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PREPARATION AND OPTICAL PROPERTIES OF ZnSe:Co FILMS

ZnSe:Co films were obtained by vacuum deposition. Optical density spectra in the region of 4-0.38eV are investigated. It is established, that in ZnSe:Co films, as compared to ZnSe films, the absorption edge is displaced to the lower energy region. The analogy of ZnSe:Co films and crystals optical absorption spectra is established. The investigated lines of ZnSe:Co films absorption are caused by electronic optical transitions from Co^{2+} ion basic condition level $^4A_2(F)$ on the excited states $^4T_1(P)$, $^4T_1(F)$ and $^4T_2(F)$ levels splitted with spin-orbit interaction.

1. INTRODUCTION

ZnSe is the perspective material for fabrication of injection electroluminescent structures and lasers which emit in blue spectral region. The possibility of this material use for creation of emission structures in the infra-red (IR) spectral region is shown last years. Doping of ZnSe with transition elements (Fe, Ni, Co, Cr) is carried out for this purpose. We suggest also a method of Co diffusion doping of ZnSe single crystals and their optical properties are investigated [1,2].

However, for fabrication of IR-region emitting structures, the film structures are most appropriate. The purpose of this study is to develope the technology of ZnSe:Co films preparation and to investigate their optical properties.

2. EXPERIMENTAL

ZnSe:Co films were obtained by vacuum deposition on quartz substrates. Crushed ZnSe:Co crystals with known cobalt concentration were used as a source. Technology of ZnSe:Co crystals preparation is described in [1]. The source temperature was no less than 1600°C during evaporation. At lower temperatures there was no evaporation of Co atoms and the undoped ZnSe films was obtained. The films thickness was in the range 5-10mkm. Obtained films had a dark grey color.

With the purpose of Co impurity activation and structure crystallization, obtained films were annealed in He and Ar atmosphere. Use of inert atmosphere hindered the films sublimation. The optimum annealing temperature was 650°C and duration of 5 hours was chosen. The lower annealing temperature hasn't led to impurity activation and film structure crystallization. Intensive films sublimation at higher temperatures was registered. After annealing the ZnSe:Co films became dark-brown. Such color was caused by the initial ZnSe:Co crystals. Estimation of the highest cobalt concentration was determined by comparison of optical absorption spectra with present data [1]. The highest concentration of cobalt in the obtained films is estimated as $10^{18}cm^{-3}$.

For comparison, the undoped ZnSe films were obtained by similar method. As a source the undoped ZnSe crystals were used in this case.

The spectra of optical density were measured by the SF-46 diffraction spectrophotometer working within the range 4.1-1.0 eV, and MDR-6 monochromator with diffraction grating of 600 and 325 grooves/mm. The first of devices was used to analyze absorption spectra within energy range 1.2-0.6eV (middle-1 IR-region), and the second – in an interval 0.6-0.4eV (middle-2 IR-region). As the recorder of light intensity in middle IR-region PbS photoresistor was used working in the mode of alternating current recording. The optical density spectra were measured at 77 and 293K.

The obtained results of ZnSe:Co films optical density measurements were compared to the results obtained for the ZnSe:Co crystals, which were used as a source for films deposition.

3. DISCUSSION

Optical-density spectra of ZnSe:Co films

The optical density spectra of ZnSe:Co and ZnSe films in the absorption edge region are investigated. The absorption spectra of undoped ZnSe films are characterized by absorption edge on 2.66eV at T=300K. Doping with cobalt results in the shift of absorption edge to the lower energy region. This shift is enlarged by cobalt concentration increase. A similar shift is observed in the ZnSe:Co crystals. The reason of absorption edge displacement in the lower energy region most, probably caused, by formation of $Zn_{1-x}Co_xSe$ solid solution.

It is established that at temperature decrease to 77K the absorption edge of the investigated films is displaced to the larger energies region by 0.11eV. The magnitude of this shift corresponds to a temperature-induced variation of the ZnSe band gap.

In the near-IR spectrum of the ZnSe:Co films the broad absorption band at 1.65eV appears (Fig. 1, curve 1). After annealing in He and Ar atmosphere the sharp series of optical absorption lines at 1.64, 1.71 and 1.78eV (Fig. 1, curve 2) appear. A similar lines were observed before in ZnSe:Co crystals (Fig. 1, curve 3). They are caused by electrons transitions from $^4A_2(F)$ basic state to splitted levels of $^4T_1(P)$ excited state of Co^{2+}_{Zn} ion. Appearance of absorption lines series after annealing could be explained by cobalt

diffusion in zinc sublattice that is confirmed by color films change.

In middle-IR region the characteristic absorption in two ranges was observed. In higher energy region ZnSe:Co films spectra were characterized by two relatively broad lines at 0.83 and 0.76 eV (Fig. 1, curve 1). The position of these absorption lines did not change with film temperature. After annealing in He and Ar atmosphere these lines as absorption lines in near-IR region become sharper (Fig. 1, curve 2). Similar absorption lines were observed in ZnSe:Co crystals (Fig. 1, curve 3). In accordance with [3], the absorption line at 0.76eV corresponds to intracenter transition from the basic state $^4A_2(F)$ to the excited $^4T_1(F)$ state splitted by spin-orbital interaction. The presence of line at 0.83eV is caused by splitting of excited state level due to spin-orbital interaction.

In the lower energy range of middle-IR region in the optical absorption spectra of ZnSe:Co films, like the absorption spectra of ZnSe:Co crystals there is the resonance absorption line at 0.43eV (Fig. 1). In accordance with [3], this line is caused by the transitions $^4A_2(F) \rightarrow {}^4T_2(F)$ between basic $^4A_2(F)$ and the nearest excited state $^4T_1(F)$.

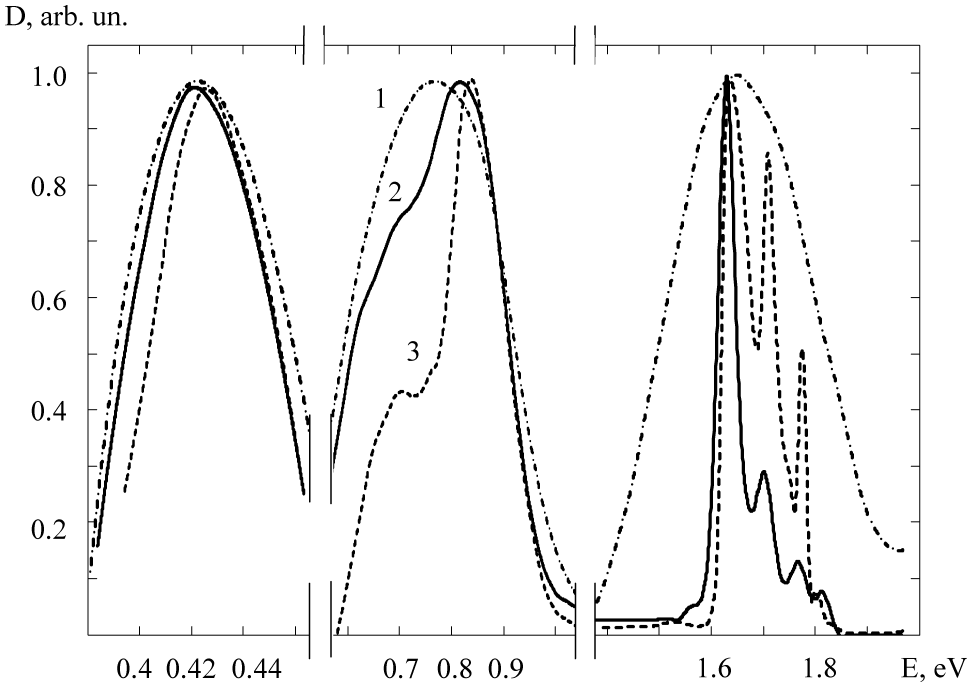

Fig. 1. Absorption spectra of ZnSe:Co films (1), (2) and crystals (3). T=77K. (Explanation in the text)

It should be noted that in undoped ZnSe films neither before nor after annealing in He and Ar atmosphere the analogous features of the absorption spectra in IR-region was not observed.

4. CONCLUSION

The studies carried out allow us to conclude the following:

1. The method of ZnSe:Co films preparation has been developed. The highest cobalt concentration in the obtained films is estimated as $10^{18}cm^{-3}$.

2. It is established that films annealing in He and Ar atmosphere results in the arrangement of films crystalline structure and effective embuilding of cobalt atoms in to zinc sublattice.

3. It is shown that observed ZnSe:Co films absorption lines are caused by electrons optical transitions from Co^{2+} ion basic state $^4A_2(F)$ level to the excited states $^4T_1(P)$, $^4T_1(F)$ and $^4T_2(F)$ levels splitted by spin-orbital interaction.

4. The present work showed indicate the absence substantial distinctions in the optical absorption spectra of films and crystals ZnSe:Co, what allows to use these films for IR spectral region structures creation.

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ZnSe:Co films were obtained by vacuum deposition. An optical density spectra in the region of 4-0.38eV are investigated. It is established, that in ZnSe:Co films, as compared to ZnSe films, the absorption edge is displaced in lower energy region. Analogy of ZnSe:Co films and crystals optical absorption spectra is established. The investigated lines of ZnSe:Co films absorption are caused by electrons optical transitions from Co^{2+} ion basic condition level $^4A_2(F)$ on the excited states $^4T_1(P)$, $^4T_1(F)$ and $^4T_2(F)$ levels split with spin-orbit interaction.

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ПОЛУЧЕНИЕ И ОПТИЧЕСКИЕ СВОЙСТВА ПЛЕНОК ZnSe:Co

Пленки ZnSe:Co были получены путем термического напыления в вакууме. Исследованы спектры оптической плотности в области 4-0.38эВ. Установлено, что в пленках ZnSe:Co, по сравнению с пленками ZnSe, край поглощения смещается в низкоэнергетическую область. Установлена аналогия спектров оптического поглощения пленок и кристаллов ZnSe:Co. Исследуемые линии поглощения в пленках ZnSe:Co объясняются оптическими переходами электронов с уровня основного состояния $^4A_2(F)$ иона Co^{2+} на расщепленные спин-орбитальным взаимодействием уровни возбужденных состояний $^4T_1(P)$, $^4T_1(F)$ и $^4T_2(F)$.

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ОТРИМАННЯ І ОПТИЧНІ ВЛАСТИВОСТІ ПЛІВОК ZnSe:Co

Плівки ZnSe:Co були отримані шляхом термічного напилення в вакуумі. Досліджені спектри оптичної густини в області 4-0.38еВ. Встановлено, що в плівках ZnSe:Co, в порівнянні з плівками ZnSe, край поглинання зміщується в низькоенергетичну область. Встановлена аналогія спектрів оптичного поглинання плівок і кристалів ZnSe:Co. Досліджені лінії поглинання плівок ZnSe:Co пояснюються оптичними переходами електронів з рівня основного стану $^4A_2(F)$ іона Co^{2+} на розщеплені спін-орбітальною взаємодією рівні збуджених станів $^4T_1(P)$, $^4T_1(F)$ и $^4T_2(F)$.