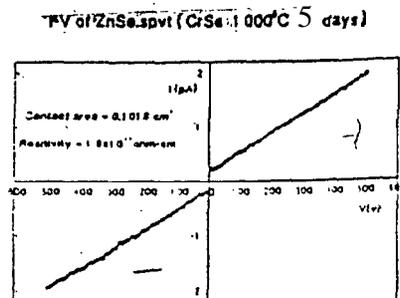


Figure 3.-4 typical I-V plot for sample annealed at 1000 °C and 5 days.

The resistance was derived from the slope of the I-V curve, and the resistivity was calculated by taking account of the contact area and thickness of the sample. The resistivity of Cr²⁺ doped ZnSe was found to be 5-8 times the order of magnitude higher than the previous undoped ZnSe. By assuming the equilibrium diffusion depth as 0.1 cm, which is deeper than the requirement to be used as solid state laser material, the diffusivity, D, can be estimated by a thin film diffusion model [10].

Summary

A new Cr²⁺ diffusion doped ZnSe process has been developed and demonstrated to yield Cr²⁺ concentrations as high as 1020 ions/cm³ which is required for tunable solid state laser material use. The crystallinity of ZnSe wafers seem to have significant influence on the Cr²⁺ concentration in this doping process. The Cr²⁺ concentration has not reached its volatility limit in the ZnSe solid solution, and it could in the future be increased by annealing at temperatures above 10000 C or at a longer time and at lower temperatures. The resistivity of doped ZnSe increases dramatically by 5-8 orders of magnitude, in the range of 10¹³ - 10¹⁶ Ω-cm compared with undoped materials. The diffusivity of Cr in ZnSe has been estimated to be in the 10-8 cm²/sec range.

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