FIZICĂ ŞI TEHNICĂ: Procese, modele, experimente, nr. 2, 2012
CZU: 621.311.592

PHOTOLUMINESCENCE OF NANOLAMELAR STRUCTURES WITH METAL DOTS OBTAINED BY GaS MONOCRYSTAL INTERCALATION

Caraman Iu.[1], Stamate M.[1], Evtodiev S.[2*], Untila D.[2], Luchian E.[3]
[1]"Vasile Alecsandri" University of Bacau, 157, Calea Marasesti, Bacau, 600115, Romania
[2]Moldova State University, 60, Alexei Mateevici str., Chisinau, MD-2009, Republic of Moldova
[*]e-mail: ievtodiev@yahoo.com

In this work are studied photoluminescence (PL) spectra from *GaS* crystals and *GaS* crystals intercalated with *Zn* and *Cd* atoms. Metal atoms were intercalated by 6 hours heat tratament at the temperature of 750 K in metal vapor atmosphere. Gallium dots are created on external surface and between *S-Ga-Ga-S* packages. This dots are aranged as distorted hexagons. *Zn* intercalation leads to formation of two PL bands with maximum at 2.12 eV and 2.84 eV, energyes. PL spectra of *Cd* intercalated crystals containes one simple contour band at 293 K, and two bands at 78 K. Band with maximum at 2.424 eV has a complex structure, composed by fononic repeats of indirect excitons emission.
Keywords: *GaS*, single crystals, intercalation, photoluminescence, thermal treatment.

În lucrare sunt studiate spectrele de fotoluminescenţă (FL) a cristalelor de *GaS* şi *GaS* intercalat cu atomi de *Zn*, şi *Cd*. Intercalarea cu *Zn*, şi *Cd*, a lamelor de *GaS* s-a efectuat prin tratament termic la temperatura 750 K, timp de 6 ore, în atmosferă de vapori ai metalului. Pe suprafaţa exterioară şi în spaţiul dintre împachetările *S-Ga-Ga-S* se formează puncte de *Ga*, aranjate preponderent sub formă de hexagoane deformate. Intercalarea cu *Zn* conduce la formarea a două benzi de FL cu maxim la 2,12 eV şi, respectiv, 2,84 eV. Spectrul de FL a cristalelor *GaS* intercalate cu *Cd* conţine o bandă cu contur simplu la temperatura T=293 K; şi două benzi la T=78 K. Banda cu maxim la 2,424 eV are structura compusă din repetări fononice ale emisiei excitonilor indirecţi.
Cuvinte-cheie: GaS, monocristale, intercalare, fotoluminescență, tratament termic.

INTRODUCTION

GaS compound is a *n* type semiconductor, with large band gap. The conduction band absolute minimum is localized on *M* point of Brillouin zone. Because valence band maximum is localized in the center of the Brillouin zone, *GaS* is a tipical semiconductor with an indirect band gap. Reserchers are interested in this material because it has optical and electrical properties making it a perspective material for optico-electronical devices in UV and visible spectra region [1-3]. Practical utilization posibility is strong related to the problem of absorbtion and emission properties control. These properties depends on impurity levels' energy localized in the band gap. Impurity levels' caracteristics can be established from photoluminescence and light absorbtion measures in undoped and doped crystals with various chemical elements. In undoped crystals by means of electrical and photoelectrical properties measures impurity levels'energies, localized at 0,17 eV, 0,45 eV, 0,56 eV have been determined [4]. The *n* and *p-GaS* crystals PL occures by donor-acceptor recombination. At low temperatures (78 K), in *n* type samples three bands are differentiated: two with low intensity, at 2,22 eV and 2,02 eV, and one intensive band at 1,59 eV [5]. *GaS* crystals doping with elements from I, II, V groupes (*Cu*, *Zn*, *P*) leads to formation of new PL bands. So, in *Zn* doped crystals, in absorption band edge region, at the same time with emission bands of indirect excitons with fonon emission at 2,510 eV, 2,550 eV, 2,534 eV, 2,521 eV, 2,480 eV, one band in red-orange region, with maximum at 1,55 eV can be observed. This band can be interpreted as emission from acceptor-vacantion complex center [6, 7]. Also, formation of recombination PL centers, by vacance-acceptor type, who emits a large PL band, with maximum at 2,12 eV takes place. I_2 molecules form deep donor levels (0,44 eV) in *GaS* crystals. *GaS* compound cristallizes as layerd packages of *S-Ga-Ga-S* type. Valence bond at packages' surface are closed. This ensures a low density of surface states. The chemical bonds betwen packages are weak, this permits intercalation of different nature atoms and molecules between *S* atoms plans, which in some conditions (concentration, temperature) forms new valence bonds. In this work PL from *GaS* lamella in wich were obtained metal dots complex structures, by intercalation with *Cd* and *Zn* atoms are studied.

EXPERIMENTAL METHOD

GaS monocrystals were grown by Bridgman method, from elementary components *Ga* (5 N) and *S* (5 N) taken in stoichiometrical quantities. From massive crystals, plates of 0,1...0,5 mm thickness, and 3÷5 cm^2 surface were cleaved. *GaS* plates together with *Zn* (*Cd*), taken in 5 % quantity of *GaS* plate weight, were introduced in SiO_2 ampulla, which were welded after air evacuation (remanent presure ~ $5 \cdot 10^{-6}$ Torr). *Cd* (*Zn*) atoms diffusion process occurs 6 hours at ~ 750 K. Metal vapors pressure at this temperature was ~ 10 mm col. Hg, for *Cd*, and ~ 2 mm col. Hg, for *Zn*.

Primary crystals had *n* type conductibility. In result of heat tratament in *Cd*, and *Zn*, vapors conductivity type has changed in *p*. Electrons concentration in undoped *GaS*, measured at 420 K, was $5 \cdot 10^{13}$ cm^{-3}. PL was measured from 78 K to 300 K. Sample temperature was measured with a T type thermocouple. PL activation was performed with *He*-N_2 laser radiation (λ=337,4 nm; average power ~ 100 mWt). Laser radiation intensity could be attenuated by ~ 30 times, using neutral filtres. PL spectra from perpendicular surface to *C* axis, were analized with МДР-2 monochromator with 600 mm^{-1} difraction grating and registred with a ФЭУ-59 photomultiplier with multialkalin cathode.

EXPERIMENTAL RESULTS

In Fig. 1 AFM image of *GaS* lamella (0001) surface, treated in *Zn* vapors at the temperature of ~750 K 30 min (a) and 6 h (b) (*Zn* concentration was ~2 mg/cm^3) is shown.

In this figure, liquid points can be clearly observed at the temperature of 303 K. Because *Zn* and his *S* and *Ga* solutions have a highest melting temperature, this points can be interpreted as *Ga* liquid points. As it can be seen, *Ga* nodes have ~10 nm dimension. Metal points are arranged in hexagones.

It can be observed that this spectrum is composed of 2 bands. The first band localized in the fundamental band region has low intensity. This band is composed from two subbands at less, with maximum at 2,49 eV and 2,52 eV.

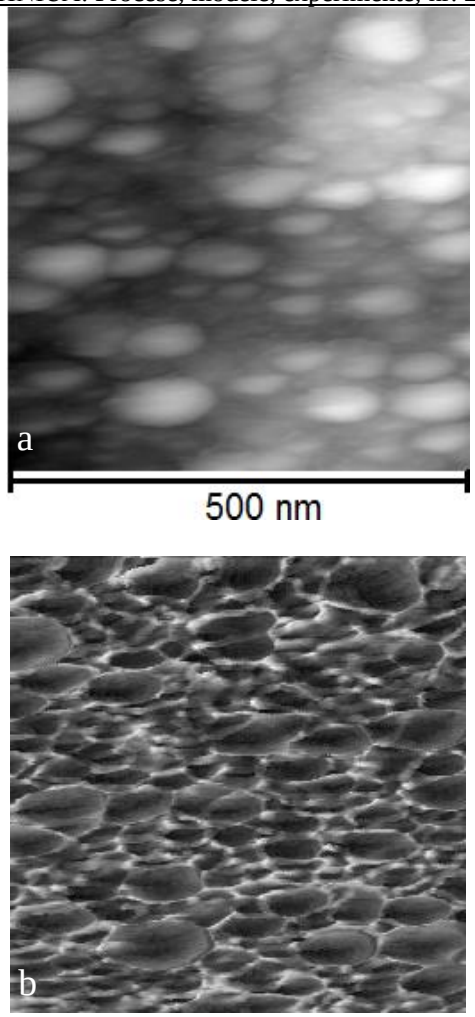

Fig. 1. AFM image of (0001) *GaS* lamella surface, treated in *Zn* vapors, at the temperature of ~750K, 30 min (a) and 6 h (b).

In Fig. 2, *GaS* lamella PL spectrum (at the temperature of 78 K) before *Zn* vapor tratament, is shown.

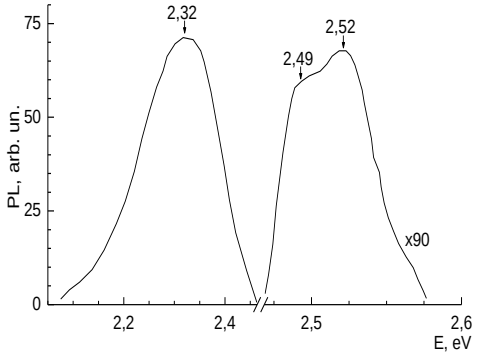

Fig. 2. *GaS* lamella PL specter, at the 78 K temperature.

This band presence is associated to radiative transitions with indirect exciton participation, with ~30 meV energy bond. The second band, has medium intensity. This band is located in the yellow-orange region, with maximum at 2,32 eV. This band is determined by distorsional defects presence, atomar planes

and *S-Ga-Ga-S* packages sliding. As a result of this distorsions acceptor type centers are formed, localized near *S*-donor centers.

In Fig. 3 micrometrical lamella heat treated (in *Zn* vapors, at ~ 2 mm col. Hg presure) PL spectra at chamber temperature (curve 1) and at 78 K (curve 2) are shown.

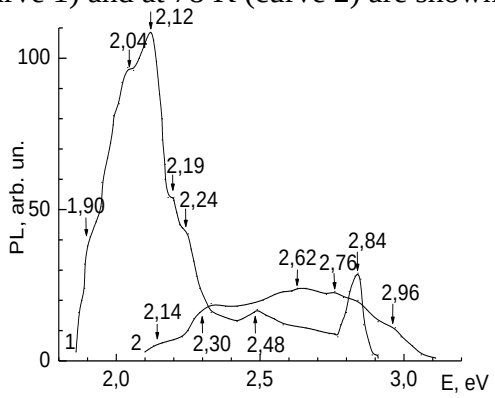

Fig. 3. *GaS-Zn* composite PL spectra, at 293 K (curve 1) and the temperature of 78 K (curve 2).

PL maximum bands' energies from Fig. 2 and Fig. 3, and their interpretations are indicated in the table below.

Table. PL maximum bands energies shown in Fig. 2 and Fig. 3 and their interpretation

Compound	Energy, eV	Interpretation
GaS	2,52; 2,49	exciton-fonon
	2,32;	donor-acceptor tranzition
GaS:Zn, at 78 K	2,84	-
	2,54÷2,35	band-band tranzition
	2,24; 2,19; 2,12; 2,04; 1,90	impuritar bands in *GaS-ZnS* compound
GaS:Zn, at 293 K	2,96	-
	2,62÷2,36	-
	2,44	-

PL spectra from *Cd* intercalated *GaS* lamella at 293 K (Fig. 4) and at 78 K (Fig. 5) are shown.

As it can be seen in Fig. 4, *GaS* PL spectra at the temperature of 293 K occurs by conduction band (in Brillouin zone *M* point) – valence band (Brillouin zone center) transitions, with 34 meV energy transversal optic phonon participation. Temperature decreasing, from 300 K to 78 K, leads to edge band displacement with ~ 70 meV to highest energies (Fig. 6).

Heat displacement coefficient of PL edge band at 140÷280 K is $4{,}2\cdot10^{-3}$ eV·K^{-1} and it corresponds to absorbtion spectra measures at 78 K to 293 K (Fig. 6, curve 2). Indirect optic band width in *GaS* crystals at 78K is equal to 2,457 eV. By this we can judge that PL band with maximum at 2,424 matches the indirect radiative transitions with 34 meV phonon emission.

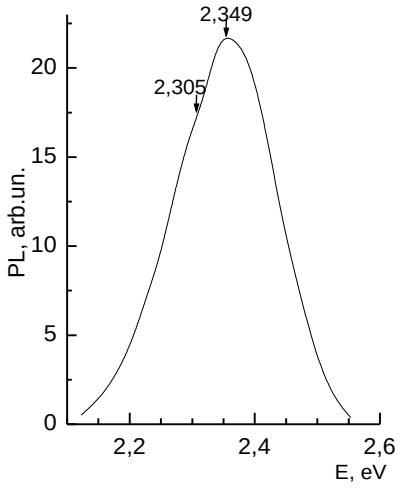

Fig. 4. PL spectrum of *GaS* lamella, *Cd* intercalated at the temperature of 750 K, 6 h. T = 293 K.

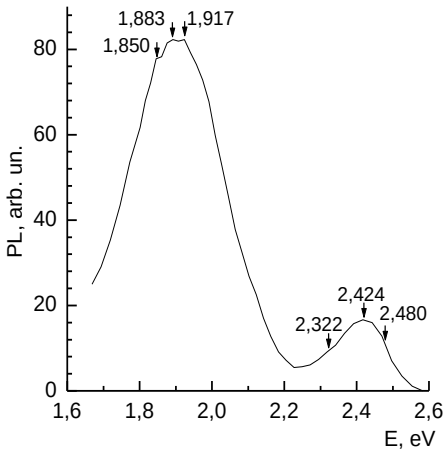

Fig. 5. PL spectrum of *GaS* lamella, *Cd* intercalated at the temperature of 750 K, 6 h. T = 78 K.

In Fig. 6 temperature dependence of edge band maximum energy is shown. Heat displacement coefficient coincidence of indirect band decreases at temperature increase with edge PL band heat displacement coeficient is a criterion that allows us to assign this band to radiative transition with phonon participation category.

In PL spectra at 78 K band with maximum of 1,883 eV prevails. Symetric contour of this band allows us to suppose that it is about emission from acceptor center associeted to *Cd* donor ion. It is known that luminescence by center is strongly attenuated at temperature increase and at the same time bands' contour increases. In reality this band completely atenuates at ~ 130 K.

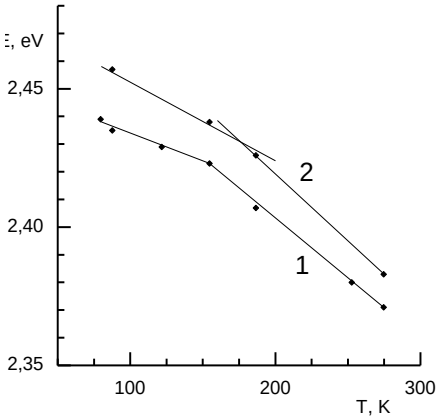

Fig. 6. Temperature dependence of edge band maximum energy, hν=2,43 eV (curve 1) and indirect band gap width (curve 2)

CONCLUSIONS

- *GaS* monocristallyne lamella PL at chamber temperature is determined by indirect radiative transitions, with 34 meV phonon participation.

- At 78 K indirect transitions with exciton and transversal optic phonon participation (with 33 meV energy) contribute to PL bands formation. Also deep impuritar levels participation transitions contribute to this PL bands formation.

- *Cd* atoms intercalated in *GaS* crystals, stimulate indirect radiative transitions with phonon emission and at the same time create donor-acceptor type PL centers.

- *Zn* atoms intercalated in *GaS* crystals form deep acceptor levels and donor-acceptor type luminescence centers asociated to *Zn* ion.

REFERENCES

1. Sasaki Y., Hamaguchi C., Nakai J. Electroabsorption of GaS around the Indirect Edge. J. Phys. Soc. Jpn., 1975, 38 (6), p. 1698-1702.

2. Okamoto N., Hara N., Tanaka H. Surface passivation of InGaP/InGaAs/GaAs pseudomorphic HEMTs with ultrathin GaS film. IEEE Trans. Electron. Devices, 2000, 47 (12), p. 2284.

3. Micocci C., Rella R., Siciliano P., Tepore A. Investigation of electronic properties of gallium sulfide single crystals grown by iodine chemical transport. J. Appl. Phys., 1990, vol. 68, p. 138.

4. Manfredotti C., Murri R., Rizzo A., Vasanelli L. Hall effect in n-type GaS. Solidi. State Commun., 1976, 19, p. 339-342.

5. Aydinli A., Gasanly N. M., Göksen K. Donor–acceptor pair recombination in gallium sulfide. J. Appl. Phys., 2000, 88, p. 7144-7149.

6. Shigetomi S., Ikari T. Radiative centers in layered semiconductor GaS doped with Zn. J. Luminescence, 2005, 113, p. 137-142.

7. Chiricenco V., Caraman M., Rusu I.I., Leontie L. On the luminescence of GaS(Cu) single crystals. J. of Luminescence, 2003, 101, p. 71-77.

Prezentat la redacţie la 14 septembrie 2012