

HYDROGEN INTERCALATION IN InSe AND GaSe SEMICONDUCTORS

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In the temperature range 77 to 293 K the transmission spectra in the range of excitonic absorption were investigated for InSe and GaSe intercalated with hydrogen. It was found that the concentration dependences of the $n = 1$ exciton maximum energy $E_{exc}(x)$ and excitonic band half-width $\Delta H(x)$ are non-monotonous. The $E_{exc}(x)$ and $\Delta H(x)$ dependences for H_x InSe and H_x GaSe hydrogen intercalates were explained starting from the known influence of the deformations induced by intercalation on the reconstruction of the energy spectrum of layered crystals. There was found that insertion of hydrogen into InSe is reversible. Thermally stimulated deintercalation of hydrogen from insertion compounds H_x InSe ($0 < x \leq 2$) is also investigated. It was established that for H_x InSe samples the hydrogen deintercalation degree gradually increases with x from 63 % ($x \approx 0.02$) to 78 % ($x \approx 2.0$)

(Received July 10, 2003; accepted August 21, 2003)

Keywords: Layered crystal, Intercalation, Hydrogen intercalate, Exciton

1. Introduction

As established before [1,2], layered semiconductors InSe and GaSe can be intercalated with hydrogen. Hydrogen intercalates of indium and gallium monoselenides are appropriate objects for basic studies and prospective for solutions to applied problems (electrodes for fuel cells, hydrogen accumulators) [3]. At the initial stage of investigation the possibility to insert hydrogen into layered single crystals InSe and GaSe was proved as well as phase-thermodynamic characteristics of the obtained intercalates [1]. Identification of the hydrogen inserted into the semiconductors InSe and GaSe was carried out by the chemical method [1] and by the nuclear magnetic resonance [2]. Later, the changes of kinetic and optical properties of indium and gallium monoselenides caused by hydrogen intercalation were studied.

In this paper we present the investigation of transmission spectra for InSe and GaSe intercalated with hydrogen measured in the range of their excitonic absorption. Intercalation – deintercalation processes in hydrogen intercalates of InSe were also investigated.

2. Experimental

Our investigations were carried out on InSe and GaSe single crystals grown by the Bridgman method as well as for their intercalates H_x InSe ($0 < x \leq 2$) and H_x GaSe ($0 < x \leq 1$). Here x is the amount of inserted ions per the formula unit. The samples for investigations were cleaved from the ingots with a razor blade. The intercalation with hydrogen was performed electrochemically by means of the method of “drawing” electrical field [1, 2] in galvanostatic conditions from a 0.1 N aqueous solutions of hydrochloric acid using a P-5827 M potentiostat. At cathodic polarization of InSe and GaSe samples a current flowing through the electrochemical cell inserts protons into bulk of these crystals. The concentration of the inserted impurity has been determined from the amount of

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electricity, which was carried through the electrochemical cell, i.e. the electrical current density and duration of the intercalation are its checking parameters. The influence of the amount of inserted hydrogen on the properties of indium and gallium monoselenides was studied. Homogeneous intercalates have been obtained by using a low current density (below $10 \mu\text{A}/\text{cm}^2$).

The transmission spectra measurements have been performed on samples of 10 to 20 μm thickness. These spectra were measured in a IKS-31 spectrometer. The spectral resolution was between 0.8 and 1.2 meV for the investigated spectral ranges, 2.095 - 2.14 eV for H_xGaSe and 0.8 - 1.2 eV for H_xInSe . A light beam was directed along the C axis of the samples. In the temperature range 77 to 300 K the dependences on temperature of the transmission spectra were measured by using a temperature controlled cryostat system UTREKS – RTR giving a stabilized temperature with an accuracy of 0.5 °C.

3. Results and discussion

The spectral location of the $n = 1$ excitonic maximum and its half-width depending on concentration of the inserted impurity were investigated for H_xGaSe intercalates in the temperature range 77 – 300 K and for H_xInSe at $T = 77$ K. In the case of H_xGaSe intercalates the room temperature concentration dependences of the excitonic maximum energy E_{exc} and the excitonic band half-width ΔH have a non-monotonous behaviour (Fig. 1). At increasing x up to the values of about 0.4 both these parameters increase. At higher values of x the opposite behaviour of the $E_{\text{exc}}(x)$ and $\Delta H(x)$ curves takes place. As one can see from the spectra measured at $T = 77$ K (Fig. 2), intercalation with hydrogen leads to the shift of the excitonic maximum energy and the broadening of the excitonic absorption band. Note that the energy location and half-width of the excitonic maximum depend on the amount of the intercalant: in the range $0.1 < x < 0.35$ the $E_{\text{exc}}(x)$ and $\Delta H(x)$ curves have constant values.

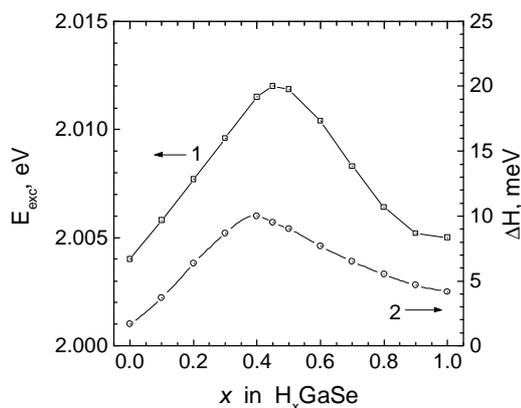


Fig. 1. Concentration dependences of the excitonic ($n=1$) maximum E_{exc} (1) and half-width ΔH of the excitonic band (2) for H_xGaSe at $T=293$ K.

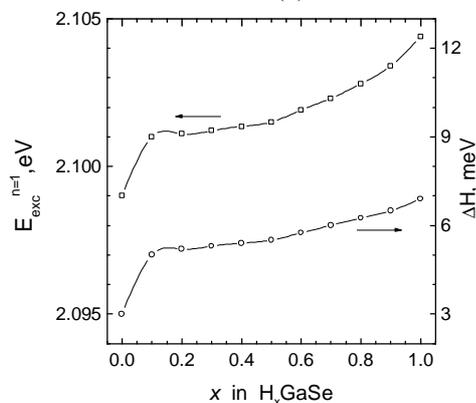


Fig. 2. Concentration dependences of the excitonic ($n=1$) maximum E_{exc} (1) and half-width ΔH of the excitonic band (2) for H_xGaSe at $T=77$ K.

Starting from the transmission spectra temperature investigations we have determined the temperature coefficients of the $n=1$ excitonic maximum shift dE_{exc}/dT and the change of the excitonic band half-width $d\Delta H/dT$ for both initial and intercalated GaSe (Table 1). They are in good agreement to the literature data [4, 5].

Table 1. Temperature coefficients of the parameters of excitonic absorption band.

Compound	dE_{exc}/dT , eV/deg.	$d\Delta H/dT$, eV/deg.
GaSe	-4.7×10^{-4}	4.0×10^{-5}
$H_x\text{GaSe}$	-5.0×10^{-4}	4.5×10^{-6}

The shift of the excitonic peak energy at 293 K can be caused by a change of the GaSe energy gap E_g and the exciton binding energy in the course of intercalation. Taking into account the peculiarities of the GaSe crystalline structure, one can point out that the contributions of the corresponding deformations (within separate layers and between them) into modification of the GaSe band structure can be changed in different ways at hydrogen intercalation. At increasing deformation tensions caused by different factors, in particular, by the increase of intercalant density, the values of the elastic constants, which characterize the bonding between hydrogen atoms inside a separate layer, grow more slowly than those between the layers [6]. The excitonic peak shift to higher energies by 7 meV (Fig. 1) at a hydrogen content $0 < x \leq 0.4$ takes place due to interlayer changes of the elastic constants what leads, according to [6, 7], to an increase of the energy gap E_g and exciton binding energy E_{exc} in $H_{x \leq 0.4}\text{GaSe}$ intercalates. As in Ref. [10], it can be explained by a change of the effective mass during intercalation. Starting from the experimental data (Fig. 1) the first factor prevails another. In the general case the E_g variation is a result of competitive contributions of inter- and intralayer deformations having the opposite signs of the deformations potentials. The opposite shift of the $E_{\text{exc}}(x)$ dependence at $x > 0.4$ can be induced by several factors, namely: i) a change of the interlayer elastic constants leading, according to [6, 7], to decreasing E_g in intercalated crystals, ii) a variation of the exciton binding energy during intercalation, preferably due to effective mass changes, iii) the band-to-band transitions with a participation of the density-of-states tail, iv) fluctuations of the energy gap edges affected by a “random” field of the inserted impurity.

The $E_{\text{exc}}(x)$ dependence at 77 K can be explained taking additionally into account the results of our previous investigations of $H_x\text{GaSe}$ intercalates by the method of proton magnetic resonance [2]. It was established that at $T \approx 140$ K the transition of a mobile phase of intercalated hydrogen to a bound one took place for $0.45 < x < 1$. As the bound phase we imply a state of hydrogen inserted into the structure of a separate layer whereas in the mobile phase it is localized in interlayer spaces of intercalates. It is worth to point out that in the mobile phase the coupling of hydrogen atoms and the orientation of H_2 molecules along the C axis take place. So, the observed difference in the behavior of the $E_{\text{exc}}(x)$ curves at 77 and 293 K is, probably, caused by the fact that at $T \leq 140$ K and $0.45 < x < 1$ the change of the elastic constants between the layers is more essential. It can be caused by the ordering of H_2 molecules in the GaSe Van der Waals gaps.

As inserted into GaSe crystals the intercalant atoms are distributed randomly, the potential relief in $H_x\text{GaSe}$ is more essential than in the initial crystals. It affects scattering of excitons [9] and the exciton radius becomes lower. These factors lead to the increase of ΔH in the ranges $0 < x \leq 0.4$ ($T = 293$ K) and $0 < x \leq 0.1$ ($T = 77$ K). To understand the difference between the $\Delta H(x)$ curves measured at 293 and 77 K, it is necessary to take into account such the factors as i) the existence of “rigidly fixed” and quasi-free states of the intercalant in the GaSe crystal lattice [10] and ii) the formation at $T \leq 140$ K of proton pairs H_2 located in Van der Waals gaps of the intercalates at $x \leq 0.45$.

At $T = 77$ K we have also investigated the excitonic maximum spectral location depending on inserted impurity amount for hydrogen intercalates $H_x\text{InSe}$ ($0 < x \leq 2.0$). As follows from Fig. 3, the $E_{\text{exc}}(x)$ dependence can be schematically divided by three parts: (i) the range of the increase of E_{exc} from the value 1.3275 eV for as-grown InSe to 1.3320 eV for $\text{H}_{0.5}\text{InSe}$ intercalate, (ii) the range of the

gradual decrease of E_{exc} to the value of 1.3295 eV in the range $0.5 < x \leq 1.0$, and (iii) the range of a approximately constant value of E_{exc} of about 1.3295 eV at $1.0 < x \leq 2.0$. Starting from the above-described experimental data for H_xInSe intercalates ($0 < x \leq 2.0$), the concentration $E_{\text{exc}}(x)$ dependence can be explained as follows. The shift of the excitonic peak energy to the high-energy range by 4.5 meV (Fig. 3) in the range of a hydrogen content $0 < x \leq 0.5$ is caused by a variation of the interlayer elastic constants what leads, according to [6, 7], to the fact that in $\text{H}_{x < 0.5}\text{InSe}$ intercalates the increase of the energy gap E_g prevails the exciton binding energy. The opposite behaviour of the $E_{\text{exc}}(x)$ dependence takes place due to the same factors as for H_xGaSe intercalates. The constant value $E_{\text{exc}} = 1.3295$ eV observed in the hydrogen concentration range $1.0 < x \leq 2.0$ means that the competitive contributions from the first and second ranges are approximately the same.

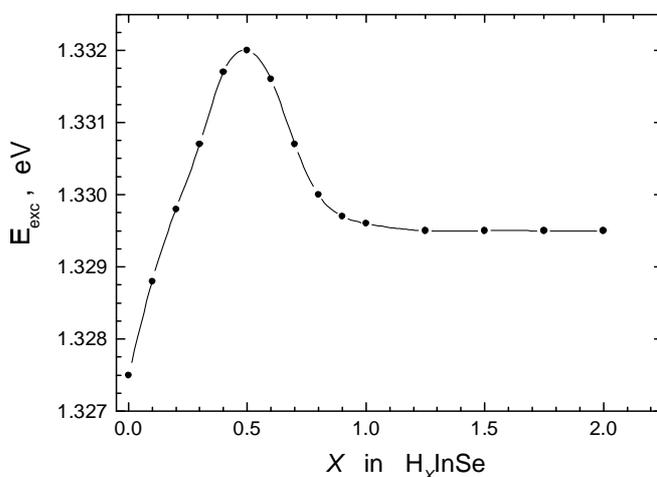


Fig. 3. Concentration dependence of the energy location of excitonic maximum E_{exc} for hydrogen intercalate H_xInSe at $T = 77$ K.

In Refs. [3, 11] it was established that layered InSe could be used as a hydrogen accumulator. Here we investigate the reversibility of hydrogen insertion into InSe. The process of thermally stimulated deintercalation of the inserted hydrogen from the insertion compounds H_xInSe has been carried out using their thermal treatment at a temperature 110°C during 3 to 9 hours at simultaneous pumping out. Registering a deintercalation degree after the thermal treatment was done by means of the comparison between the “standard” (for a not thermally treated sample) concentration dependence of the excitonic peak energy at $T = 77$ K and those for thermally treated samples H_xInSe ($0.02 \leq x \leq 2.0$), i.e. undergone to thermally stimulated deintercalation. Fig. 4 shows the concentration dependence of the reversibility of hydrogen insertion for H_xInSe after a thermal treatment during 6 h. As it follows from this plot, the deintercalation degree gradually increases with increasing x from 63 % at $x \approx 0.02$ to 78 % at $x \approx 2.0$. In order to explain the concentration dependences of the hydrogen insertion reversibility $N(x)$ for H_xInSe , it is necessary to take into account that the intercalant in the crystal-matrix exists in bound and quasi-free states [10]. It was established [12], that for hydrogen intercalates of layered GaSe the bound state took place only at $x > 2$. In order to understand the abrupt increase of N , especially in the range $x > 1.25$, it is necessary to take into account the spectra of proton magnetic resonance for hydrogen intercalates of layered semiconductors [13]. They indicate that the quasi-free intercalant, existing in the Van der Waals gaps, consists of “quasi-liquid” and “viscous” hydrogen films. It leads, probably, to more intensive deintercalation of hydrogen from InSe in the range $1.5 < x \leq 2.0$.

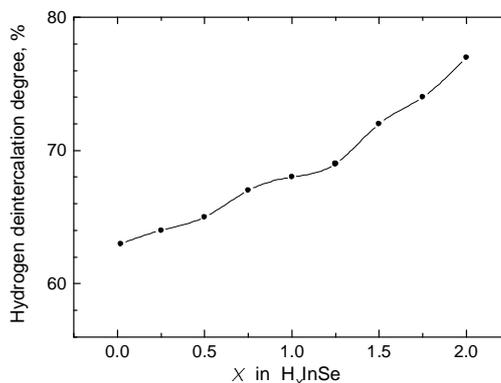


Fig. 4. Concentration dependence of hydrogen insertion reversibility for H_xInSe . Duration of thermal treatment is 6 h.

4. Conclusion

Hydrogen intercalates based on layered semiconductors InSe and GaSe represent a new kind of hydrogen insertion compounds. The investigation of InSe and GaSe based hydrogen intercalates shows the appearance of new effects caused by hydrogen insertion and are important for possible applications.

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