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TITLE: Progress in Semiconductor Materials for Optoelectronic Applications Symposium held in Boston, Massachusetts on November 26-29, 2001.

Mat. Res. Soc. Symp. Proc. Vol. 692 © 2002 Materials Research Society H9.43

Development of $A^{II}B^{VI}$ Semiconductors Doped with Cr for *IR* Laser Application

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ABSTRACT

Electrical and optical measurements obtained with CdSe single crystals doped with chromium from a gas source CrSe over a wide temperature range (500-1050 °C) are compared with ZnSe annealed in liquid metal (Zn). These processes are intended to control the concentrations of the impurity and intrinsic defects. The low temperature annealing of CdSe crystals in CrSe atmosphere allows obtaining high electron mobility up to 9000 cm^2/Vs at 80 K and demonstrates the low native defect concentration. A high temperature annealing gives rise to increased electron concentration with decreased mobility. Optical absorption measurements show that at the high annealing temperature effective doping with Cr takes place. The impurity absorption beyond the absorption edge is interpreted by the excitation of Cr^{++} and Cr^{+} deep levels.

INTRODUCTION

Compact, tunable, room-temperature, solid-state laser sources operating in the mid-*IR* (1.5 – 3 μm) spectral region are of interest for a number of applications such as eye safe laser radar, chemical sensing, IR counter-measures and spectroscopy. Efficient room temperature lasing has been demonstrated with Cr^{++} active ions doped into II-VI chalcogenides such as ZnSe and CdSe [1, 2]. Transition metals incorporated into Zn(Cd)Se substitute metallic atoms and create deep levels in the band gap [3]. Only one strong emission at 2.67 eV is observed in the spectrum of the undoped ZnSe, which corresponds to the room temperature band gap energy in ZnSe. The luminescence of doped compounds exhibits two new bands near 2.2 and 1.4 eV corresponding to the photogeneration ($Cr^{++} + e_{VB} \rightarrow Cr^{+}$) and photoionization ($Cr^{+} \rightarrow Cr^{++} + e_{CB}$) processes in ZnSe. Hence the positions of Cr^{+} and Cr^{++} states were found 1.24 and 2.26 eV beneath the conduction band edge [4]. From the intensities of Cr^{+}/Cr^{++} related processes a relatively large capture cross section of the Cr^{++} ion has been deduced.

In addition to these high energy transitions, a typical room temperature absorption spectrum of CdSe:Cr^{++} reveals a peak at 1.9 μm [5] corresponding to the inter-center transition ${}^5T_2 \rightarrow {}^5E$ of Cr^{++} in CdSe [6]. Mid-infrared tunable laser media based on II-VI semiconductors doped by transition metals were demonstrated in [7] based on this transition. Tetrahedrally-coordinated Cr^{++} ions are especially attractive as laser centers on account of high luminescence quantum yields for emission in the 2-3 μm range. The strength of the emission depends on the concentration of the Cr^{++} ions in the material. In developing of a II-VI:Cr laser material we consider two questions: (a) The total amount of the Cr dopant atoms depends on the available metallic vacancies for replacement by Cr. To investigate the vacancy replacement process we studied the annealing of ZnSe crystals in Zn melt. (b) The fraction of Cr^{++} may be controlled by the free electron concentration in the crystal and its IR absorption. Annealing at different temperatures and Se vapor pressures determine the free electron concentration. In the present paper doping approached of CdSe and ZnSe crystals are investigated with the aim of optimizing the materials for laser application. CdSe was doped with Cr and compared with ZnSe crystals annealed in Zn melt. The electronic and optical properties of the crystals were characterized.

EXPERIMENTAL DETAILS

ZnSe single crystals were grown by the high-pressure Bridgman method using ZnSe powder with a purity of 6N. All samples were cut from one as-grown ZnSe single crystal and then mechanically polished so that they have the shape of wafers with dimensions about 5×5×1 mm^3. CdSe crystals were grown by the Czochralski technique. Regular X-ray diffraction was used to determine the quality of crystals. The CdSe crystals have a surface orientation <0001> and thickness ≈ 1 mm. The *n*-ZnSe samples were prepared by long-term high temperature treatment (500 - 950 °C) of the originally high ohmic ($\rho \approx 10^{10}$ Ωcm) single crystals in zinc melt. The self diffusion coefficient is $D_{Zn} = 9.8$ (cm^2/s) exp(-3 eV/kT) [8]. Increasing of the duration of the treatment of the ZnSe crystals causes the increase of the electron concentration which reach saturation after 100 hours. Diffusion of Cr from a gaseous source (CrSe) was used for doping the CdSe specimens, allowing to maintain a constant level of surface Cr concentration during a 100 hr diffusion anneal. The selenium gaseous source generates an overpressure of Se and prevents decomposition of the crystals during the heat treatment. The concentration of Cr in CdSe crystals was varied by changing the annealing temperature between 500 to 1050 °C.

DISCUSSION

The temperature dependence of the Hall coefficient R_H and the electron mobility $R_H\sigma$ (σ is the conductivity) of ZnSe:Zn samples are shown in figures 1 and 2.

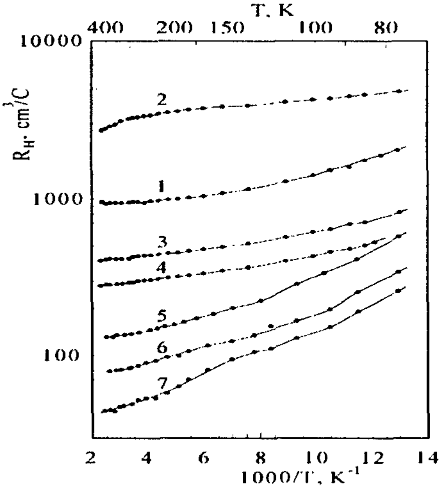

Figure 1. The temperature dependence of the Hall coefficient R_H for CdSe:Cr and ZnSe:Zn crystals annealed at different temperatures. 1- CdSe as grown, 2-4 - CdSe:Cr, 5-7 - ZnSe:Zn. Annealing temperatures: (2) 500 (3) 600, (4, 5) 700, (6) 800, (7) 950 °C.

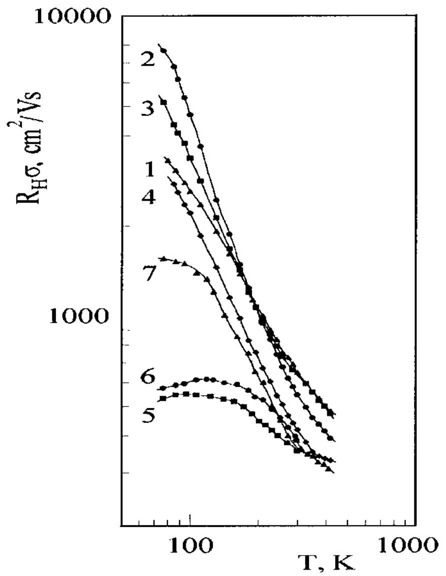

Figure 2. Hall mobility $R_H\sigma$ as a function of temperature in CdSe:Cr and ZnSe:Zn crystals. 1- CdSe as grown, 2-4 - CdSe:Cr, 5-7 - ZnSe:Zn. Annealing temperatures: (2) 500 (3) 600, (4, 5) 700, (6) 800, (7) 950 °C.

With increasing the annealing temperature, one observes increase both of the free electron concentration and of their mobility. In the low temperature range the $R_H(T)$ dependence is determined by electron activation from shallow donor states to the conduction band. The $R_H(T)$ dependence becomes weaker in the high temperature range. The donor concentration for ZnSe:Zn samples calculated by the electrical-neutrality equation reaches $N_D = 1.6\times10^{17}$ cm^{-3} as the annealing temperature increases to 950 °C. The carrier concentration and therefore the concentration of donors increases with increasing of the annealing temperature, namely, the compensation ratio decreases. With temperature decrease the mobility monotonously increases in conformity with a power law (figure 2) and has a maximum only near the liquid nitrogen temperature. This indicates a combination of phonon and ion scattering. The increase of the mobility with annealing temperature indicates the decrease of electron scattering by the charged impurity ions and is caused by a decrease of the compensation.

The temperature dependence of the Hall coefficient R_H and the Hall mobility for the CdSe:Cr samples are also shown in figures 1 and 2. The Hall mobility $R_H\sigma$ in the CdSe:Cr samples annealed at low temperature (500 °C) has a high values of 9000 cm^2/Vs at 77 K and of 520 cm^2/Vs at room temperature indicating the high perfection and purity of the crystals. In the temperature range from 77 to 400 K (figure 1), the character of the $R_H = f(10^3/T)$ dependence remains similar to the ZnSe:Zn crystals and is unchanged with varying the Cr content: the Hall coefficient decreases with increasing temperature. This is caused by the activation of electrons from shallow donors (Se vacancies). The R_H dependence becomes weaker with tendency to saturation near 400 K. Also the mobility monotonously increases in conformity with a power law, in similarity with the ZnSe crystals (figure 2).

Unlike the ZnSe:Zn crystals, the Hall coefficient and the electron mobility increase at the low treatment temperature relative to the as-grown crystal. These are explained as the result of filling of selenium vacancies by selenium from the CrSe source with a concomitant reduction of the concentration of these native defects. Doping at higher temperatures leads to a decrease of the mobility in the CdSe:Cr crystals, due to the introduction of chromium scattering centers. Indeed, the increase of chromium concentration at high doping temperatures is manifested by changes in the optical absorption.

Room temperature optical transmission near the band gap was measured for CdSe:Cr crystals annealed at different temperatures. The absorption coefficient α was calculated from the measured transmission I/I_0, by the relation:

$$I = I_0(1-R)^2 \, exp(-\alpha d),$$

where d is the thickness of the wafer and R is the wavelength dependent reflectivity [9]. Results of the calculated α as a function of the wavelength for CdSe samples annealed at different temperatures are shown in figure 3.

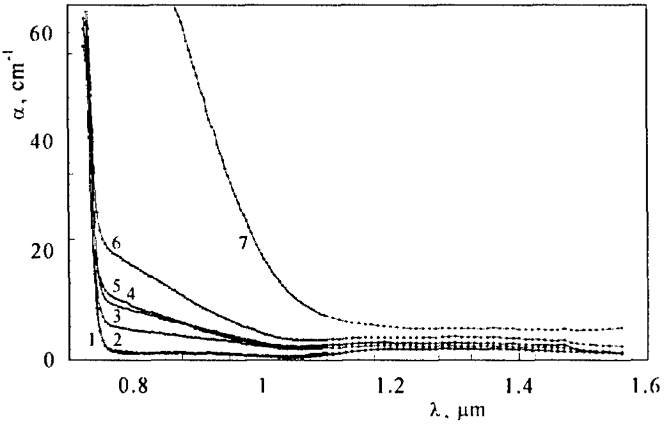

Figure 3. Optical absorption coefficient α in CdSe:Cr crystals versus wavelength for various Cr concentrations. 1- CdSe as grown, 2-7 - CdSe:Cr. Annealing temperatures: (2) 600 (3) 700, (4) 900, (5) 950 (6) 1000, (7) 1050 °C.

The doping of CdSe crystals by Cr moves the effective absorption edge to the IR range. The fundamental absorption edge does not change by doping with Cr but the absorption at energies lower than the fundamental absorption edge regularly increases with raising the annealing temperature and is remarkable after annealing at 1050 °C. This is clearly the result of the increase of Cr concentration.

CONCLUSSIONS

The principal possibility to dope CdSe single crystals by Cr from gaseous CrSe source has been demonstrated. High temperature doping is the outcome of the occupation of metallic vacancies by Cr atoms thus decreasing the acceptor Cd vacancies concentration and leaving the main influence to the shallow donor Se vacancies. In these conditions the electron concentration increases to 10^{16} cm^{-3} but the electron mobility is reduced. The doping effect on carrier concentration is similar to the annealing of ZnSe crystals in Zn melt. The introduction of Cr atoms at the high doping temperatures creates strong absorption *beyond* the fundamental edge of the absorption. The magnitude of the impurity absorption grows with increasing the chromium concentration. This absorption is interpreted by the excitation of Cr^{++} and Cr^{+} deep levels.

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