EXCITONIC AND RADIATIVE EFFECTS IN GaSe-C_{60} STRUCTURES

I. Evtodiev, P. Lozovanu, E. Cuculescu, M. Caraman

Faculty of Physics, Moldova State University, 60, A. Mateevici str., MD-2009, Chisinau, Republic of Moldova
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Abstract

The absorption and photoluminescence spectra of GaSe intercalated in C_{60} fullerene has been investigated at 293 K and 78 K. C_{60} and C_{60}-toluene molecules intercalated in-between GaSe stratified "packing" cause the appearance of localized levels revealed in low energy wing of n=1 excitonic of the absorption and determine the exciton-phonon interaction. It has been established that C_{60} and C_{60}-toluene molecules form new recombination levels in GaSe crystals and determine the 1.7÷1.75 eV photoluminescence band.

1. Introduction

The Gallium Selenide (GaSe) crystallizes in hexagonal lattice as layers, Ga and Se atomic planes being oriented perpendicular to C_6 axis. The atomic layers form "stratified packings" of Se-Ga-Ga-Se type. The bonds between stratified "packings" are of polarization origin (van der Waals), while the bonds inside a "packing" are predominantly covalent. This peculiarity of gallium monoselenide structure allows the localization of impurity atoms and molecules in the space between "packings". The valence bonds are practically closed at the surface of stratified "packings"; thus, the intercalation of atoms and molecules of different nature contributes to formation of new bonds between chalcogen planes. So, the electrons energetic spectrum is modified as well.

Considering that the C_{60} molecule diameter of ~ 14 Å [1] is much bigger than the covalent radia of Ga and Se of 1.26 Å and 1.16 Å, respectively, the C_{60} molecules can be localized predominantly in the space between "stratified packings" (chalcogen planes) bonded by polarizational forces. This configuration can result in formation of new valence bonds and, as a consequence, to changes in the electronic states structure in GaSe crystals. The thickness of the "stratified packings" is equal to "*c*" parameter of the crystalline lattice, allowing fabrication of nanostructures on the basis of stratified single crystals. Note that insular nanostructures on the basis of GaSe/MoS_2 and InSe/MoS_2 heterojunctions have been manufactured by molecular beam epitaxy [2].

Some optical properties of the GaSe crystals intercalated with C_{60} molecules by diffusion from C_{60}-toluene and vapor phase are analyzed in this paper.

2. Experimental

The GaSe compound has been synthesized of elementary components Ga (99.9998) and Se (99.99). The GaSe single crystals have been grown by Bridgman method. In order to diminish the probability of material contamination, GaSe single crystals have been obtained within a single synthesis cycle – single crystal growth.

The material intercalated with C_{60} fullerene has been obtained by burning the pure spectral graphite electrodes in electric arch in Ar+He atmosphere.

The material purification has been carried by double sublimation at ~ 610 K. It was used the saturate C_{60}-toluene solution as well.

The 2÷2.5 cm^2 GaSe plates with thicknesses in the range of 2÷2.5 mm have been obtained by cleavage of GaSe single crystals. The intercalation of GaSe plates with C_{60} has been realized by two methods namely from C_{60}-toluene solution and from C_{60} vapor phase. The first method consisted of GaSe plates dipping in C_{60}-toluene solution for ~ 280 hours at constant temperature of + 48 °C. The solution temperature was stabilized with ± 2 °C precision. Then, the samples have been dried in vacuum at +65 °C for 48 hours. The vapor phase intercalation has been realized for GaSe plates with the thicknesses of 1.5÷2 mm and 1÷1.5 cm^2. GaSe together with an amount of 0.3÷0.5 g mixture of fullerene, nanotubes, and graphite with a composition of 28-32% of C_{60} have been placed in quartz ampoules. The ampoules have been pumped down to 10^{-5} mm Hg and annealed for 24 hours at ~ 680 K. The ampoules volume did not exceed 15 cm^3. The average thickness of GaSe plates annealed in C_{60}-toluene solution and dried in vacuum increased by 12.5%, while the thickness of the plates annealed in C_{60} vapors increased by ~ 9%. A comparison treatment of GaSe in Ar ambient has been carried out. After a 24 hours annealing step, the plate thickness increased by ~ 3 %. The intercalation process was followed by the cleavage of the GaSe plates into thinner ones, thickness varying from 12 μm up to 300 μm, for optical transmission measurements.

The optical transmission T and reflection have been measured at 78 K and 293 K by use of a Specord M40 spectrophotometer. The photoluminescence measurements have been carried out on a spectrophotometric device based on grating monochromator (600 mm^{-1}). For low temperature measurements (78 K) the samples have been placed in an optical transparent cryostat in liquid nitrogen vapors.

3. Results and discussion

The GaSe single crystal intrinsic absorption band edge is localized at 1.95÷2.00 eV at 293 K. As one can see in Fig. 1, the absorption coefficient exponentially decreases together with the energy within wide range of absorption coefficients: by more than 2 degrees of magnitude.

The figure offers for comparison the spectral dependence of absorption coefficient for primary GaSe crystals. A linear dependence $lg\alpha=f(\hbar\omega)$ is seen for a quite large limits of absorption coefficients: $(2\div1,5)\cdot10^3$ cm^{-1} for primary GaSe samples. As one can see from this figure (curves 1 and 2), the GaSe plates treatment in C_{60}-toluene solution modifies the aspect of the $\alpha=f(h\nu)$ function for low values of the

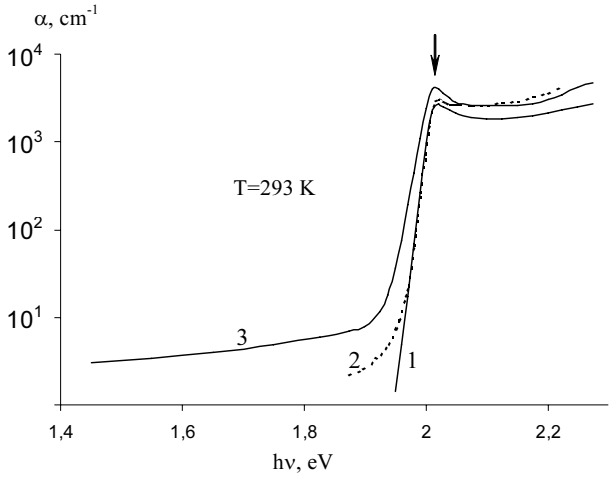


Figure 1. The absorption spectra at 293 K for primary ε-GaSe (curve 1), C_{60}-intercalated from C_{60}-toluene single crystals (curve 2) and from C_{60} vapors (curve 3)

absorption coefficient ($\alpha \leq 20$ cm^{-1}) (curves 1 and 2). Curves 1 and 2 practically coincide for absorption coefficients in the range of 20 cm^{-1} up to ~10^3 cm^{-1}. Taking into account that the exponential dependence of the absorption coefficient on energy in the fundamental absorption band is determined by the exciton-phonon interaction mechanism [3] and, by its means, with structural defects, one can conclude that through diffusion of the C_{60}-toluene solution in the space between the stratified "packings" of Se-Ga-Ga-Se type, localized states appear in the vicinity of the valence band maximum of GaSe crystals; this procedure does not change the type of majority of charge carriers (holes).

The constant of the exciton-phonon interaction increases in GaSe crystals annealed in C_{60} vapors (curve 3). At the same time, it is obvious that, as a result of this technologic procedure, a wide spectrum of localized states is formed. The latter determines the wing of the absorption band for energies $h\nu$<1.93 eV (curve 3, Fig. 1).

In such a way, the C_{60} carbon molecules, having dimensions larger (>10 times) than the metal (Ga) covalent radius, are predominantly localized in-between layers and, as a result, multilayered structures of C_{60}-Se-Ga-Ga-Se-C_{60}-Se-Ga-Ga-Se-C_{60}-... type are formed.

The temperature decreases from 293 K down to 78 K (Fig. 2); this leads to excitonic band formation. A well known structure [4] of the absorption band edge is obtained for primary crystals with two absorption bands for n=1 ($\hbar\omega_{n=1}$ = 2.099 eV) and n=2 ($\hbar\omega_{n=2}$=2.113 eV) (curve 1, Fig. 2). As one can see in Fig. 2 (curves 2 and 3), in the C_{60} and C_{60}-toluene intercalated crystals the n=2 band is not revealed. At the same time, the absorption coefficient for the n=1 excitonic maximum decreases. The presence of the C_{60} and C_{60}-toluene molecules in GaSe is revealed by the decrease of the absorption coefficient relative to initial crystals for $h\nu$<2.099 eV at 78 K and $h\nu$<1.93 eV at 293 K. The stronger absorption is revealed for the crystals for which the C_{60} molecules diffused at ~ 680 K from the vapour phase.

The photoluminescence (PL) spectra for the GaSe crystals with C_{60} (curve 3), C_{60}-toluene (curve 2) as for comparison

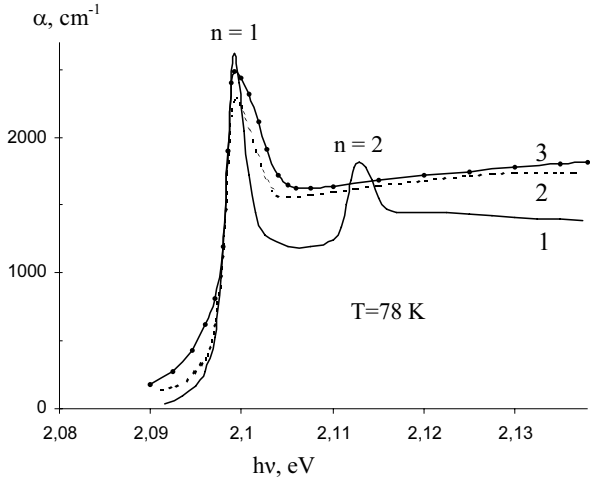


Figure 2. The absorption spectra of primary ε-GaSe single crystals (curve 1), C_{60}-intercalated from C_{60}-toluene (curve 2) and from C_{60} vapours (curve 3) at 78 K

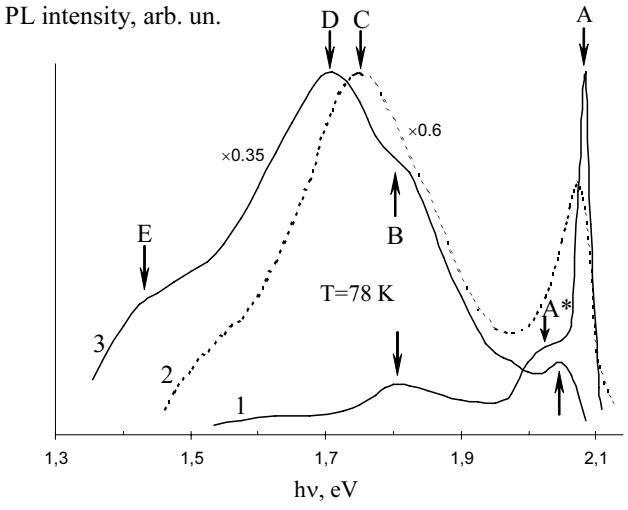


Figure 3. The photoluminesence spectra of primary GaSe single crystals (curve 1), C_{60}-intercalated from C_{60}-toluene (curve 2) and from C_{60} vapors (curve 3) at 78 K

with GaSe primary crystals (curve 1) are presented in Fig. 3. As it can be seen (curve 1), the photoluminescence in GaSe crystals at T=78 K is dominated by exciton emissional anihilation $h\nu_{max}$=2.085 eV (band A). At the same time, the band A*, originating from D-A transitions ($h\nu$=2.01 eV), is highlighted and a broader, much weaker band with peak energy at 1.8 eV, appears. As it has been shown in [5], the excess of Ga atoms in GaSe leads to formation of a new impurity PL band with peak energy at ~ 1.78÷1.80 eV. As one can easily observe from Fig. 3 (curves 2 and 3), a PL band is found in this energetic interval for GaSe crystals, in which the C_{60} molecules have been intercalated by diffusion. Thus, the C_{60} carbon molecules do not modify the structure of the PL bands determined by the defects in the metals sublattice, inside a stratified "packing", and, so, the specific of the absorption spectra; that is, absorption in the $h\nu$<1.95 eV at 293 K and $h\nu$<2.099 eV at 78 K energy range is determined by the C_{60} carbon molecules, localized in the space between the stratified "packing".

The PL spectrum for GaSe intercalated with fullerene from C_{60}-toluene solution has a more complex structure. So, in the fundamental edge region a photoluminescence band is highlighted due to, probably, weakly bound excitons ($h\nu_{max}$=2.075 eV). The binding energy is ~ 15 meV. This PL band is superimposed with the D-A recombination band. As a result of the superposition, an asymmetrical band is formed, with a powerful extension to lower energies.

In GaSe (C_{60}-toluene), the rate of emissional electronic transitions ocures by means of C-band with maximum at 1.75 eV, which extends to ~1.45 eV. A ~ 30 meV shift to lower energies of the edge band maxima (band A) in the PL spectra of the GaSe with C_{60} crystals is observed at the same time. The intensity of this band is up to 0.1 of the intensity of excitonic PL band in primary crystals. So, the C_{60} molecules intercalated in-between "stratified packings" form localized states, which screen the electron-hole bands; the average distance between electron and hole is 60 Å.

The maximum intensity of the PL in the GaSe (C_{60}) crystals is localized at ~ 1.7 eV (peak D) and is shifted relative to C-peak ~ 50 meV to lower energies. One can clearly see a PL band in the lower energy region with peak intensity at ~ 1.43 eV (peak E). The E-band (curve 3, Fig. 3) is superimposed with an intense band D. As a consequence, the maximum of the D band is shifted to lower energies. As it has been mentioned, the diffusion of the C_{60} molecules takes place at ~ 680 K, but as it has been shown in [6], as a result of thermal annealing, emission energetic states are formed in GaSe crystals, which results in formation of a broad emissional band in this spectral region.

It is known [7] that the structure of the electron energetic states is revealed by reflection bands. The reflection spectra for GaSe(C_{60}) (curve 1), GaSe (C_{60}-toluene) (curve 2), and for comparison GaSe primary crystals (curve 3) are given in Fig. 4.

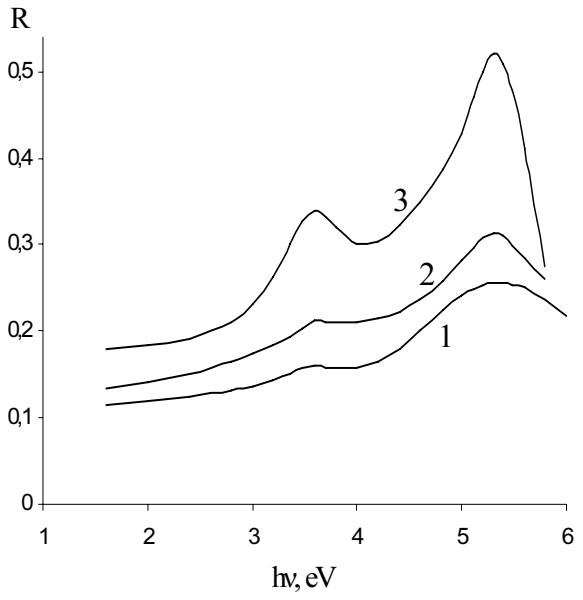


Figure 4. The reflection spectral dependency for primary GaSe single crystals (curve 1), C_{60}-intercalated from C_{60}-toluene (curve 2) and from C_{60} vapours (curve 3) at 293 K.

As one can see from this figure, C_{60} intercalation causes the reflection band intensity decrease. This fact is expected due to the structure of this spectrum, being determined by the lattice field inside a "stratified packing", and the presence of impurity molecules in the space between "packings" does not form new valence bands, which can influence the energetic spectrum of electrons in these crystals.

4. Conclusions

The C_{60} molecules have been intercalated into GaSe crystals by thermal diffusion.

The C_{60} and C_{60}-toluene molecules intercalated in the space between "stratified packings" create localized levels, form low energy wings of the n=1 excitonic bands, and determine the exciton phonon interaction mechanism.

The C_{60} and C_{60}-toluene molecules form new recombination levels in GaSe crystals, which determine the appearance of the 1.7÷1.75 eV PL bands.

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