
Spectral Properties of GaS Nanoparticles Obtained by Laser Ablation

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Abstract: Bulk single crystals of GaS were grown by Bridgman-Stockbarger method in an evacuated (10^{-6} Torr) quartz ampoules of optical quality. Nanoparticles of quasi 2-D GaS crystals were obtained by laser ablation (LA) technique (KrF Excimer laser at 248 nm (COHERENT COMPex 201), and characterized by: XRF, GDOES, SEM, TEM and UV-VIS absorption spectroscopy. Nanoparticles obtained for the first time were ablated by using of excimer KrF laser operated at $f = 50$ Hz with pulse duration $\tau = 4$ ns and maximum energy 200 mJ. Obtained results are analyzed with respect to particle size. Absorption spectra of particles with diameter less than 18 nm turned out to be shifted in the blue range of spectra. Blue shift in the optical absorption spectra of GaS nanoparticles with decreasing the particle sizes was explained by presence of nanocrystals in the quantum size regime. These results are consistent with a perturbation of GaS band structure due to carrier confinement, resulting in a widening of the forbidden gap.

Keywords: Nanoparticles, Layered Crystals, 2-D Materials, Spectral Properties, Laser Ablation

1. Introduction

Semiconductor nanostructures are promising building blocks for future electronic and photonic devices. Nanostructures based on layer-type (2- D) semiconductors, such as GaSe- type (GaS, InSe, GaTe) are of particular interest in terms of the optical, non-linear optical (NLO), solar, X- ray and particles detection applications [1-10]. Gallium selenide is accepted by world scientific community as an outstanding NLO material [1].

For the last years our research groups at the National Aviation Academy of Azerbaijan, Scientific-Research Institute of Transport and Anionic Problems, Baku/Bina, Azerbaijan Republic and the Trakya University, Trakya, Turkey have been focused on growth and investigation of highly anisotropic semiconductors, especially, GaSe, InSe and GaS due to increasing interest of their NLO and other applications (photovoltaics, particle detection etc.). We used the modified Bridgman-Stockbarger method [1] for growth of bulk crystals of GaS and the LA (Laser Ablation) method

to obtain the nanoparticles of this material with a given size and to examine elemental content (XRF- X- ray Fluorescence, GDOES- Glow Discharge Optical Emission Spectroscopy), structural (X- ray, TEM- Transition Electron Microscopy and SEM- Scanning Electron Microscopy), optical (absorption in VIS- Visible) and vibrational (Raman and confocal Raman) spectroscopy.

Highly anisotropic crystal structure (Figure 1) leads to observation some effects in layered materials, which are not observable in crystals with isotropic or “normally” anisotropic structure. Among these are: splitting of each vibrational or electronic states into a number of component equal to a number of isolated units in a primitive unit cell, easy mechanical cleavage of crystal in the direction perpendicular to the optical c- axis with a thickness up to several tenth of nanometers etc. The ϵ - modification is the main component for GaSe-type crystals obtained from the melt. It is noncentrosymmetric, contains 2 layers per unit

cell, and belongs to space group (SG) D_{3h}^1 .

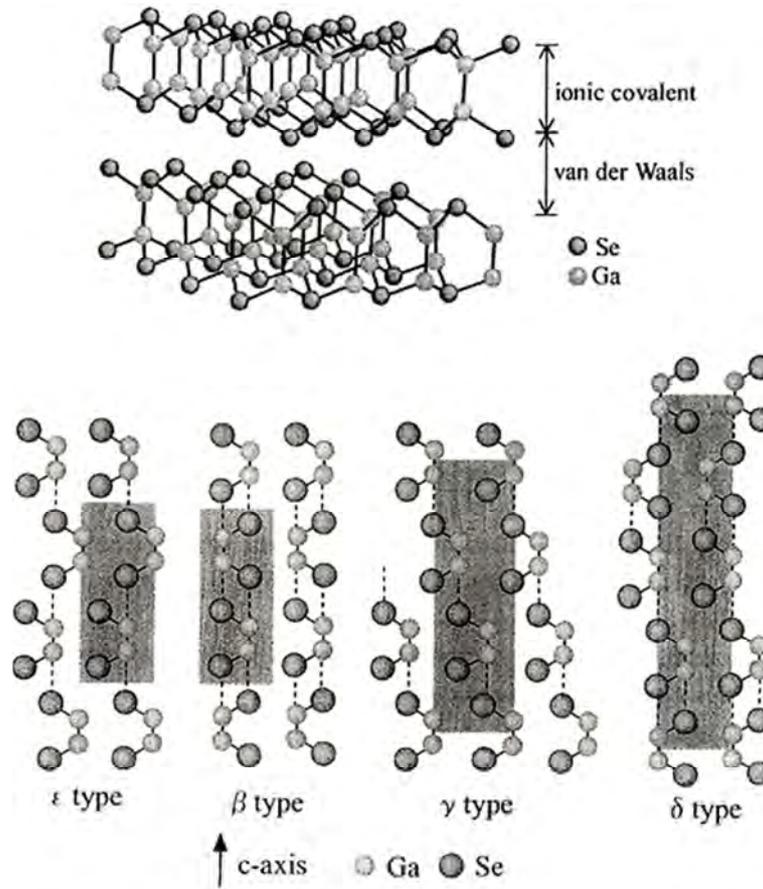


Figure 1. Schematic view of unit layer and different polytypes for GaSe. Notice the three-fold coordination of Se atoms which exist within the layer [1]. Same structures are typical for GaS-polytypes – only with Se atoms (in GaSe-case) substituted by S atoms (in case of GaS).

The hierarchy of weak forces and the ability of these materials for easy cleavage together with the low density of electronic states on freshly cleaved surfaces (does not exceed $\sim 10^{10} \text{ cm}^{-2}$, water absorbs on a surface without any reaction and forms 3-D clusters on the (0001) planes) and existence of different polytypes and other unique properties- is one of the main reason why GaSe-type layered semiconductors were extensively investigated since about 1960th up to the present time [1-3]. GaS crystallizes in a space group (SG) of D_{6h}^4 and the elementary unit cell consists of 2 layers of atoms in sequence of $-S-Ga-Ga-S$. The crystals of GaSe characterize by: melting point $T_m = 965^\circ\text{C}$ (1238 K), density 3.86 gcm^{-3} , molecular weight 101.79. Small amount of S added to GaSe (or some GaSe-GaS solid solutions) leads to increase the transparency range of NLO material. Latter is important in NLO.

Existing more than 1000 papers on thermodynamic-, structural-, electrical-, linear optical-, and other electronic and vibrational properties - indicate that GaS is an interesting material for optoelectronic application. All these and other peculiarities make interesting to grow and characterize the bulk crystals as well as nanoparticles of GaS and other GaSe-type crystals. The latter is highly interesting because GaS nanoparticles may have a single tetra-layer structure consisting of covalently bond $-S-Ga-Ga-S-$ tetra-layers.

Some of GaSe-type crystals have band gaps in the range of 1.1-1.5 eV (solid solutions of GaS-GaTe) which make them and their nanoparticles suitable materials for photovoltaic applications.

The remainder of this paper is follows. In Section 2. the Methodology used is described including growth techniques for bulk crystals as well as nanoparticles. In this section also method for characterization of nanoparticles and the equipment, facilities and methods used for characterization of bulk crystals and nanoparticles are presented. In Section 3. Experimental results obtained are described including an average size of synthesized nanoparticles, spectral dependence of grown nanoparticles versus gas pressure used and the results of theoretical explanation of blue shift of the absorption spectra with decreasing the size of nanoparticles. In Section 4 Conclusions summarizing the results obtained are presented.

2. Methodology

The starting materials were prepared by mixing quantities of high-purity (99.999%) gallium and sulfur pellets in the atomic proportion 1/1. Especially un-doped GaS crystals were grown by the Bridgman-Stockbarger method in an evacuated quartz tube (10^{-6} Torr). GaS single crystals 20 mm

in diameter and 60 mm in length with yellow color were successfully obtained. From the boules (\varnothing 20 mm), slabs of different thickness were easily cleaved with a razor blade for further preparation of powder. Powder was obtained by grinding the single crystal plates in an agate grinder. Then the powder was pressed into a form of pellets and used as a target in the LA experiments.

Nanoparticles were grown by home built LA apparatus during stay of Prof. K. Allahverdiyev at the Institute of Material Sciences, Tsukuba University, Tsukuba, Japan (Prof. K. Allahverdiyev are indebted to Prof. S. Onari for his hospitality during stay at Tsukuba University). KrF Excimer laser at 248 nm (COHERENT COMPex 201), with the repetition frequency $f = 10$ Hz and pulse duration $\tau = 10$ ns, 25 mJ and 200 mJ pulses were used and the particles were deposited at different gas pressures. The average size of grown GaS nanoparticles were controlled by a change in the pressure of the noble gases and the laser energy. In the present paper the results only for nanoparticles deposited onto the quartz plates will be presented and discussed.

Equipment, facilities and methods used in the present research for characterization of GaS bulk crystals and nanoparticles were as follows: XRD- (Shimadzu X-ray diffraction XRD-600); X-ray fluorescence XRF- (Philips PW 2404); GDOES (Glow discharge optical emission spectrometer)- High Resolution HR 10000 Glow Discharge

Profiler (Jobin Yvon); very small drops of samples were dropped onto carbon support film coated copper TEM grids. JEOL-2100 HR TEM (Transmission electron microscope) operating at 200 kV (LaB₆ filament) and equipped with an Oxford Instruments 6498 EDS system; JEOL-JSM-6335F FEG-SEM (Scanning electron microscope) equipped with Oxford EDS system, operated at 20 kV and INCA software; double-pass spectrometer (Jobin Yvon U-1000) with the photon counting system equipped with a photomultiplier (RCA-C31034) and a multichannel analyzer (Canberra Series 40) for UV-, VIS-, for the transmission measurements.

3. Results

Growth from the melt (Bridgman-Stockbarger method) provided large single crystals sufficiently homogeneous and free of defects which allows the fabrication of samples destined for optical or transport phenomena measurements. A little thin slice of single-crystal sample was ground into powder and its XRD pattern was recorded. The results showed the presence of diffractions characteristic of hexagonal phase for GaS (D_{6h}^4 space group). The XRD pattern indicated that the as-prepared products have high crystallinity. The cell parameters are in agreement with that presented in Figure 2 and in accordance with given in Ref. [1].

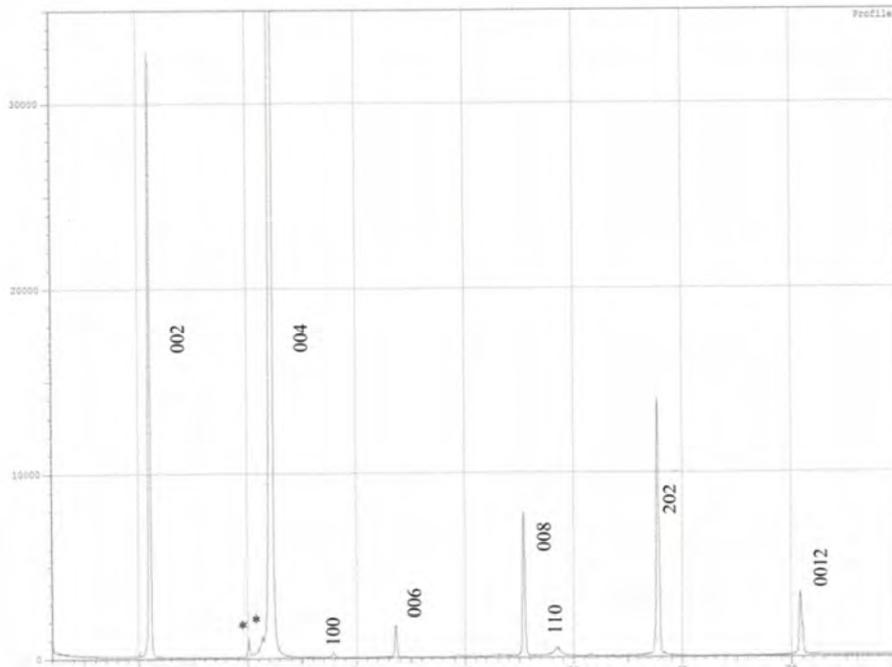


Figure 2. XRD pattern obtained from freshly cleaved [(001) plane] GaS single crystal plate (thickness, $t = 2.00$ mm). Pattern was obtained by using X-ray source with the parameters: Ni filtered CuK_{α} radiation of $\lambda = 1.54056$ Å. Measurements were done at RT in 2θ range of $5^{\circ} - 80^{\circ}$ with scanning step width of 0.01° and 10 s scanning time per step. Annealing the pellets at vacuum (10^{-6} Torr) at temperatures up to $100^{\circ}C$ practically did not change neither pattern nor type of conductivity (all as grown crystals were *p*-type). Similar results were obtained for polycrystalline pellets of GaS samples.

Lattice parameters obtained from XRD pattern presented in Figure 2 ($a = 3.65$ Å, $c = 14.78$ Å) are in good agreement with those presented in Ref. [1] for β - modification of GaS (D_{6h}^4 - space group; 2 -S-Ga-Ga-S units in a primitive unit cell).

Optical band gap of GaS measured in the present work is $\Delta E = 2.5$ eV and in good agreement with existing data [1, 9]. Elemental content analysis of grown crystals are as follows: the results obtained by the GDOES confirmed nearly stoichiometry content (49.5 at % of Ga and 49.3 at % of S).

XRF measurements performed on series of GaS crystals showed nearly the same content. Energy dispersive X-ray spectrometer (EDS) analysis indicated only presence of O (oxygen) element in the spectrum, indicating the high purity of grown crystals.

The average size of grown GaS nanoparticles were controlled by a change in the pressure of the noble gases and

the laser energy. The size of grown particles was estimated by direct observation with a TEM operated at 200 kV. All measurements were carried out at room temperature.

The particles with the size in the range of 8 – 15 nm were obtained at conditions- when the shape of plume was close to the theoretical one (upper right Picture presented in Figure 3).

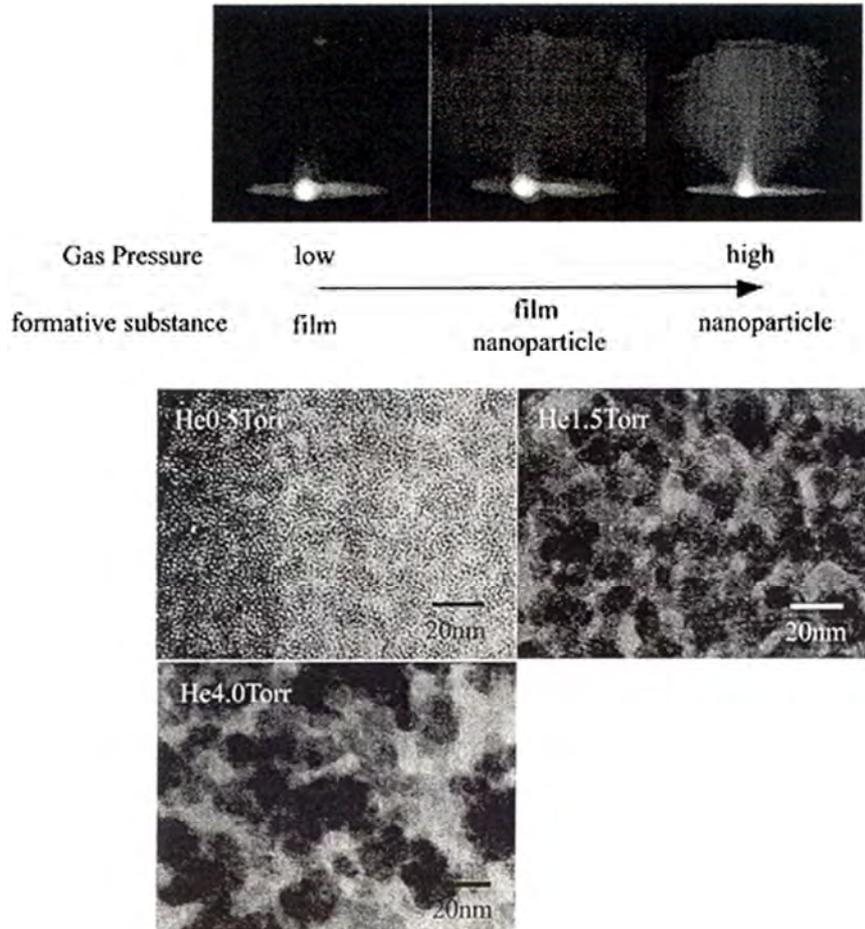


Figure 3. Shape of plume formed during ablation in dependence on the gas pressure (less than 0.07 Torr- upper left; 0.6 Torr-middle; 1.7 Torr- right). Lower 3 pictures represent the TEM of GaS particles ablated at different He gas pressure.

Spectral dependences of optical density of grown particles versus gas pressure (Ar and He) for GaS particles for different laser powers were built, analyzed and by using these data absorption gap versus gas pressure were built. It was established that characteristic feature of these dependences is that with increasing gas pressure optical density shifts to lower energies. It was seen that absorption gap increases with increasing pressure up to about 0.6 Torr (He gas, laser pulse power 220 mJ and He gas, laser pulse power 30 mJ) and then decreases. With increasing the distance between the target and substrate gas pressure value from which the gap of particles start to decrease and shifts to higher gas pressure (at $\sim 0.2 - 0.17$ Torr at distance 30 mm and at ~ 0.28 Torr at distance 70 mm).

We associate the blue shift in the optical absorption spectra of GaS with decreasing the particle sizes to the presence of nanocrystals in the quantum size regime (nearly same as it

was reported earlier for GaS and InSe [5]). According to Brus [6] an analytical expression for the first excited electronic state of the quantum particle is:

$$E = \frac{h^2 \pi^2}{2 R^2} \left[\frac{1}{m_e^*} + \frac{1}{m_h^*} \right] - \frac{1.8 e^2}{\epsilon R} + \text{polarization terms} \quad (1)$$

where: the first term is the quantum energy of localization; the second term is the Coulomb attraction; the third term (smaller term) arises from Coulomb interaction in the presence of a crystalline surface; R is the radius of the particle; m_e^* and m_h^* are the effective masses of electron and hole, respectively, and e is the charge of an electron, ϵ is the dielectric constant at the optical frequency. The value of E represents the energy shift with respect to the value of the band gap for bulk crystal. It was shown, that for nanoparticles of GaS the combination of Coulomb term and relatively large effective masses (compared to GaAs, InSb

etc.) keeps the excited state energy near the bulk forbidden gap for diameters larger than approximately 20 nm (very similar to that for GaSe and InSe).

4. Conclusions

1. Polycrystals of GaS were synthesized by horizontal method.

2. High optical quality single crystals of GaS were grown by the Bridgman-Stockbarger method having a size of 20 mm in diameter and 60 mm in length. The space group (D_{6h}^4) of grown crystals are in good agreement with the existing data.

3. The nanoparticles of GaS have been synthesized using Laser Ablation method. The size of nanoparticles was successfully controlled by selection of the experimental parameters of rare gas species of Ar or He: at pressures lower than 0.1 Torr the particles with diameter more than 15 nm were obtained. Increasing the gas pressure more than 0.1 Torr results to formation of particles with diameter 5 nm and less (at gas pressure 1 Torr). Further increasing the pressure leads to increasing the particle sizes (12 nm at 5 Torr).

4. Blue shift in the optical absorption spectra of GaS nanoparticles with decreasing the particle sizes was explained by presence of nanocrystals in the quantum size regime. These results are consistent with a perturbation of GaS band structure due to carrier confinement, resulting in a widening of the forbidden gap.

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