Technical Physics, 2024, Vol. 69, No. 4

08

Effect of substrate temperature on the Ga-S films properties prepared by PECVD

© *M.A. Kudryashov,*[1,2] *L.A. Mochalov,*[1,2] *M.A. Vshivtsev,*[1] *I.O. Prokhorov,*[1,2] *Yu.M. Spivak,*[3] *V.A. Moshnikov,*[3] *Yu.P. Kudryashova,*[2] *P.V. Mosyagin,*[2] *E.A. Slapovskaya,*[2] *V.M. Malyshev*[1]

[1] Nizhny Novgorod State Technical University n.a. R.E. Alekseev,
603155 Nizhny Novgorod, Russia
[2] Lobachevsky State University,
603022 Nizhny Novgorod, Russia
[3] St. Petersburg State Electrotechnical University „LETI“,
197022 St. Petersburg, Russia
e-mail: ymkanageeva@yandex.ru

Received June 26, 2023
Revised December 30, 2023
Accepted January 17, 2024

Gallium sulfide (GaS) has a great potential for applications in optoelectronics and energy storage. In view of the sufficiently large Eg, thin films of gallium sulfide can be used as a buffer layer in a solar cell. GaS also provides efficient passivation of the GaAs surface. In this work, Ga-S thin films were obtained for the first time by plasma-chemical vapor deposition. High-purity elemental Ga and S were used as precursors. The plasma was excited by an RF generator (40.68 MHz) at a reduced pressure of 0.1 Torr. The composition, structural and optical properties of Ga-S films were studied depending on the substrate temperature. All films were highly transparent (75%) in the range of 400−1100 nm.

Keywords: gallium sulfide, films, PECVD, structure, optical properties.

DOI: 10.61011/JTF.2024.04.57536.156-23

Introduction

A high interest to 2D (2*D*) materials lead to extensive studies of their physical, chemical and mechanical properties. Monochalcogenides of the third group elements, such as gallium sulphide, selenide, telluride, GaX (X=S, Se, Te), are one of the last additions into the family of 2*D*-materials and are of a special interest for optoelectronic applications of UV within visible range due to their high width of the band gap [1]. GaS is of a special interest among them, which has the highest width of the band gap about 2.4 eV for 3D material [2], which is increased due to the effects of quantum limitation up to 3.2 eV for monolayer [3]. Though gallium monosulphide is an indirect band gap semiconductor, its direct band gap was discussed in 3.04 eV [4].

GaS is a non-toxic material having a high chemical and thermal stability, as well as resistance to oxidation. It shows a high Young's modulus (173 GPa) and bursting stress of about 4.5% [5]. Gallium monosulphide is crystallized into a hexagonal laminar structure consisting of a pile of covalently bound tetralayers S−Ga−Ga−S along the axis c, with Van der Waals weak forces between them. The most stable form under normal condition is β-GaS ($a = b = 3.585$ Å, $c = 15.50$ Å), which represents a diamagnetic semiconductor [6]. Gallium-enriched GaS relates to n-type semiconductor, and sulfur-enriched GaS, — relates to p-type semiconductors [7]. It was found that 3D GaS of p-type demonstrates quite high mobility of holes along the axis c ($80\,\mathrm{cm^2{\cdot}V^{-1}{\cdot}s^{-1}}$) for that material [8]. Moreover, gallium monosulphide manifests photoluminescence within the green-blue region [9], and demonstrates broad band transparency in infrared and terahertz ranges [10].

The results of studies of electronic and optical responses of gallium monosulphide both in 3D and 2D forms show that GaS can be used in transistors, gas sensors, photodetectors, non-linearly optical devices, catalysts, solar cells, etc. [11–16].

There quite many methods of production of GaS films, among of which we distinguish chemical vapor-phase deposition [17], magnetron sputtering [18], molecular-beam epitaxy [19], atomic layer deposition [20], deposition from solution [21], ion-beam sputtering [22] etc. However, we did not find papers devoted to production of gallium monosulphide by plasma-chemical vapor-phase deposition of elementary precursors. It is known also that deposition conditions could impact structural, optical and electrical properties of thin films. In relation therewith we produced GaS films by plasma-enhanced chemical vapor deposition (PECVD), where elementary gallium and sulphur were used as precursors, and the impact of substrate temperature on their properties was studied. Such method allows resolving the problem of contamination of finished materials as a result of incomplete conversion of precursors, and the purity of deposited films in this case is determined only by the purity of initial substances.

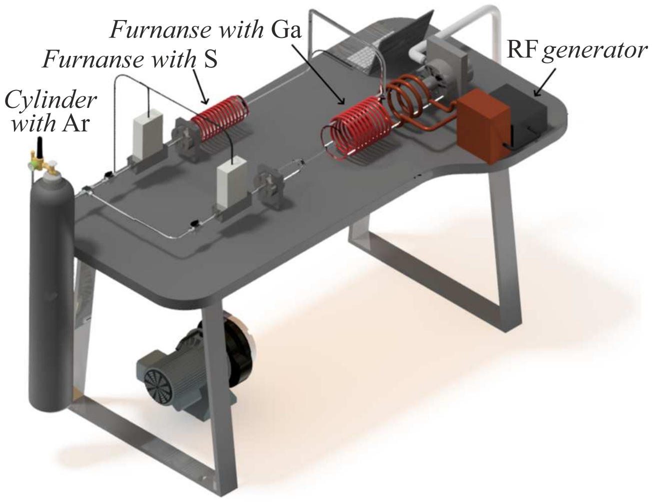

Figure 1. Diagram of plasma-chemical facility for thin GaS films synthesis.

1. Experimental part

The plasma-chemical facility diagram is shown in Fig. 1. This facility consists of the initial substances feeding system, quartz tubular plasma-chemical reactor, high-frequency generator with interface and external inducer, as well as pumping out system. Similar type of a facility was earlier discussed in the papers [23–25].

Gallium with purity of 6N and elementary sulphur with purity of 5N were loaded into special feeding tanks made of a high-purity quartz and equipped with external resistive heating elements and thermocouples for temperature control. The gallium source temperature was 850°C, the sulphur source temperature was — 120°C. High-purity argon (99.999 vol.%) was blown through precursors with the flow rate of 10 ml/min. Plasma discharge was driven by external four-winding HF inducer, the plasma power was 50 W. The films were deposited onto sapphire (001) with the size of 10×10 mm. Cover glass was also used in certain experiments. The substrates temperature varied within the range 150–350°C. Total pressure in the system during experiments was kept constant at 0.1 Torr. Average thickness of films measured by means of Linnik interferometer microscope MII-4M, was about 50 nm. The films growth rate in our experiments was about 25 nm/h.

The composition of produced films was studied by means of X-MaxN 20 energy-dispersive attachment (Oxford Instruments) of JSM IT-300LV scanning election microscope (JEOL). X-ray diffraction analysis was performed by using Bruker D8 Discover diffractometer at the angles 2θ from 10 to 60° with the pitch 0.1°. Morphological condition of the gallium sulphide films surface was studied by atomic-force microscopy (AFM) with the use of SPM-9700 scanning probe microscope (Shimadzu, Japan) in contact mode. We used arithmetic roughness, which was assessed by AFM from the sample area $10 \times 10\,\mu$m, as the surface assessment. Initial roughness of sapphire substrate surface used in the experiments was ~ 0.1 nm. Transmittance spectra were registered at UV mini-1240 spectrophotometer (Shimadzu, Japan) within the wavelength range 200–1100 nm with the pitch of 1 nm. All measurements were performed at room temperature.

2. Results and discussion thereof

The substrate temperature determined the composition of the produced gallium sulphide films (see Table).

At the temperatures of 150 and 250°C the compositions were near-stoichiometric GaS. However, at the highest temperature of the substrate, a considerable increase in sulphur content in the films was observed.

Fig. 2 shows impact of the substrate temperature on the structure of produced gallium sulphide films. At the minimum substrate temperature (150°C) the film was X-ray amorphous. Temperature increase up to 250°C enabled the growth of a film, which is close to texture. In this case diffraction peaks were observed near to 11.4° and 23°, corresponding to planes (002) and (004) β-GaS. Reflexes of β-GaS are quite wide, which indicates that the films have defects and are polycrystalline, with a small size of domains. XPA curve inclination indicates the presence of amorphous phase. The presence of peaks (002) and (004) only indicates a preferred orientation of the axis c. The diffraction pattern of thin gallium sulphide film produced at

GaS films composition depending on the sapphire substrate temperature

Substrate temperature, °C	Composition, at.%
150	$Ga_{47}S_{53}$
250	$Ga_{48}S_{52}$
350	$Ga_{45}S_{55}$

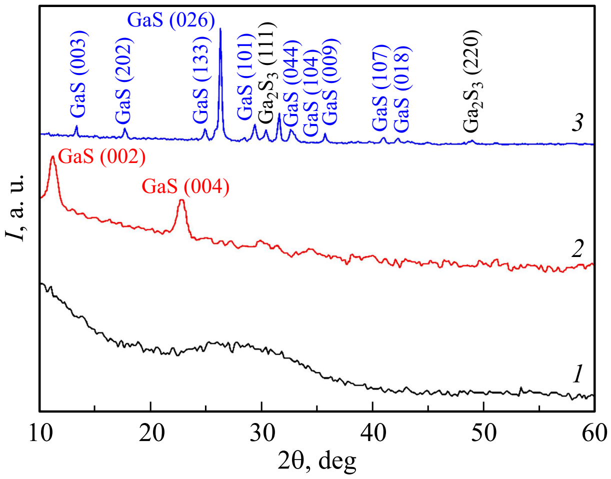

Figure 2. Diffraction patterns of gallium sulphide films deposited onto sapphire at various temperatures of the substrate: 150 (*1*), 250 (*2*) and 350°C (*3*).

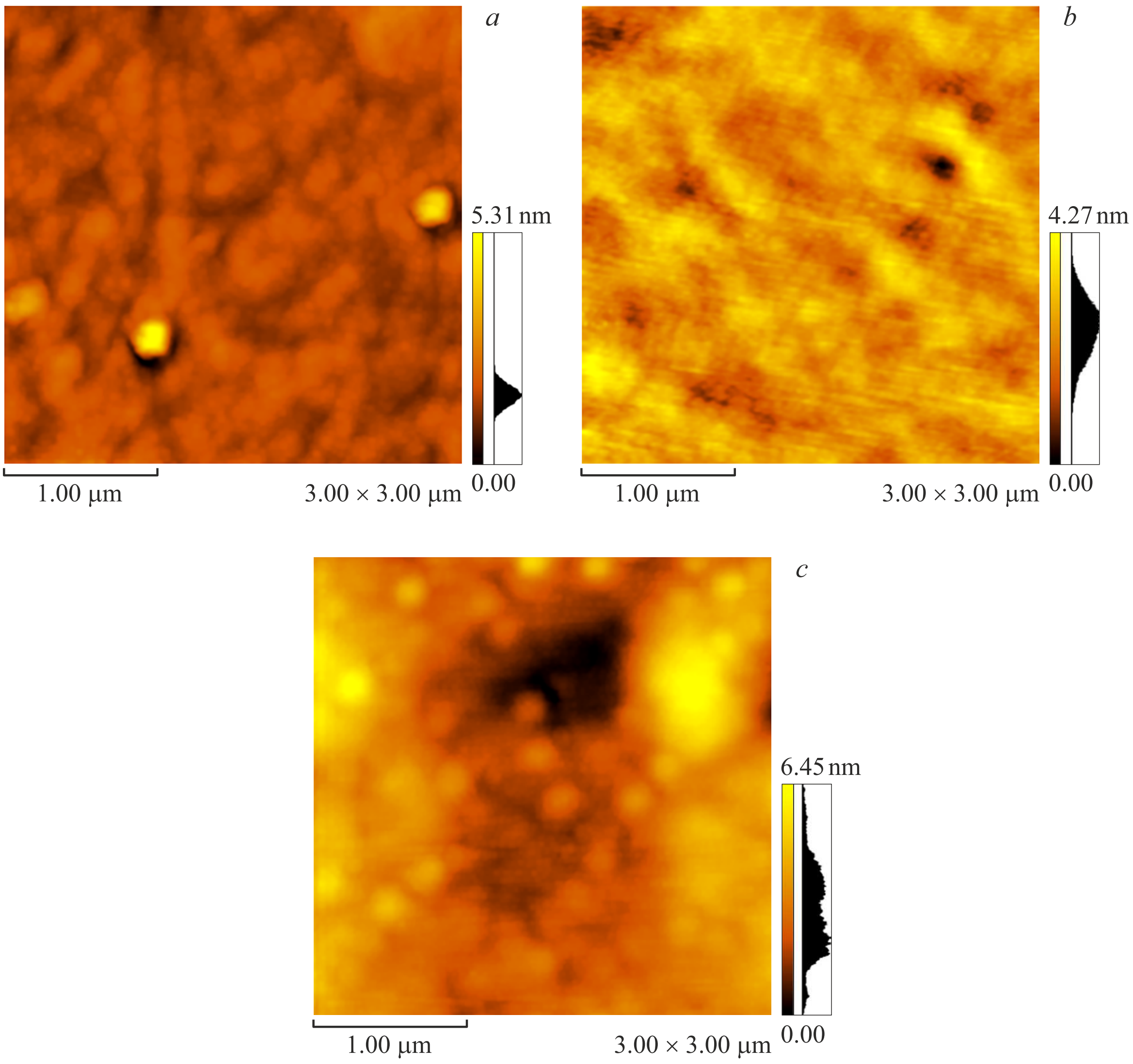

Figure 3. AFM images of gallium sulphide films deposited onto sapphire at various temperatures of the substrate: 150 (*a*), 250 (*b*) and 350°C (*c*).

the maximum temperature of the substrate 350°C (curve *3*), indicates that the film is polycrystalline. XPA curve analysis indicates that the phases are β-GaS and α-Ga_2S_3. It correlates the results of the films composition study, where the highest sulphur content is observed at 350°C. Different phases can be produced in various growth conditions in some of semiconductor crystals, and it is one of the principal inherent properties of semiconductors $A^{III}B^{VI}$ [26].

The substrate temperature also had an impact on the surface morphology of the produced gallium sulphide films (Fig. 3). Temperature increase of the sapphire substrate from 150 to 250°C and further up to 350°C lead to the roughness increase from 0.22 to 0.44 and to 0.97 nm, accordingly. This fact relates to the increase of the film microstructure grain sizes. It can be clearly seen on the AFM image of the film, taken at the maximum substrate temperature (Fig. 3, *c*), where formation of spherical grains with the size of 240 nm was found. Similar behavior, which is expressed insignificantly though, was found in the paper [27]. Formation of such a smooth film on sapphire refers to the layer-by-layer growth according to the Frank-van der Merve growth mode.

More noticeable increase in the grain size and surface roughness depending on the substrate temperature was found in the case of using a cover glass (Fig. 4), where the grain size grow from 130 to 200 nm, and the roughness from 3.26 to 10.12 nm. More developed surface of films on the glass substrate is associated, apparently, with the Volmer–Weber isle growth mode.

Fig. 5 presents dependences of GaS films transmittance spectra on the substrate temperature. All films are highly transparent in visible and near IR ranges (75%). Subject to low reflection of light from the films the absorption coefficient (α) was derived from the transmittance coefficient (T) and the film thickness (d), as $\alpha = \ln(T)/d$.

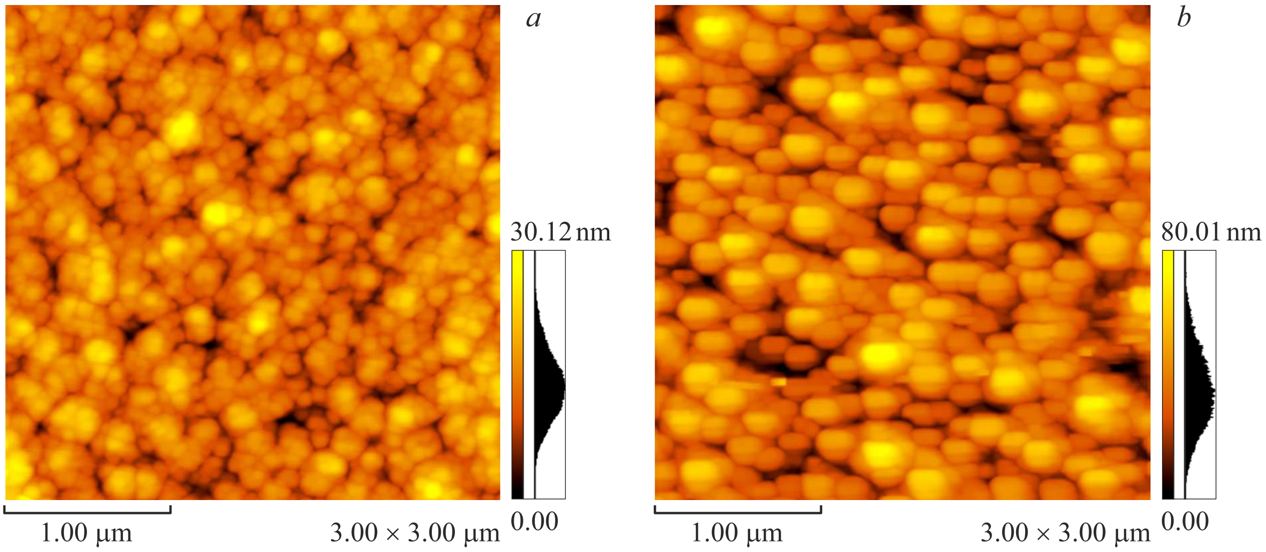

Figure 4. AFM image of gallium sulphide films deposited onto a cover glass at the substrate temperatures of 150 (*a*) and 250°C (*b*).

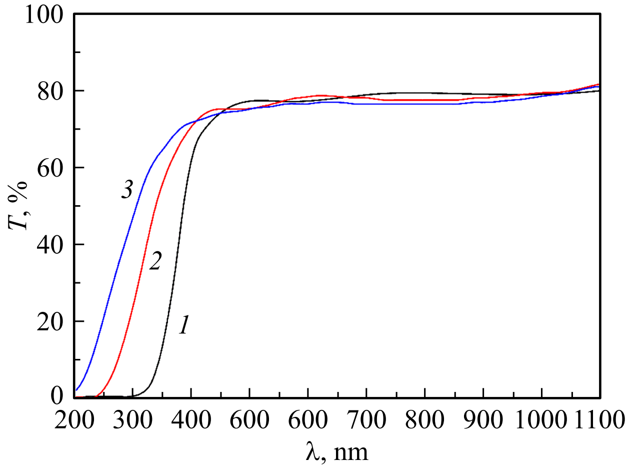

Figure 5. Transmittance spectra of gallium sulphide films deposited onto sapphire at various temperatures of the substrate: 150 (*1*), 250 (*2*) and 350°C (*3*).

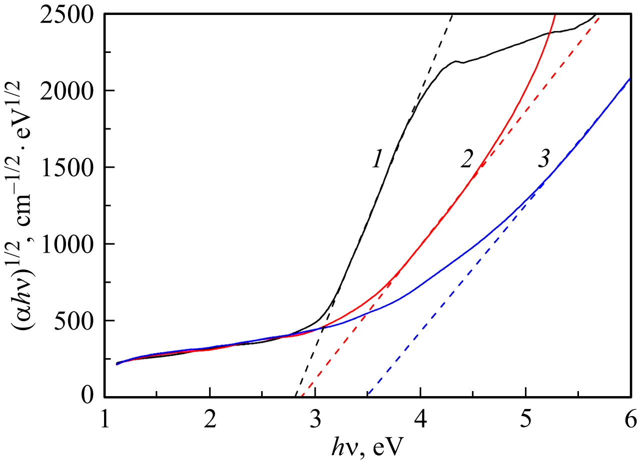

Figure 6. Absorption spectra in the coordinates $ah\nu^{1/2}$ from $h\nu$ for gallium sulphide films deposited onto sapphire at various temperatures of the substrate: 150 (*1*), 250 (*2*) and 350°C (*3*).

Since the films contain either amorphous phase or a combination of two crystalline phases, according to the X-ray diffraction analysis, the band gap width was determined from the dependence $\alpha h\nu = A(h\nu - E_g)^{1/2}$. This dependence is shown in Fig. 6. For a pure X-ray amorphous film $Ga_{47}S_{53}$ the band gap was about 2.81 eV, and for the films $Ga_{48}S_{52}$ and $Ga_{45}S_{55}$ — 2.87 and 3.48 eV, accordingly. It should be noted that the deposition method and conditions considerably impact on structural, optical and electric properties of thin gallium sulphide films. For example, for GaS films produced by deposition from solutions and thermic evaporation, the energy of direct band gap was 2.76 [21] and 2.55 eV [28], accordingly; by atomic layer deposition — 3.1−3.3 eV [20]; by chemical deposition with modulated flux — 3.2−3.6 eV depending on the substrate temperature [27]. In our case we associate the growth of the band gap width of a film produced at the substrate temperature of 350°C also with the occurrence of the phase α-Ga_2S_3, which initially has a high value E_g, than the phase β-GaS.

Conclusion

Thin films of GaS were produced in the conditions of low-temperature non-equilibrium plasma at different temperature of the substrate. The substrate temperature determined the composition and properties of films. The temperature growth leads to modification of the film structure from X-ray amorphous to polycrystalline one. GaS film produced at the maximum substrate temperature (350°C) contains two phases — β-GaS and α-Ga_2S_3. Increase in sapphire substrate temperature leads to the increase of roughness of the films surface from 0.22 to 0.97 nm. Wherein all films are highly transparent (75%) within the range 400−1100 nm, and their band gap width increases from 2.81 to 3.48 eV. The band gap width growth for a film produced at the substrate temperature of 350°C, apparently, is associated with occurrence of the phase α-Ga_2S_3. The most optimum substrate temperature for the growth of β-GaS films in our conditions was 250°C.

Funding

The study was supported by the Russian Science Foundation, grant № 22-19-20081, https://rscf.ru/en/project/22-19-20081/.

Conflict of interest

The authors declare that they have no conflict of interest.

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Translated by D.Kondaurov