

# Growth of Cr- and Co-Doped CdSe Crystals from High-Temperature Selenium Solutions

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Transition metals in the group II-VI semiconductors have attracted considerable attention for their application as tunable mid-infrared (IR) lasers at room temperature. Very recently, Co-doped II-VI hosts have been considered as saturable absorber materials.<sup>1</sup> In the present study, we have grown both Cr-doped and Co-doped CdSe by a high-temperature solution growth technique using Se as solvent. The Cr-doped CdSe was grown in 4,000-ppm concentration. The Co-doped CdSe crystals were grown in concentrations of 2,000 ppm and 4,000 ppm. The crystals were characterized by optical-absorption spectroscopy. The absorption-peak position for Cr was 1.92  $\mu\text{m}$ , and for Co, the peak position was 1.8  $\mu\text{m}$ . The doping concentrations for Cr-doped samples were estimated from optical-absorption spectra using the Beer-Lambert law. Good-quality, crack-free single crystals were grown; however, our near-IR transmission microscopy showed Se inclusions, which were also confirmed by differential scanning calorimetry (DSC). The electrical-resistivity dependence on doping concentrations is presented and discussed. Glow discharge mass spectrometric (GDMS) measurements for the Co-doped sample are reported. The absorption cross section for Co was calculated for the first time using the Beer-Lambert law.

**Key words:** II-VI semiconductor, optical transmission, electrical resistivity, glow discharge mass spectrometric (GDMS), Beer-Lambert law, mid-infrared solid-state laser

## INTRODUCTION

Several studies on CdSe have demonstrated its optical, electrical, and photoelectrochemical properties. Cadmium selenide has also been used for several applications in thin-film and quantum-dots technologies. However, a potential new class of lasers tunable in the mid-infrared (IR) spectral region is being developed based on CdSe doped with transition metals.<sup>2</sup> Other II-VI materials, such as ZnSe and ZnS doped with transition metals, have demonstrated room-temperature laser action in the 2–3- $\mu\text{m}$  spectral region.<sup>3,4</sup>

In this report, CdSe doped with Cr and Co transition metals were grown separately from a high-temperature selenium solution. The crystals were characterized using optical-absorption spectroscopy, optical-transmission microscopy, and differential scanning calorimetry (DSC). From optical-absorption spec-

troscopy, the concentration of the chromium ions and its effective segregation coefficient were calculated. The optical-transmission microscopy and the DSC measurements were carried out for the investigation of the presence of Se precipitates. Current-voltage (I-V) measurements were performed on the Co-doped CdSe samples for the 2,000-ppm and 4000-ppm concentration. Glow discharge mass spectrometric (GDMS) measurement was performed on the CdSe doped with Co to measure the concentration of Co. The result of the concentration of Co was used to find the absorption cross section for the Co-doped CdSe sample.

## EXPERIMENTAL PROCEDURE

### Growth of Cr<sup>2+</sup>:CdSe and Co<sup>2+</sup>:CdSe from High-Temperature Selenium Solution

Chromium selenide and cobalt selenide of 95.5% purity from Alfa Aesar (Ward Hill, MA) and CdSe reagent of 99.999% purity purchased from Alfa

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Aesar were used as the starting materials for both growths. Sublimation under a dynamic vacuum was performed on the CdSe-starting materials using a prebaked quartz ampoule. The Cr-doped CdSe was grown in a 4000-ppm concentration. The Co-doped CdSe crystals were grown in concentrations of 2,000 ppm and 4,000 ppm. For the Cr<sup>2+</sup>:CdSe growth, the mixture of the starting materials (CdSe plus CrSe) was placed on top of selenium inside an ampoule. Selenium served as the solvent that helped to dissolve the CdSe and reduced the growth temperature for CdSe. The quartz ampoule (12-mm inner diameter and 14-mm outer diameter) had a conical tip where the crystal starts growing (crystal-nucleation site). The ampoule was sealed under a vacuum of  $2 \times 10^{-7}$  torr. The sealed ampoule was placed inside a two-zone vertical furnace with its conical tip located at the 3°C/cm temperature-gradient region. The temperature of the furnace was slowly (0.83°C/min) raised to 1,200°C and allowed to stabilize for 120 h. The temperature was slowly (0.052°C/min) reduced to 1,080°C and stabilized at that level for 3 days. The temperature was further lowered (0.05°C/min) to 1,050°C and kept centered there for 1 day. It was slowly dropped down to 830°C at 0.07°C/min and stabilized for 2 days. At a cooling ramp of 0.28°C/min, it was brought to 427°C and stabilized for 1 day. Finally, the temperature was lowered to room temperature at 0.26°C/min. The crystallization took place during the slow cooling process. The ingots were single crystal except the Se-rich region. The Co-doped crystals were grown from the selenium solution by the vertical-Bridgman technique.

The ingots are removed from the ampoule and cut into wafers perpendicular to their growth axis. A diamond-coated wire saw was used for this purpose. The samples were then mechanically polished using a microcloth and an alumina-suspension, 0.05- $\mu$ m abrasive from Buehler (Lake Bluff, IL). After polishing the wafers, the wafers were later cleaned with pure trichloroethylene and methanol. Optical-absorption spectroscopy was performed on the wafers using a Cary (Varian, Inc.) 500 spectrophotometer operating from mid-IR to ultraviolet spectral region.

Optical-transmission microscopy was performed to investigate the presence of elemental precipitates (Se) along the ingots. The optical-transmission-microscopy images were acquired via a charge-coupled device camera connected to the computer for capturing and processing images. A differential scanning calorimeter (TA Instruments (U.S.A.) DSC model 2010) was further used to confirm the previous observations. The DSC measurements, with sample weights ranging from 32–40 mg, were performed from room temperature to 300°C at a rate of 10°C/min.

Prior to I-V measurements, an etching solution of bromine methanol was used on the samples to remove the damaged layer caused by the previous

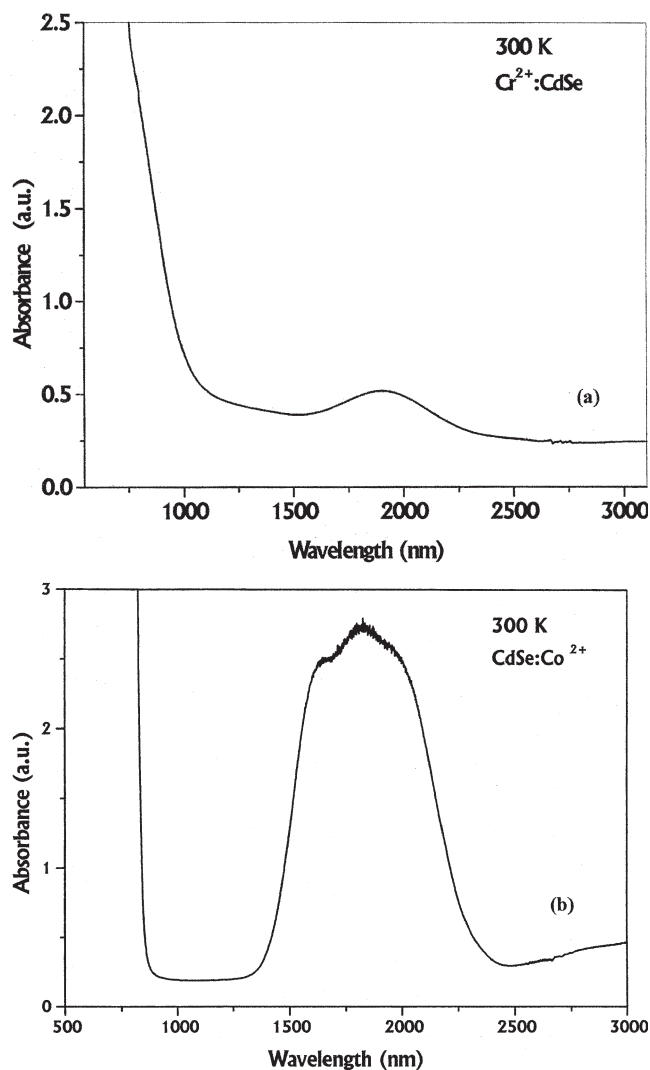


Fig. 1. The room-temperature optical-absorption spectrum for doped samples of CdSe (a) CdSe:Cr<sup>2+</sup> and (b) CdSe:Co<sup>2+</sup>.

mechanical polishing. Gold-electrical contacts, deposited by a sputtering technique, were subsequently applied. Thin (0.001 in.) Pd leads were attached using a graphite suspension in water (“aquadag” from Acheson Inc. (Bridgewater, MA)). The contacts were covered with a protective coating (“Humiseal” from Chase Corp.) to isolate them from the ambient and to improve the mechanical stability of the electrical contact.

A programmable Keithley (U.S.A.) high-voltage power supply (KI 237) was used for applying bias to the sample and measuring the resulting current flowing through the sample. Both forward and reversed bias voltages were applied.

## RESULTS AND DISCUSSION

Chromium in CdSe mostly substitutes for Cd. The second-oxidized state of chromium ions (Cr<sup>2+</sup>) is responsible for the absorption band (1.6–2.2 μm) of Cr<sup>2+</sup>:CdSe. An optical-absorption spectrum at room temperature in the 400–3,200-nm spectral region is given in Fig. 1a. Zunger reports that the peak at

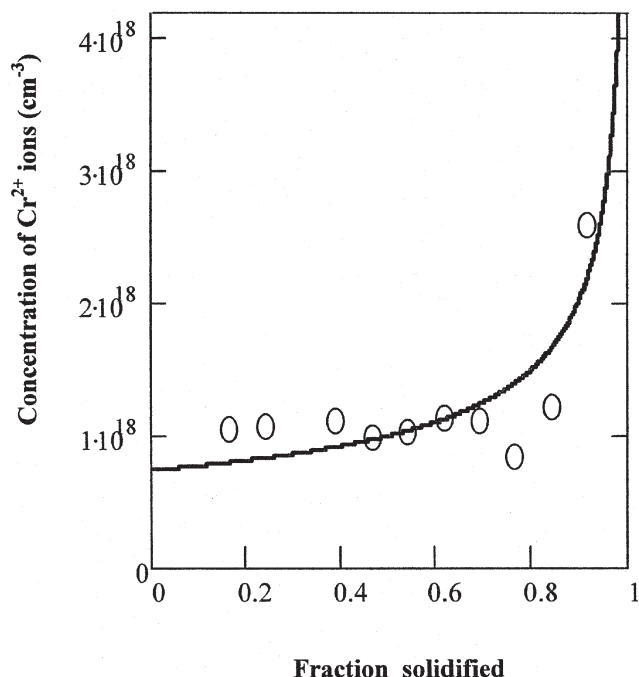


Fig. 2. The axial distribution of Cr<sup>2+</sup> ions in the Cr<sup>2+</sup>:CdSe ingot. The circles are data obtained from optical-absorption spectra. The solid line corresponds to the normal freezing model (Eq. 2).

1.92 μm corresponds to the intracenter transition (<sup>5</sup>T<sub>2</sub> → <sup>5</sup>E) of Cr<sup>2+</sup> in CdSe.<sup>5</sup> Similarly, the cobalt in CdSe mostly substitutes for the Cd, and the second-oxidized state of cobalt ions (divalent Co) is responsible for the (1.4–2.4 μm) absorption band of the Co<sup>2+</sup>:CdSe. The optical-absorption spectrum at room temperature in the 400–3,200-nm spectral region is given in Fig. 1b.

The average Cr<sup>2+</sup> concentration was calculated using the Beer-Lambert law from the optical-absorption spectrum, as shown in Fig. 2.

The following relation was used:

$$A = \frac{\delta \times C \times \sigma_a}{\ln(10)} \quad (1)$$

where A is the absorbance, δ is the sample's thickness, and σ<sub>a</sub> and C are, respectively, the absorption cross section and the concentration of the absorbing species. The absorption cross section for Cr<sup>2+</sup> in CdSe (σ<sub>a</sub>) used was 3 × 10<sup>-18</sup> cm<sup>2</sup>.<sup>6</sup>

The concentration of Co determined from GDMS measurement was 0.2 at.% for the sample whose corresponding optical absorption is in Fig. 1b. The value of the concentration of the absorbing species was then applied to Eq. 1 to calculate the absorption cross section of Co and was found to be 1.21 × 10<sup>-18</sup> cm<sup>2</sup>. The concentration of the absorbing species for Cr ions was calculated using the maximum height of the absorption peak at 1.92 μm for Cr, with the value of σ<sub>a</sub> taken from the literature.

The distribution of Cr<sup>2+</sup> ions along the ingot depends on the experimental conditions and the growth techniques. Ndap et al.<sup>6</sup> have reported a decrease of the concentration of Cr<sup>2+</sup> ions from the

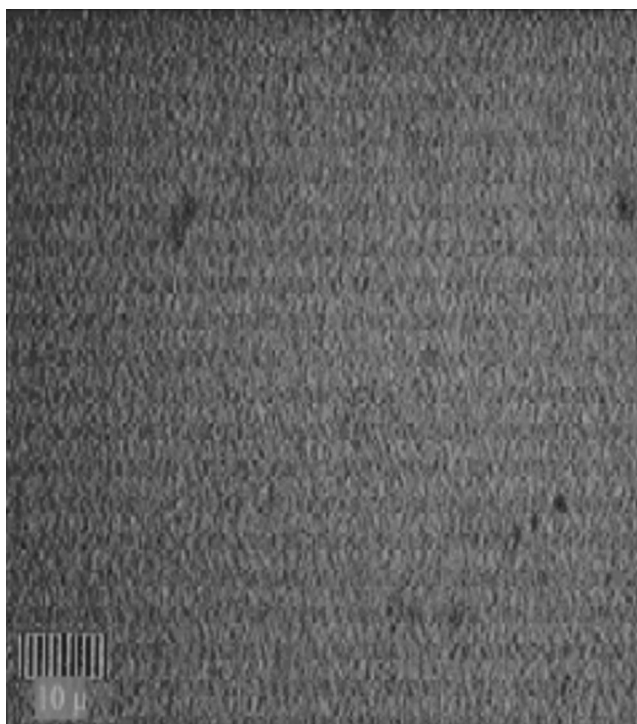
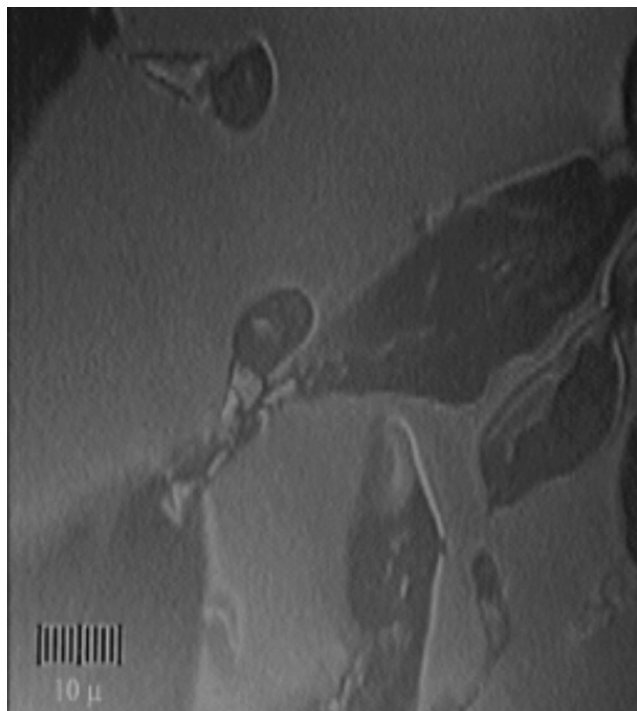


Fig. 3. The optical-transmission micrograph of (a) Cr-doped CdSe and (b) Co-doped CdSe crystals.

first-to-freeze to the last-to-freeze regions of the ingot covering the 1 × 10<sup>18</sup>–1.5 × 10<sup>17</sup> cm<sup>-3</sup> range. In this study, we observed in Fig. 2 that the concentration of the Cr<sup>2+</sup> increases from the first-to-freeze to the last-to-freeze regions of the ingot covering the 2.9 × 10<sup>18</sup>–8.63 × 10<sup>18</sup> cm<sup>-3</sup> range. This result suggests that the effective-segregation coefficient of Cr<sup>2+</sup> here is less than 1.

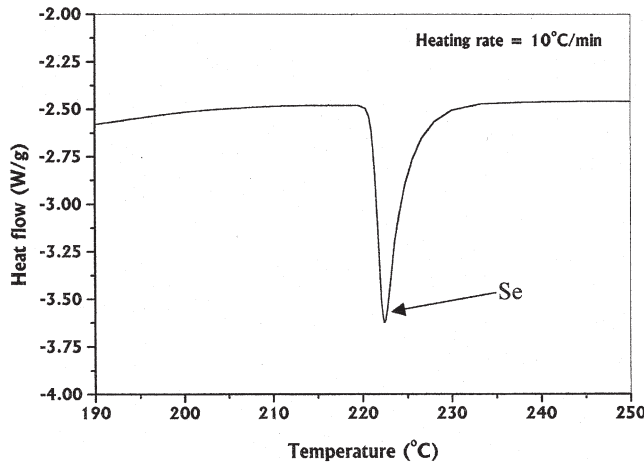


Fig. 4. The result of the DSC plot for the Co-doped CdSe sample.

Using the trend of the axial variation of  $\text{Cr}^{2+}$  ions observed, following the normal freezing model, Eq. 2 was used to calculate an effective segregation.

$$C(g) = C_o K_{\text{eff}} \times (1 - g)^{k_{\text{eff}} - 1} \quad (2)$$

where  $C$  is the initial concentration,  $k_{\text{eff}}$  is the effective segregation, and  $g$  is the fraction solidified. From the model for an initial concentration,  $C_o = 1.32 \times 10^{18} \text{ cm}^{-3}$  and  $k_{\text{eff}} = 0.55$  were obtained.

Figure 3a and b shows optical-transmission micrographs of two wafers of CdSe doped with different transition metals, Cr and Co, respectively.

In order to identify the precipitates observed in the transmission microscopy, a DSC measurement was performed. Figure 4 shows a variation of the heat flow measured in one of the samples as a function of the temperature (heating rate of  $10^\circ\text{C}/\text{min}$ ). From the endothermic peak, one can evaluate the melting point of selenium ( $221^\circ\text{C}$ ) as well as the energy necessary in melting it. The peak at  $221^\circ\text{C}$  confirms the presence of selenium in the grown crystals.

The resistivities for the Co-doped CdSe samples were found to be  $5.14 \text{ } \Omega\text{cm}$  and  $30.1 \text{ } \Omega\text{cm}$  for the 4,000-ppm and 2,000-ppm concentrations, respectively. These values are low when compared to the resistivity value reported earlier by Ndap et al.<sup>6</sup> for the Cr-doped CdSe sample.

## CONCLUSIONS

Good-quality Cr-doped and Co-doped CdSe were successfully grown. The crystals were crack free with the occasional presence of Se impurity. The absorption cross section for Co was calculated to be  $1.21 \times 10^{-18} \text{ cm}^2$ . The effective segregation for Cr ions obtained was 0.55. The resistivity increases after Cr doping, while Co doping reduces the resistivity drastically.

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## REFERENCES

1. T.-Y. Tsai and M. Birnbaum, *J. Appl. Phys.* 87, 25 (2000).
2. J. McKay and K.L. Schepler, *Opt. Lett.* 24, 1575 (1999).
3. R.H. Page, L.D. Deloach, G.D. Wilke, S.A. Payne, and W.F. Krupke, *IEEE J. Quantum Electron.* 32, 885 (1996).
4. K.J. Schaffers, R.H. Page, L.D. Deloach, G.D. Wilke, F.D. Patel, J.B. Tassano, S.A. Payne, W.F. Krupke, K.T. Chen, and A. Burger, *IEEE J. Quantum Electron.* 33, 609 (1997).
5. A. Zunger, *Solid State Phys.* 39, 275 (1986).
6. J.-O. Ndap, O.O. Adetunji, K. Chattopadhyay, C.I. Rablau, S.U. Egarievwe, X. Ma, S. Morgan, and A. Burger, *J. Cryst. Growth* 211, 290 (2000).