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The effect of tin on the properties of gallium nitride grown by hydride vapor-phase epitaxy

© A.V. Osipov¹, Sh.Sh. Sharofidinov², E.V. Osipova¹, A.V. Redkov³, S.A. Kukushkin^{3,¶}

¹ Institute for Problems in Mechanical Engineering of the Russian Academy of Sciences, St. Petersburg, Russia

² Ioffe Institute, St. Petersburg, Russia

³ St. Petersburg State University, St. Petersburg, Russia

¶ E-mail: sergey.a.kukushkin@gmail.com

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An *n*-type GaN layer doped with Sn was grown by hydride vapor-phase epitaxy (HVPE). Tin doping was carried out by a chemical reaction with the formation of SnCl₂ and its subsequent decomposition in the presence of NH₃. It has been shown that doping with tin leads to the disappearance of cracks and a decrease in the roughness of GaN. The optical properties of tin-doped GaN have been investigated. It is shown that in the Raman spectrum of GaN:Sn a thick zone of lines appears in the region from 620 to 740 cm⁻¹, associated with fluctuations in Sn–N bonds. The conduction electrons produced by doping GaN with tin absorb light in the region of 2.2–3.3 eV. Using the density functional theory, it is shown that Sn atoms strongly interact with each other in a GaN crystal in an anisotropic manner, determining the local symmetry group of the doped crystal.

Keywords: gallium nitride, density functional theory, hydride vapor-phase epitaxy, ion radius, Raman spectrum.

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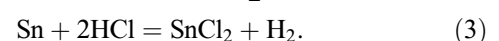
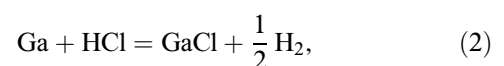
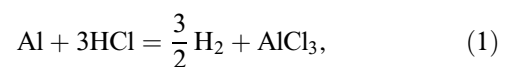
1. Introduction

It is known that gallium nitride (GaN) has a set of benefits as compared to silicon: larger band gap, high electric strength, high mobility of electrons, high work temperature, high drift speed of electrons saturation [1]. Combination of high concentration of conductivity electrons and high mobility of electrons significantly decrease resistance of GaN transistors in open state, and hence energy losses in power converters [2]. So, the problem of creation of high concentration of doping substance in GaN is rather actual [3,4]. Frequently as *n*-impurity silicon Si is used, but due to that ionic radius of Si is by 30% lower than ionic radius of Ga, GaN heavily doped with Si grown on sapphire cracks higher [5]. Besides, after achievement of the electron density 10¹⁹ cm⁻³, it starts decreasing due to compensation of the charge carriers [5]. The use of germanium Ge as a dopant results in a large number of pits due to Ge droplets. As the ionic radius of Sn is by 17% larger than the ionic radius of Ga, there is idea on tin Sn use instead of Si [5]. Since Sn increases the mobility of Ga atoms, it is expected that the addition of Sn shall also make GaN smoother. And, finally, it can increase the coefficient of thermal expansion of GaN, and, therefore, decrease cracking of GaN on sapphire. It is difficult to implement the method of metalloorganic vapor-phase epitaxy (MOVPE) by doping with tin due to absence of appropriate precursor. Method of hydride vapor phase epitaxy (HVPE) is known as most commercially successful

method of GaN substrates manufacturing as it ensures high growth rate with simple control of conductivity type and conductance due to doping by impurities. In the present paper GaN samples heavily doped with Sn were grown by this method. The Sn precursor was obtained as a result of the chemical reaction of Sn with HCl. The optical properties of the obtained samples were studied.

2. Experimental procedure

Growth of GaN:Sn was performed by method of hydride epitaxy on substrates SiC/Si and Al₂O₃ in set-up HVPE. The set-up comprises quartz reactor with diameter 76 mm with five heated zones using furnaces with resistive heating. As chemicals ammonia (NH₃) hydrogen chloride (HCl) were used, and high purity argon (Ar) was used as transport gas. Melts of gallium (Ga), aluminium (Al) and tin (Sn) were used as sources. Temperature in zone of sources varied from 600°C to 850°C depending on metal (for Ga lower, for Al higher). In zone of GaN growth the temperature was 1040°C. The hydrogen chloride enters in reaction with melted metal forming appropriate chloride



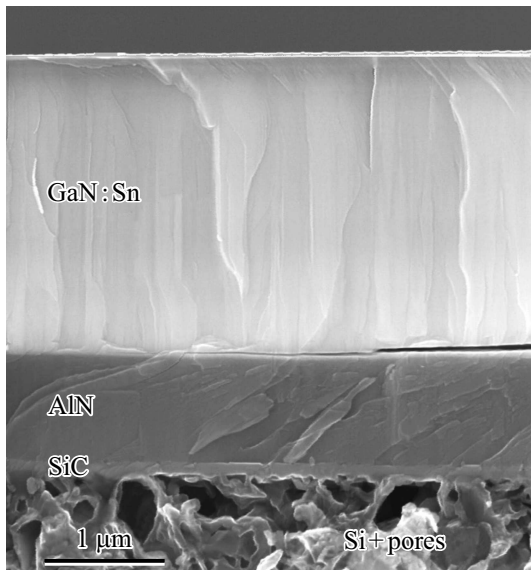
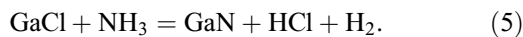
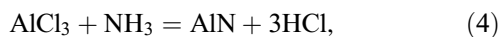


Figure 1. Image of section of sample GaN:Sn/AlN/SiC/Si, obtained by scanning electron microscope.

The such obtained chlorides were mixed with another chemical NH_3 and enter in reaction with it on substrate surface



Tin chloride does not enter in reaction with NH_3 , but upon its presence disintegrates with formation of pure tin



The thermodynamic calculations show that in ideal situation at pressure 0.01 atm the maximum number of disintegrated molecules SnCl_2 are formed at temperature 840°C and is 26%.

As substrates the plates of silicon Si with orientation (111) with grown on them layer of silicon carbide of cubic polytype SiC-3C 50–100 nm thick were used. The silicon carbide was grown by method of coordinated replacement of atoms [6] due to chemical reaction of Si with gas CO [7]. Feature of this method of SiC growth is absence of mismatch dislocation of lattices and presence of porous layer in Si under layer with SiC [6,7]. These substrates proven themselves to be excellent for growing thick GaN layers for LEDs [8].

Before loading into the reactor, the substrates were subjected to standard chemical treatment to remove unnecessary impurities. First of all buffer layer of AlN 500–700 nm thick was grown at temperature 1080°C due to reaction (4). Then on obtained layer GaN was grown by reaction (5) with addition of tin (Sn) and without it (for comparison). The ratio of gallium Ga to tin Sn in reactions (2) and (3) is about 10 : 1. The growth temperature was 1040° . Total flow of argon Ar was 4 l/min, growth rate of GaN was about $0.5 \mu\text{m}/\text{min}$.

3. Study results

Figure 1 shows image of section of sample GaN:Sn/AlN/SiC/Si, obtained by scanning electron microscope. AlN layer has thickness about 800 nm, GaN — $2.5 \mu\text{m}$. Under layer of silicon carbide ~ 100 nm thick we clearly see pores and voids in bulk of silicon substrate, which were formed as result of reaction of agreed replacement of atoms [6,7].

Figure 2, *a* shows image of surface of film GaN:Sn in electronic microscope. We see complete absence of large cracks that present in sample GaN without tin (Figure 2, *b*). Insert to Figure 2, *a* shows image of surface of film GaN:Sn in electronic microscope. Surface roughness of GaN:Sn, measured by optical profilometer Zygo NewView6000, was equal to about 10 nm, which is about 2 times lower the roughness of film GaN without tin (19 nm).

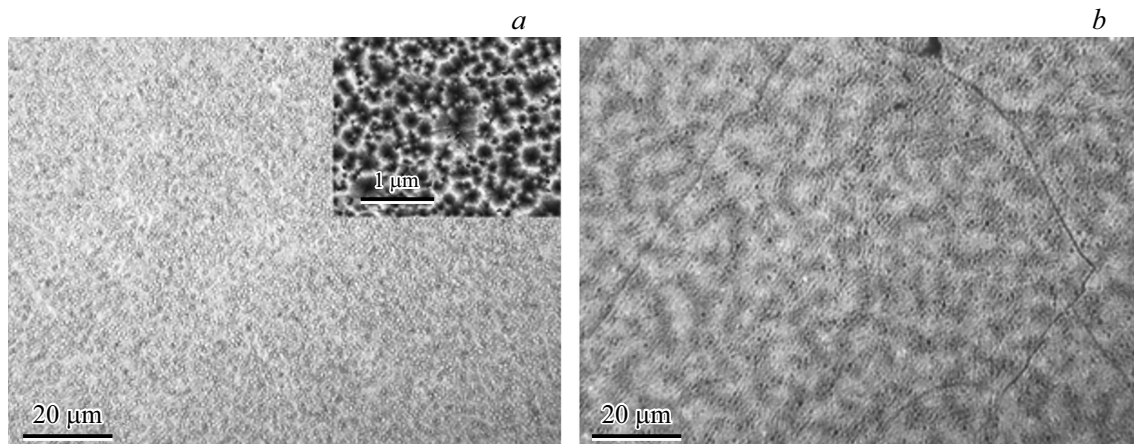


Figure 2. Image of surface of film GaN with tin (*a*) and without tin (*b*) in optical microscope. Insert to part (*a*) shows image of surface off film GaN:Sn in electronic microscope.

Values of energy of cluster $\text{Ga}_{47}\text{SnN}_{48}$, calculated from minimum possible state, depending on group of symmetry

Group of symmetry	P31m	P31c	CC	P63mc	Cmc21	Cm	P3m1	21	P3
Energy, eV	0.0	0.06	0.14	0.22	0.28	0.42	0.52	0.60	0.60

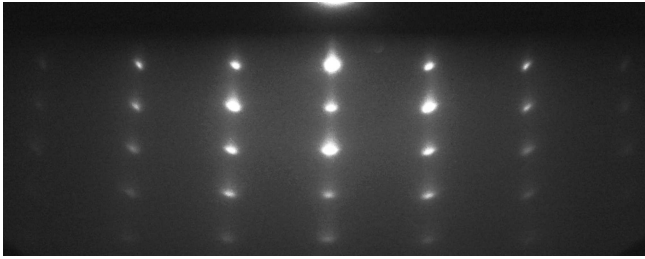


Figure 3. Pattern of diffraction on high-energy electrons on reflection with energy of 50 KeV from the surface GaN:Sn obtained by electron-diffraction instrument EMR-100.

Pattern of high-energy electron diffraction on reflection with energy of 50 KeV from the surface GaN:Sn is shown in Figure 3. It is shown that surface GaN:Sn completely corresponds to hexagonal crystal of polytype 2H. Visible defects of the diffraction pattern such as polycrystalline circles or amorphous halos are completely absent.

Figure 4 shows the Raman spectra of $\text{GaN}/\text{AlN}/\text{SiC}/\text{Si}$ samples with and without tin, obtained under the same conditions and measured with a WiTec Alpha300R confocal Raman microscope. Figure 4, *a* corresponds to pure GaN without the dopant Sn, and Figure 4, *b* corresponds to Ga:Sn at ratio of flows Ga:Sn 10:1. The main lines are signed. It is seen that doping with tin leads to the appearance of an additional zone of lines in the region from 620 to 740 cm^{-1} and the disappearance of the line $A_1(\text{LO})$.

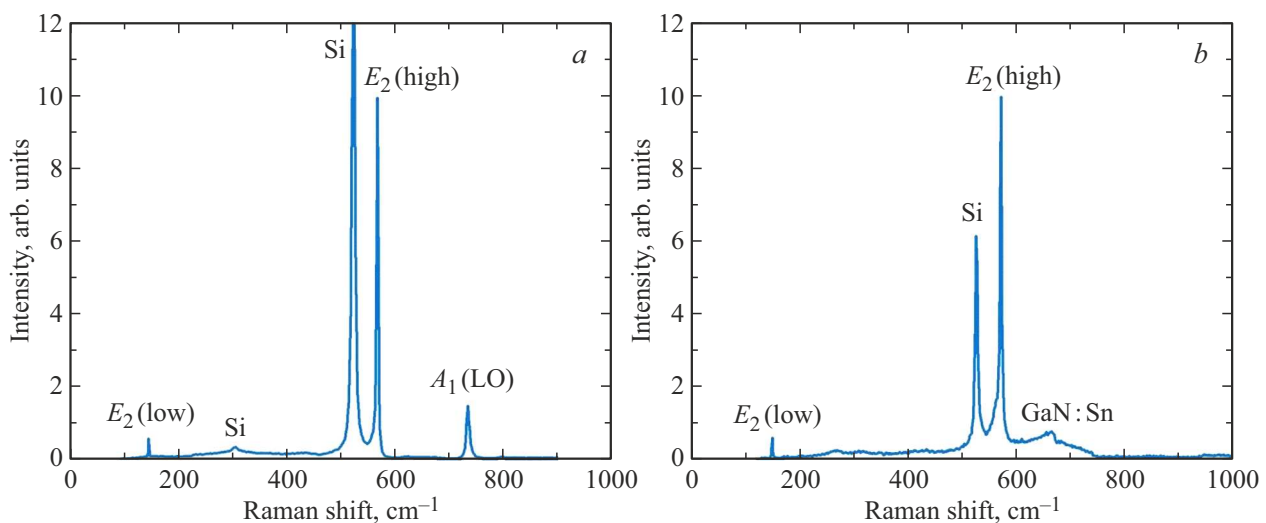


Figure 4. Raman spectra of pure GaN (*a*) and GaN , doped with Sn (*b*), obtained under same conditions.

Besides, it is obvious that the main line $E_2(\text{high})$ during doping becomes noticeably thicker at the base. The silicon line becomes weaker by approximately 2 times, which is explained by the light absorption by conduction electrons formed during GaN doping with tin.

To study the nature of the change in Raman spectra when doping GaN with tin, the density functional method was used with the software Medea-Vasp [9]. In all calculations, periodic boundary conditions were used for all three dimensions, the exchange-correlation contribution was calculated using the gradient functional PBEsol [10]. For integration in Brillouin zone grid of k -points was used, generated as per Monkhorst–Pack scheme [11], distance between them was maximum 0.3 \AA^{-1} . The pseudopotentials using Bloch projector augmented wave (PAW) method were applied in all calculations [12]. Cut-off energy of plane waves in all calculations was 500 eV. Initially the theoretical group analysis of Sn atoms distribution over GaN crystal was made. As the studied system the cluster $(\text{GaN})_{288}$ of 576 atoms was selected. 6 Ga atoms were replaced by 6 Sn atoms in all possible ways, and all possible symmetry groups of the new cluster were found. Then, after optimizing the system geometry, i.e. minimizing the energy by the coordinates of the atoms and the volume of the system, the most favorable configurations of the atoms were found. Calculations showed that the most favorable configuration of the system, where each of 48th Ga atoms is replaced by Sn atom, is the configuration with the symmetry group P31m (see Table). It is shown in Figure 5.

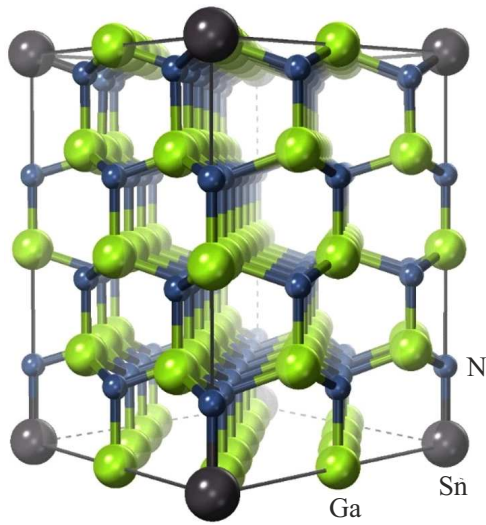


Figure 5. Most favorable configuration $\text{Ga}_{47}\text{SnN}_{48}$ with dimensions $a = b = 10.94 \text{ \AA}$, $c = 10.32 \text{ \AA}$, $\alpha = 60^\circ$, corresponding to trigonal group of symmetry $P3m1$.

From Table's data it is obvious that replaced Sn atoms strongly interact with each other, at that anisotropically. If each 48th Ga atom is replaced by Sn atom, the system volume increases by 1%, and concentration of Sn atoms becomes equal to $9.35 \cdot 10^{20} \text{ cm}^{-3}$. Calculation of Raman spectrum of pure GaN and $\text{Ga}_{47}\text{SnN}_{48}$ with symmetry group $P3m1$ by method of density functional is shown in Figure 6.

From Figure 6 it is obvious that GaN doping with tin leads to the disappearance of the $A_1(\text{LO})$ line, which is most likely explained by change in the symmetry group and thickening of the main line $E_2(\text{high})$ and occurrence of new line $\sim 700 \text{ cm}^{-1}$, associated with oscillations of bonds Sn–N.

The analysis carried out by the density functional method shows that Sn atoms are practically motionless due to their mass, and only N atoms oscillate. Figure 7 shows the directions of oscillations of N atoms, which give the main contribution to the new line of the Raman spectrum of GaN:Sn. In general, we can conclude that the modeling

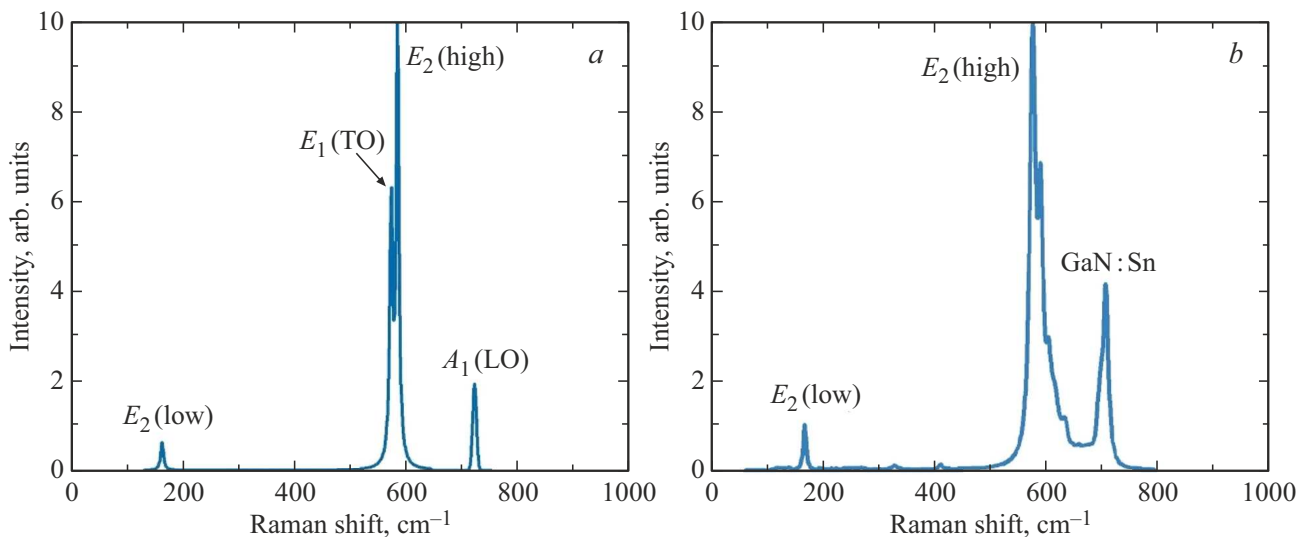


Figure 6. Raman spectra of pure GaN (*a*) and $\text{Ga}_{47}\text{SnN}_{48}$ with symmetry group $P3m1$ (*b*).

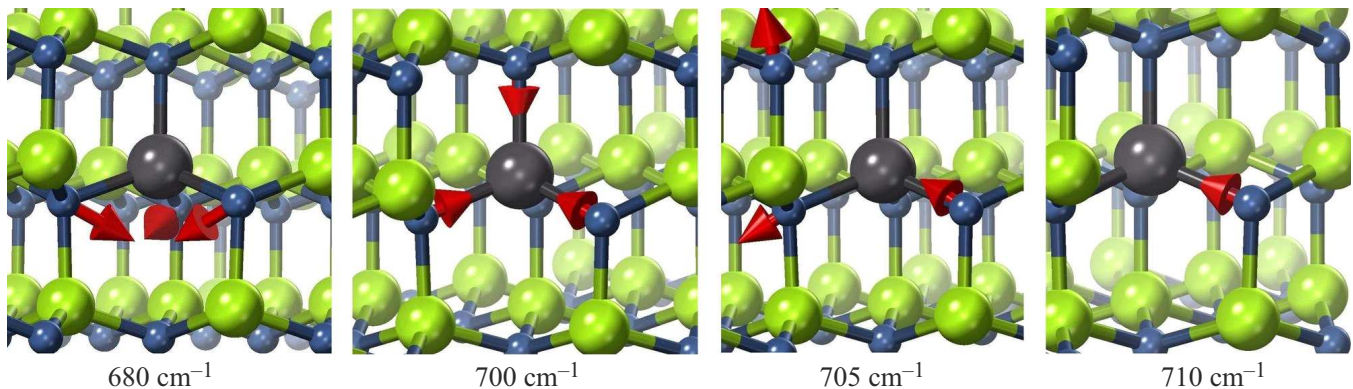


Figure 7. Visualization of oscillations, which give the main contribution to the new line of the Raman spectrum of GaN:Sn. Direction of oscillations of N atoms is shown by red arrows.

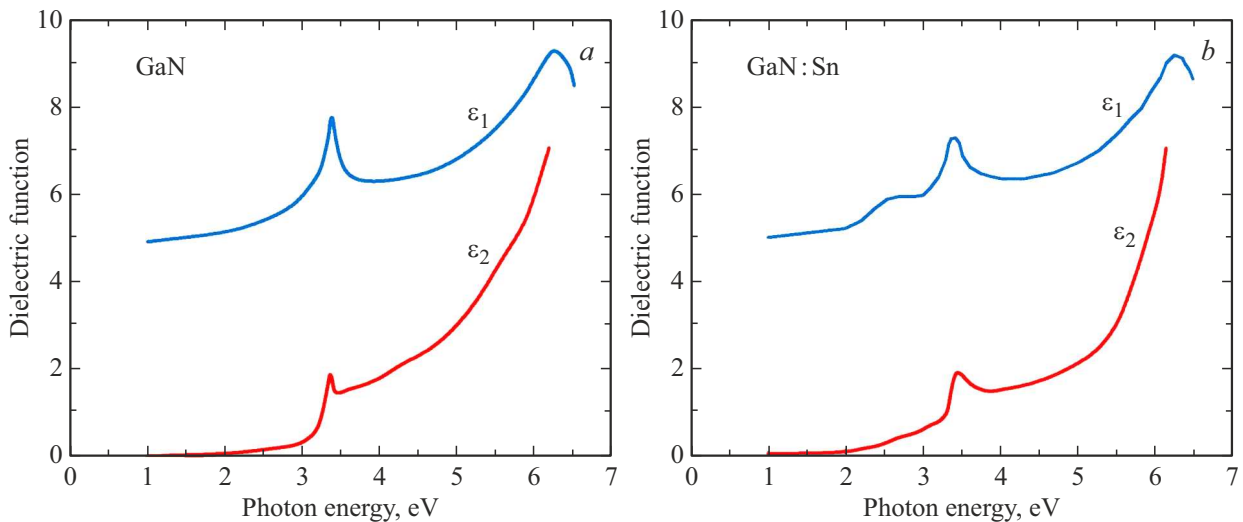


Figure 8. Dielectric permittivity vs. energy of photons of pure GaN (a) and GaN, doped with Sn (b), obtained under same conditions.

of the Raman spectrum (Figure 6) coincides well with the experimental data (Figure 4). If we suppose that amplitude of new line of Raman spectrum GaN:Sn ($680 \pm 60 \text{ cm}^{-1}$, Figure 4, b) is directly proportional to concentration of Sn atoms, then comparing the experimental and theoretical curves, see Figure 4, b and Figure 6, b, respectively, we can evaluate concentration of Sn atoms in obtained sample as 10^{20} cm^{-3} .

Using ellipsometer WVASETM (0.7–6.4 eV) J.A. Woolam measured ellipsometric spectra of samples with and without tin. Then by standard methods [13,14] information was extracted from them on dielectric permittivity of pure GaN and GaN:Sn, see Figure 8. It is obvious that the main difference between them is the additional light absorption by the conduction electrons of the doped sample in the region 2.2–3.3 eV. It is because of this absorption the silicon line in the Raman spectrum of GaN:Sn is approximately by 2 times weaker than that of GaN, since the laser radiation is absorbed more strongly.

4. Conclusion

In this paper heavily tin-doped GaN samples are grown by hydride vapor phase epitaxy. It is shown that tin doping leads to the disappearance of cracks and decrease in the roughness of GaN, which is apparently due to higher mobility of Ga atoms in the presence of Sn. The optical properties of tin-doped GaN are studied. It is shown that a thick band of lines appeared in the Raman spectrum of GaN:Sn in the region from 620 to 740 cm^{-1} , associated with oscillations of bonds Sn–N. It is determined that the modeling of the Raman spectrum GaN:Sn by density functional method coincides well with the experimental data. The oscillations that make the main contribution to the Raman emission lines are visualized. Conduction electrons, occurred during GaN doping with tin, absorb light in region

2.2–3.3 eV, making it less transparent in this region as compared to pure GaN. Sn atoms interact strongly with each other in GaN crystal in anisotropic manner, determining the local symmetry group of the doped crystal. Possibility of GaN doping with impurity of *n*-type with concentration up to 10^{20} cm^{-3} and over is due to that ionic radius of tin is larger than in gallium (by 17%). Thus, the use of additives with large ionic radius, in particular tin, is very promising in growth of crystals A^3B^5 by hydride vapor phase epitaxy method.

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Conflict of interest

The authors declare that they have no conflict of interest.

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