

Synchrotron photoemission study of zinc-modified oxide/GaSb film structures

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GaSb-based device structures obtained by zinc diffusion from the gas phase have been studied by means of high-resolution photoelectron spectroscopy using the synchrotron radiation. It is shown that the method of creating the oxide film on GaSb significantly affects the Zn atomic concentration in the subsurface area of the substrate, and that this impurity, in turn, improves the useful properties of the passivation layer. The results demonstrate the high potential of photoelectron spectroscopy for the characterization of semiconductor device structures at the atomic level.

Keywords: synchrotron-radiation photoelectron spectroscopy, GaSb, oxide, diffusion, photovoltaic converter.

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Introduction

Semiconductor surfaces interacting with the environment are subject to oxidation even in vacuum conditions at residual pressure of $\sim 10^{-7}$ – 10^{-6} mbar and above [1]. The oxide films that are formed spontaneously on such surfaces usually lack long-range order and contain multiple broken bonds. This can cause unwanted states in the band gap and accordingly deteriorate the operation of semiconductor devices. Therefore, detailed understanding of the mechanisms for the formation of oxide/semiconductor interfaces and their physical and chemical properties at the atomic level in the device structures, on the one hand, and use of the controlled conditions for their growth, on the other hand, should assist the development of the technology and design of the materials with the specified parameters.

One of the important practical systems, where the surface oxide film properties play a significant role, are the photovoltaic converters based on gallium antimonide [2–10]. Most of solar cells, thermal and laser photovoltaic converters are fabricated by diffusion into a GaSb-substrate [2–9]. Besides, the substitution of a natural oxide on its surface with a film developed in an electrolyte under the controlled conditions (anode oxide) can improve the characteristics of the obtained structures. Thus, previously in the technology of GaSb-converters, the anode oxide films were used successfully to accelerate the penetration of zinc in formation of p – n -junction [2,7], to develop the simplest antireflection coatings [2,3,6,9], to control the surface concentration of the impurity in the photoactive area [2–4,9] and to form the device structure with the complex profile [2,5].

From the above it is clear that for further improvement of semiconductor devices based on gallium antimonide, the comparative research is necessary on the device structures

of oxide/GaSb, obtained in the different conditions. Until now the number of such papers in the literature is very limited [11–13]. To replenish (at least partially) the specified gap, this article for such systems conducted the comparative analysis of the phase composition with the help of the high-resolution photoelectronic spectroscopy (PES) in its variant, where electrons emitted from the core (inner) levels of atoms are collected (core-level photoelectron spectroscopy), and their photoionization is conducted with the help of synchrotron radiation [14]. Core electrons, contrary to the valence ones, are localized near the atom nucleus, and for this reason are chemically inert, i.e. do not participate directly in formation of the bonds between atoms. However, the energy of the core shells is very sensitive to the change of the chemical environment and electronic state of atoms (for example, in process of oxidation of the semiconductor crystal surface). From here it follows that the analysis of the fine structure of photoelectronic spectra of core levels and determination of energy shifts from them for various atoms in the film structures make it possible to receive information on the nature of various phases in these systems. The important role in such studies is played by synchrotron radiation, since its application makes it possible to vary the depth of photoelectron escape from the sample and to optimize the sensitivity of the recorded spectra to the surface and bulk.

In the earlier studies, the high resolution PES method using synchrotron radiation studied the structures of oxide-GaSb(100) type, which were created in vacuum conditions by exposure of the substrate with atomically clean surface in molecular oxygen at the specified dose (dry oxidation) [15]. The data obtained in these papers, despite their fundamental significance, can not always explain the issues related to the technology of device structures. This study presents the PES

results for the structures based on GaSb, which are used directly for the manufacturing of photovoltaic converters. Its purpose was to find the differences observed for the samples with oxide layers of two types, and, finally, explain the role of the oxide on the surface of gallium antimonide in process of formation of p - n -junction in the substrate bulk by zinc diffusion. It is assumed that the obtained data will make it possible to formulate important recommendations for the improvement of the technological process, and will also demonstrate the potential of the PES method for diagnostics of device structures.

Experimental method

The samples were formed at the Ioffe Institute. n -GaSb(100) substrates doped with tellurium were used. The surface of the substrates was covered with a layer of natural oxide or oxide layer developed by intentional anode treatment [2,3]. Further such film structures will be specified by 1 and 2 respectively. Upon anode treatment, the substrate was soaked in electrolyte based on 3%-solution of tartaric acid and ethylene glycol in the ratio of 1:2 with addition of NH_4OH to obtain pH 6 [16,17]. The thickness of the oxide film obtained in this manner was ~ 40 nm. The oxide growth rate was 2.2 nm/V [2,3], and the supplied density of current — 1–5 mA/cm². The films formed by the specified method have the high homogeneity by thickness and good reproducibility. Besides, this mode will prevent erosion of the substrate [17]. Zinc diffusion from the gas phase was conducted into substrates with oxide films of both types in a hydrogen flow in the quasi-closed graphite cassette on a fluid epitaxy unit at temperature of $\sim 450^\circ\text{C}$. Depth of p - n -transition in samples 1 and 2 was ~ 0.5 – $1.0\ \mu\text{m}$ [2,4]. After zinc diffusion the samples were studied by PES method.

Photoemission measurements were carried out in an experimental station NANOPES of a specialized source of synchrotron radiation KISI-Kurchatov [18,19]. The spectra were recorded using a semispherical analyzer SPECS Phoibos 225 at room temperature and normal angle of electron escape from the sample. Energy resolution was ~ 0.25 eV (at photon energy of $h\nu = 900$ – 1100 eV). The area of surface lighting with a photon flux was $100 \times 300\ \mu\text{m}$.

Spectrum fitting features

The quantitative analysis of photoelectronic spectra was conducted by their decomposition into components by the least square method. The background was subtracted from the spectra using Shirley method [20]. The decomposition used linear combinations of model Voigt functions, which represented a convolution of the Lorentzian and Gaussian forms of the line. For Zn $2p$, Sb $3d$ and Ga $3d$ levels the values of spin-orbit splitting were equal respectively to 22.97, 9.38 and 0.43 eV. The intensity ratio of two sublevels of doublets $2p_{1/2}$ – $2p_{3/2}$ was 1:2, and doublets

$3d_{3/2}$ – $3d_{5/2}$ — 2:3. Lorentzian (or natural) broadening of the lines caused by the finite hole lifetime at the core level in the excited state of the atom, was 0.10 eV for the levels of Zn $2p$, 0.04 eV for Sb $3d$ and 0.15 eV for Ga $3d$. All the above parameters did not change in process of fitting. The variable parameters were the number of components in the spectrum, their intensity, the energy position and the Gaussian broadening.

To fit O $1s$ - and $2s$ -spectra, the linear combinations of singlets were used, which were described with a Gaussian profile with a small additive of Lorentzian shape. The best reproduction of the experimental data was obtained in the case when the Lorentzian contribution was from 0 to 4% of the total intensity of the components. This result matches well with the recent data [21–24].

For all spectra the criterion for the selection of the optimal fitting parameters was the use of the minimum possible number of components (N). This means that the introduction of the new additional component into the decomposition, i.e. use of the fitting scheme with the number of components equal to $N + 1$, will not actually improve the quality of decomposition. At the same time the use of the fitting scheme with a smaller number of components, for example $N - 1$, will not yet allow to accurately reproduce the experimental data. Other features of the procedure for the spectra decomposition may be bound in publications [25,26].

Results and discussion

Fig. 1 presents the survey photoelectronic spectra for the film structures 1 and 2 at photon energy $h\nu = 900$ eV. The depth which they provide information from, is ~ 5.4 – 6.4 nm (this value was adopted as equal to 3λ , where λ — inelastic mean free path of electrons with kinetic energy of ~ 720 – 900 eV). As you can see from Fig. 1, for both structures there is a series of lines provided for by the emission of electrons from different core levels of Sb, Ga and Zn atoms (marked in the chart). Their comparison can lead to several important conclusions. First of all, as it follows from the analysis of peak intensities of Zn $3s$, Zn $3p$ and Zn $3d$, the content of zinc in the sample 2 is higher than in the sample 1. This result agrees well with the data of the previous studies conducted with the help of mass spectrometry of secondary ions [2]. Besides, it is noteworthy that the values of zinc signals are comparable to the similar values for gallium and antimony given in Fig. 1. With account of the probability of photoionization of the corresponding core shells [27] this means that the concentration of Zn atoms in the near-surface layers of the samples 1 and 2 is $\sim 10^{21}$ – $10^{22}\ \text{cm}^{-3}$.

Secondly, the intensities of the lines of gallium and especially antimony for sample 1 is noticeably higher than the intensities of the corresponding lines for sample 2. Obviously, one of the possible reasons for such difference can be related to a higher concentration of zinc in the

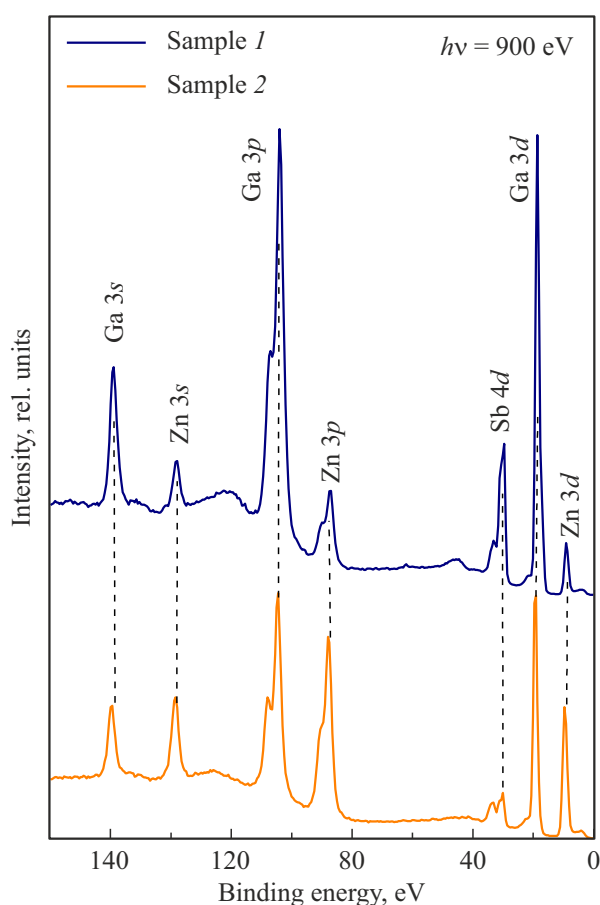


Figure 1. Survey photoelectron spectra of samples 1 and 2. The binding energy is marked on the abscissa axis. The photon energy is 900 eV.

second sample. Indeed, the more of its atoms are embedded into the substrate, the stronger must be the screening of antimony and gallium signals. Other potential reasons will be discussed below.

Finally, thirdly, the shape of line Sb 4d varies substantially when transitioning from one sample to another. This means that the electronic and chemical state of antimony atoms in the studied structures is not equivalent. Therefore, the above features of the spectra in Fig. 1 make it possible to conclude that the phase composition of oxide-GaSb film structures and concentration of Zn atoms introduced into them depend on the method of oxide film development on the surface of the substrate.

To obtain more detailed information, the quantitative analysis of the fine structure of photoelectronic lines was conducted. The spectra were fitted for the levels that have the largest cross sections of photoionization [27]. For gallium and antimony such are 3d-levels. For gallium the binding energy of 3d-shell is equal to ~ 19 eV, which corresponds to the depth of electron escape of ~ 5.8 nm at excitation energy of 900 eV. For antimony the binding energy 3d_{3/2}- and 3d_{5/2}-sublevels is 537 and

528 eV respectively. In this case the depth of escape is approximately 2.7 nm.

Another feature of 3d-spectra of Ga and Sb is the fact that they partially overlap with the photoemission of oxygen, namely with lines O 1s (~ 23 eV) and O 2s (~ 531 eV) respectively. This means that the decomposition of such spectra makes it possible to simultaneously obtain information on the chemical and electronic state of atoms of all three elements in the film structures.

As for the zinc photoemission, for this element the most intense line is the 2p one. The binding energy of its 2p_{1/2}- and 2p_{3/2}-sublevels is equal to ~ 1145 and 1122 eV respectively. Therefore, to record such spectra, this paper used the excitation energy of $h\nu = 1100$ eV. The electron escape depth under such conditions was ~ 1.34 nm.

2p-level spectra of Zn for 1 and 2 structures are given in Fig. 2, a. From their comparison one can see that the quantity of zinc in the second structure is approximately twice higher than its quantity in the first one. The results of fit of these spectra are shown in Fig. 2, b (for visual clarity, only the data for 2p_{3/2}-sublevel are present). The experimental points are shown by round symbols. The results of the quantitative analysis are indicated by solid lines. Even without the fit one can notice that both maxima in Fig. 2, b have, strictly speaking, asymmetrical shape: their „center of gravity“ is somewhat displaced to the area of lower energies. This means that the spectra can not be described with the help of the only spin-orbit doublet, and each film structure includes inequivalent atoms of zinc with different environment. Indeed, according to the conducted analysis, for the reproduction of the fine structure of the spectra in Fig. 2, two components are necessary. One of them, (ξ_1), is found at energy of ~ 1021.7 eV (Fig. 2, b). It is necessary for the precise adjustment of the low-energy „tail“ of the lines. The other component (ξ_2) is found in the area of energies of ~ 1023.4 – 1023.5 eV. Its shift relative to ξ_1 is ~ 1.7 – 1.8 eV. The values of Gaussian broadening ξ_1 and ξ_2 are equal to 1.16 and 1.48 eV respectively. Therefore, Zn atoms introduced into film structures 1 and 2 can exist in two chemical states.

The position of peak ξ_1 at the energy scale corresponds to the emission from metal zinc [28]. In the studied samples the Zn atoms may in principle interact with atoms of Sb, Ga and/or O. The electronegativity of Sb (2.05) and Ga (1.81) atoms would not differ much from a similar value for Zn (1.65). This means that when bonds are formed between these atoms, for example Zn-Sb, no substantial transfer of the charge would likely happen, and, therefore, the binding energy of 2p-level of zinc atoms surrounded by atoms of Sb and/or Ga, should not differ too much (within the model of the initial state) from a similar energy for the metallic zinc.

A different situation should be expected in the case when Zn atoms form bonds with O atoms. Substantial difference in their electronegativity (1.65 and 3.44 accordingly) must provide for the substantial transfer of the charge from the metal to oxygen. This should result in noticeable decrease of 2p-level in zinc atoms and, therefore, to shift of the existing

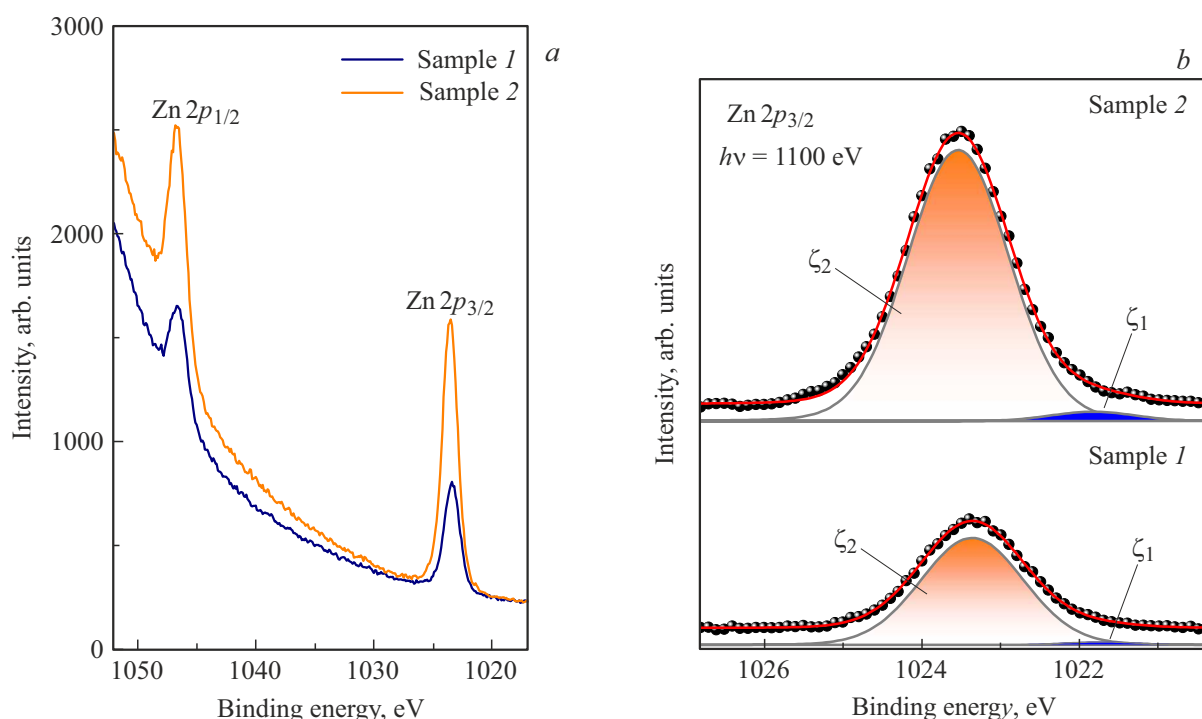


Figure 2. (a) Spectra of 2p-level of Zn and (b) results of their fitting for samples 1 and 2. The chart (b) contains data only for the $2p_{3/2}$ -sublevel. Photon energy is $h\nu = 1100$ eV. Other details are available in the text.

component in the photoelectronic spectra towards higher bond energies.

From the analysis that has just been made, one can easily understand the atomic nature of ζ_1 and ζ_2 components. The first can be assigned to the Zn atoms, which are surrounded with atoms of the substrate and do not engage in the exchange interaction with oxygen. The second one corresponds to the Zn atoms, which form bonds with O atoms. The ratio of peak intensities of ζ_1 and ζ_2 in Fig. 2, b is equal to 1:42 for structure 1 and 1:34 for structure 2. One can draw a conclusion then that almost all atoms of the diffused impurity in the film structures react with oxygen and form an oxide. Such conclusion is not surprising. The strength of Zn-O bonds significantly exceeds the strength of Zn-Zn bonds: the energy of rupture of the former (65 kcal/mol) is much higher than of the latter (4.4 kcal/mol) [29]. This means that the formation of the zinc oxide in the studied structures is energetically favorable. The absence of other components that depend on the bonds of Zn atoms with oxygen indicates that the positions of such atoms are identical. Seemingly, this is related to the fact that the only stable zinc oxide at temperatures of $\geq 200^\circ\text{C}$ is ZnO [30]. The useful properties of this oxide were previously noted for GaAs [31]. This compound is stable, optically transparent, and its ultrafine layers passivate the surface of the semiconductor. Besides, the zinc diffusion is a simpler and less expensive method than the atomic layer deposition, used in paper [31] for ZnO growth.

Now let us proceed to the comparison of the fine structure of 3d-spectra of Ga and Sb for samples 1 and 2. In order to interpret them correctly, let us first consider similar spectra for a single crystal substrate GaSb(100), the surface of which contains no foreign atoms, and the same substrate covered with an oxide film. Such spectra and their interpretation can be found in paper [15]. Let us briefly list the main features. In the ultrahigh vacuum the clean GaSb(100) surface has a reconstruction with the (4×3) unit cell [32,33]. This fact noticeably influences the type of photoelectronic lines. The Sb 3d spectrum for such substrate includes four spin-orbit doublets. One of them is provided for by Sb atoms, which form bonds with Ga atoms in the crystal bulk (bulk component, bond energy ~ 528.2 eV). Another doublet is provided for by Sb atoms, which are bonded to the Ga atoms on the surface (its surface shift relative to the bulk component is -0.7 eV). Other doublets are provided for by Sb atoms surrounded with similar atoms, on the surface and in the bulk (Sb-Sb bonds). Their energy shifts are 0.35 and 0.8 eV respectively.

A similar, even though a somewhat simplified situation was observed for Ga 3d-spectra [15]. They include a bulk component (Ga-Sb bonds in the crystal bulk) and a surface component (Ga-Sb bonds on the surface) with a shift equal to 0.66 eV.

After a layer of oxide is formed on the GaSb(100) surface (in [15] it was developed by filling of O_2 into the vacuum system, the dose was 10^3 – 10^5 Langmuir (L), and temperature of the substrate was varied from $\sim 23^\circ\text{C}$

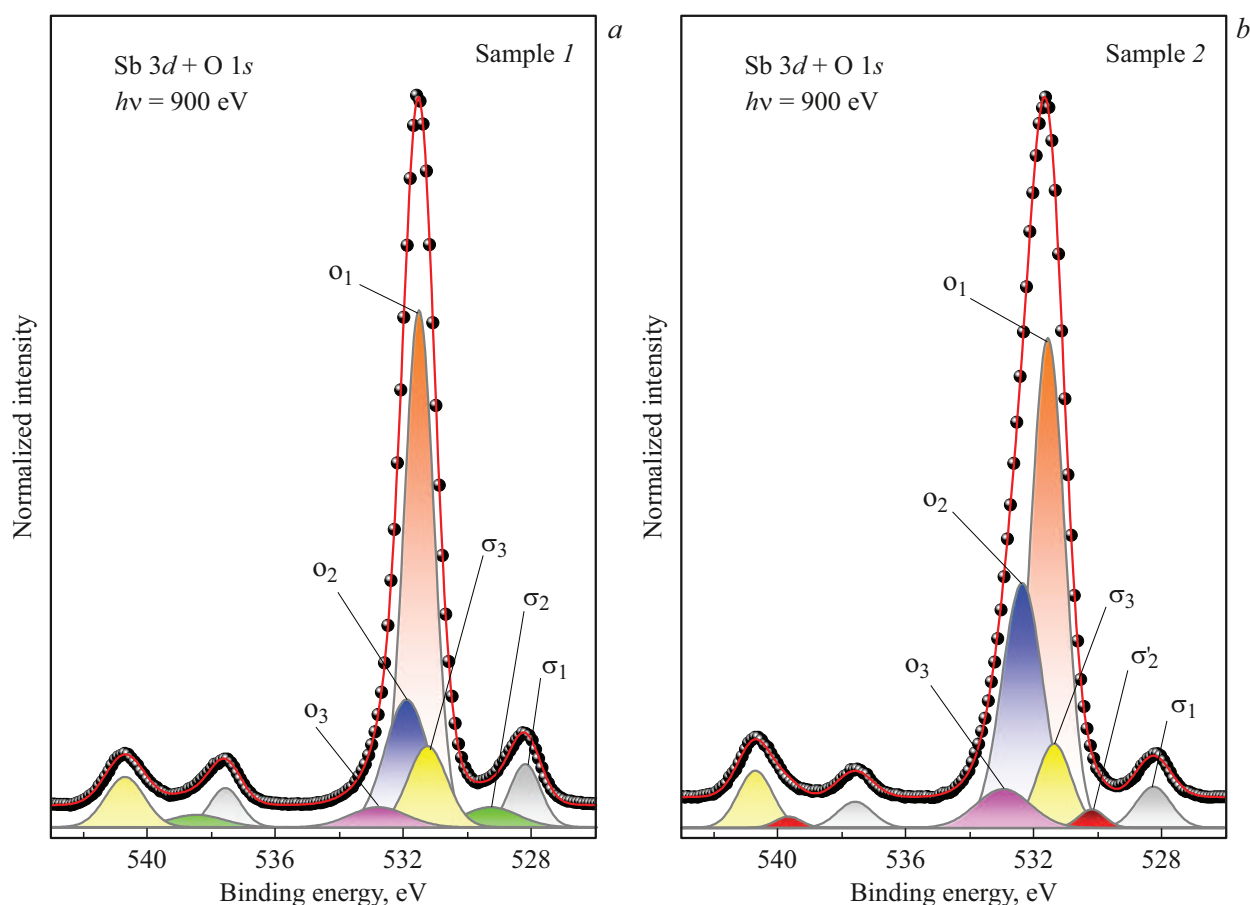


Figure 3. Normalized spectra of Sb 3d- and O 1s-levels and results of their fitting for various film structures: *a* — sample 1, *b* — sample 2.

to 300°C), the spectra appearance underwent significant changes. First of all, new components appeared in them, which were provided for by bonds of Sb and Ga atoms with oxygen. Three new doublets were found in Sb 3d spectra, and these doublets were shifted by 1.9–3.2 eV towards higher energies relative to a bulk component. They were interpreted as emission from antimony atoms in the surface phases with mean stoichiometry of Sb_2O_3 , Sb_2O_4 and Sb_2O_5 . Besides, at ~ 531 –533 eV the Sb 3d spectrum had 1s-line of oxygen imposed upon it, including three singlets (their shifts relative to $3d_{5/2}$ -sublevel of the bulk component of Sb were 2.5–4.3 eV). These peaks were assigned to various O atoms, bonded to Ga and/or Sb atoms.

In the Ga 3d-spectrum after formation of an oxide film, two new components appeared due to Ga-O bonds with chemical shifts of 0.9 eV (surface phase of Ga_2O) and 1.4 eV (surface phase of Ga_2O_3). As in the case of antimony, such spectrum overlapped with the line of oxygen (O 2s). This line was formed by three singlets with shifts in the interval of ~ 3.1 –5.0 eV (the count started from the position of $3d_{5/2}$ -sublevel of the bulk component of Ga). The specified singlets were assigned to O atoms in a different environment of Ga and/or Sb atoms. More detailed information can be found in [15].

The normalized Sb 3d and O 1s spectra obtained in this paper for 1 and 2 film structures are presented in Fig. 3. For structure 1 (Fig. 3, *a*) to precisely reproduce the shape of the line, three spin-orbit doublets σ_1 – σ_3 are required, which are provided for by emission from antimony atoms, as well as three singlets σ_1 – σ_3 , which are provided for by emission from oxygen atoms. Their energy shifts are given in Table 1. The need to use σ_1 – σ_3 doublets in the expansion results from the analysis of the spectral line in the energy range of 536–541 eV. Under such energies the spectrum depends on emission from $3d_{1/2}$ -sublevel of Sb atoms, and O atoms do not contribute. As for σ_1 – σ_3 singlets, they are required to reproduce the maximum at 531–532 eV. Therefore, the optimal pattern of spectrum expansion in Fig. 3, *a* includes six components. This means that in film structure 1 there are at least three inequivalent Sb atoms and three inequivalent O atoms.

The position of σ_1 component on the energy scale is very close to the position of the bulk component for clean GaSb(100) substrate. Based on this, σ_1 can be assigned to atoms of antimony, which are bonded to zinc and/or gallium atoms (Table 1). Components σ_2 and σ_3 are displaced relative to σ_1 towards higher values of energy, and their shifts are equal respectively to 1.0 and 3.1 eV. The

Table 1. Components identified in spectra in Fig. 3, their energy shifts and suggested atomic nature. For oxygen the shifts of singlets σ_1 , σ_2 and σ_3 are counted from the position of $3d_{5/2}$ -sublevel of the spin-orbit doublet of σ_1 in the antimony spectra. The Gaussian broadening of Sb $3d$ -components, except for σ_2 , is equal to ~ 1.2 – 1.3 eV. For σ_2 it is 2.0 eV. For singlets of oxygen σ_1 , σ_2 and σ_3 the broadening is equal to 1.2, 1.6 and 2.0 eV respectively

Sample 1			Sample 2		
Component	Shift, eV	Atomic nature	Component	Shift, eV	Atomic nature
σ_1 (Sb $3d$)	0	Sb-Zn(Ga)	σ_1 (Sb $3d$)	0	Sb-Zn(Ga)
σ_2 (Sb $3d$)	1.0	Sb-Sb	σ_2' (Sb $3d$)	1.9	Sb-O (Sb_2O_3)
σ_3 (Sb $3d$)	3.1	Sb-O (Sb_2O_5)	σ_3 (Sb $3d$)	3.1	Sb-O (Sb_2O_5)
σ_1 (O $1s$)	3.3	O-Ga	σ_1 (O $1s$)	3.3	O-Ga
σ_2 (O $1s$)	3.8	O-Zn	σ_2 (O $1s$)	4.0	O-Zn
σ_3 (O $1s$)	4.6	O-Sb	σ_3 (O $1s$)	4.7	O-Sb

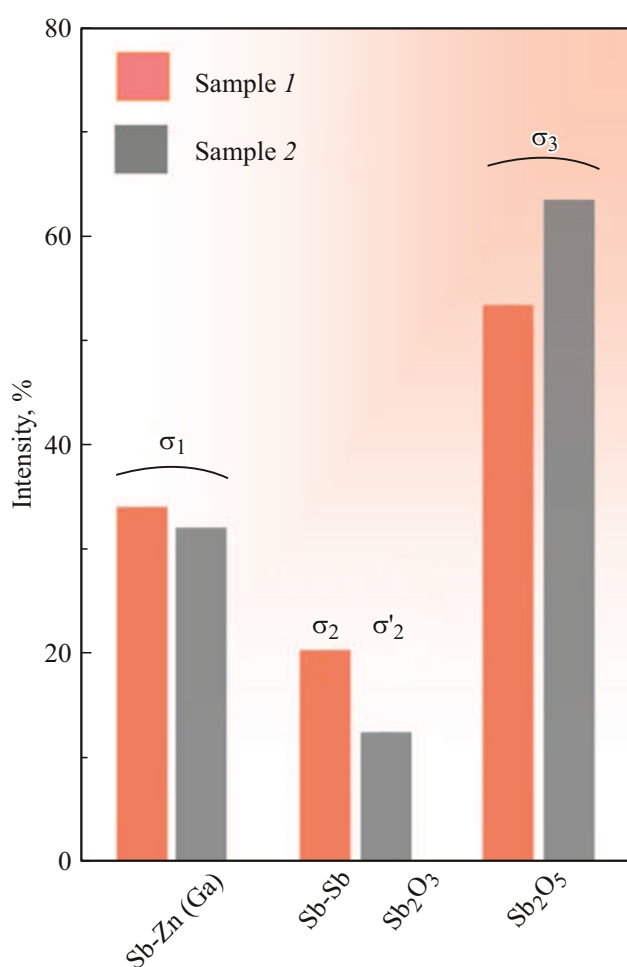


Figure 4. Ratio of component intensities in Sb $3d$ -spectra for samples 1 and 2. The intensity is given as percentage ratio.

comparison of these values with the shifts in paper [15] justifies the assumption that the first of these components is provided for by atoms of antimony surrounded by the same atoms (Sb-Sb, metallic antimony), and the second one — by antimony atoms surrounded by oxygen atoms in the surface phase (Sb_2O_5). It should be noted that the spectrum

contains no components that could have been assigned to the (4×3) surface reconstruction. This result is not surprising. It indicates that the oxide film is entire and fully covers the substrate surface, resulting in the disappearing of (4×3) reconstruction.

The spectrum of sample 2 (Fig. 3, *b*) also includes six components, three of which are provided for by Sb atoms, and the rest — by O atoms (Table 1). Among them two spin-orbit doublets (σ_1 and σ_3) are observed at the same energies as the corresponding components in Fig. 3, *a*. Therefore, one can assume that the atomic origin of σ_1 and σ_3 doublets in both structures is similar. Component σ_2' in Fig. 3, *b* has a shift of 1.9 eV, and its analog in structure 1 (Fig. 3, *a*) is absent. Taking into account the position in the energy scale, σ_2' can be interpreted as the emission from antimony atoms present in the surface phase of Sb_2O_3 [15]. Therefore, Sb $3d$ -spectra in Fig. 3 indicate that film structures 1 and 2 have a different phase composition, and antimony atoms in them — inequivalent chemical environment. The ratio of intensities of Sb $3d$ -components for each sample is presented in the form of a histogram in Fig. 4. It can be concluded from it that when going from sample 1 to sample 2 the antimony atoms to a larger extent become coordinated with the oxygen atoms. It should also be noted that the phase of the metallic antimony (σ_2 component in Fig. 3, *a*) is observed only for structure 1. It is absent in structure 2. From the practical point of view the presence of multiple Sb-Sb bonds causes reduction in the characteristics of devices, since the formation of such bonds is accompanied by the formation of electronic states of donor type in the band gap and pinning of Fermi level [34]. As it is shown above, the method of anode oxidation prevents the decrease in the antimony oxidation degree in the dielectric/GaSb structure and makes it possible to successfully eliminate such bonds in the near-surface area of the sample. It seems that the formation of zinc oxide in anode oxidation makes it possible to also eliminate the Fermi level pinning in the GaSb band gap as it was observed for $\text{Al}_2\text{O}_3/\text{GaSb}$ structures in [34].

Components σ_1 , σ_2 and σ_3 in Fig. 3 have the same or very close shifts for both samples (Table 1). The component with

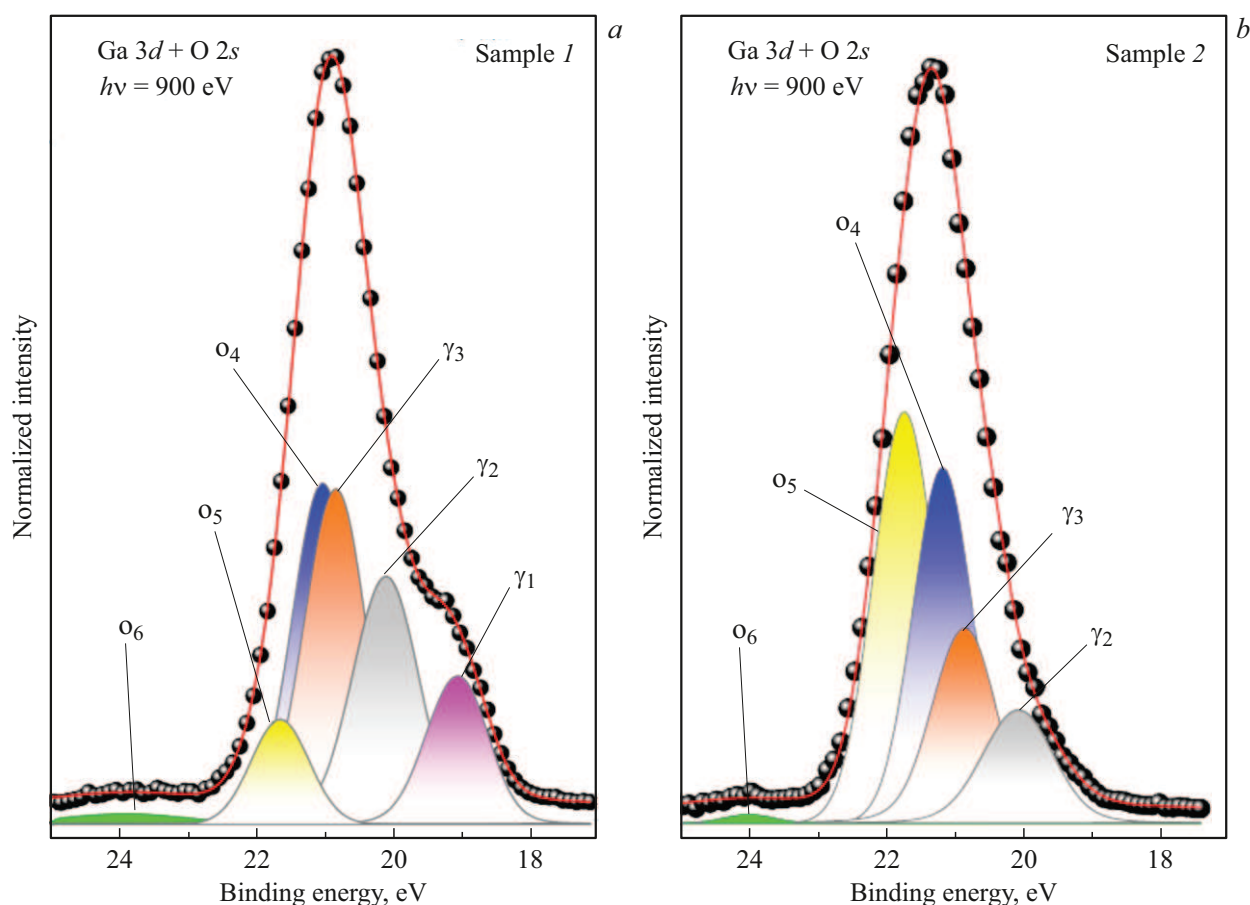


Figure 5. Normalized spectra of Ga 3d- and O 2s-levels and results of their fitting for various film structures: *a* — sample 1, *b* — sample 2.

the highest energy value (o_3) can be assigned to oxygen atoms that form bonds with Sb atoms, and the component with the least value (o_1) — to oxygen atoms that form bonds with Ga atoms. Such interpretation fully agrees with the conclusions of paper [15]. As for singlet o_2 , it is logical to bring it in compliance with oxygen atoms interacting with zinc atoms. As seen in Fig. 3, when going from structure 1 to structure 2 this singlet increases noticeably, which supports this interpretation. One can also assume from the comparison of intensities of O 1s-components in Fig. 3 that after diffusion of zinc the near-surface areas in both structures become depleted of antimony and enriched with gallium. Most likely, Sb atoms at the same time are removed from the samples. More detail about this will be provided further.

Spectra of Ga 3d- and O 2s-levels are presented in Fig. 5. For sample 1 (Fig. 5, *a*) the emission from Ga atoms consists of three components γ_1 – γ_3 (Table 2). As in the case of antimony, their interpretation is based on the results of paper [15]. The component γ_1 (bond energy 19.1 eV) corresponds to the atoms, whose closest neighbors are Sb atoms and which do not interact with O atoms. Two other components shifted to the higher binding energies can

be assigned to atoms bonded to oxygen in oxide phases of Ga_2O (γ_2) and Ga_2O_3 (γ_3).

For sample 2 only γ_2 and γ_3 components are observed, and γ_1 is absent. Most likely this is related to a higher concentration of zinc and oxygen atoms in the film structure and, therefore, to the increase in the thickness of the surface film of oxide that fully screens the Ga atoms bonded with antimony. The distribution of γ_1 – γ_3 components by intensity in two samples is shown in Fig. 6. There you can see that except for γ_1 component, the film structures 1 and 2 have a close phase composition. The dominant phase in the oxide films of these structures is Ga_2O_3 sesquioxide. At the same time Ga_2O_3 is not harmful for the devices based on A_3B_5 compounds [35–37].

O 2s spectra for samples 1 and 2 include three o_4 – o_6 components (Table 2). o_6 has a shift equal to 5.0 eV, and, according to data of [15], can be assigned to oxygen bonding with antimony. The intensity of this component is very low. This confirms the previous conclusion on depletion of antimony in the surface layers. Shifts and intensities of two other components make it possible to presume that o_4 and o_5 are provided for by O atoms bonded with gallium and zinc respectively. The peak intensity of o_5 for

Table 2. Components identified in spectra in Fig. 5, their energy shifts and suggested atomic nature. For oxygen singlets o_4 , o_5 and o_6 the shifts are counted from the position of $3d_{5/2}$ -sublevel of the spin-orbit doublet of gallium γ_1 for sample 1. The Gaussian broadening of Ga $3d$ -components is equal to $\sim 0.8 - 0.9$ eV. For oxygen singlets o_4 and o_5 it amounts to ~ 1.0 eV, and for $o_6 - 2.0$ eV

Sample 1			Sample 2		
Component	Shift, eV	Atomic nature	Component	Shift, eV	Atomic nature
γ_1 (Ga $3d$)	0	Ga-Sb		—	
γ_2 (Ga $3d$)	1.0	Ga-O (Ga_2O)	γ_2 (Ga $3d$)	1.0	Ga-O (Ga_2O)
γ_3 (Ga $3d$)	1.8	Ga-O (Ga_2O_3)	γ_3 (Ga $3d$)	1.8	Ga-O (Ga_2O_3)
o_4 (O $2s$)	2.1	O-Ga	o_4 (O $2s$)	2.2	O-Ga
o_5 (O $2s$)	2.7	O-Zn	o_5 (O $2s$)	2.8	O-Zn
o_6 (O $2s$)	5.0	O-Sb	o_6 (O $2s$)	5.0	O-Sb

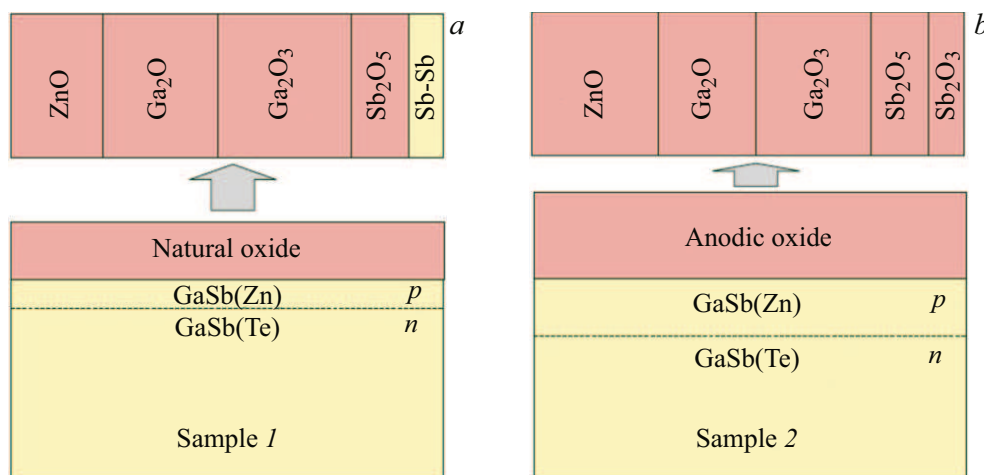


Figure 7. Phase composition of oxide films in samples: *a* — 1 and *b* — 2. The diagram shows the properties of film structures qualitatively, but not quantitatively.

sample 2 noticeably exceeds the intensity of a similar peak for sample 1, which agrees with the above results.

Another important conclusion from the results in Fig. 5 is the fact that in Ga $3d$ -spectra there are no components that could have been assigned to metallic gallium. Indeed, from the energy point of view, formation of Ga-Ga bonds (energy of rupture of 32 kcal/mol) is less beneficial than formation of Sb-Sb, Sb-O and Ga-O bonds (energies of rupture 70, 92 and 90 kcal/mol respectively) [29].

The obtained results can be generalized as two diagrams that represent schematically the phase composition of the studied film structures. They are shown in Fig. 7. As shown in them, zinc diffusion into oxide/GaSb structures causes qualitative transformation of film surfaces: the considerable fraction in it after diffusion is taken by ZnO compound, having good passivating properties. Besides, the fraction of antimony oxides without such properties decreases substantially. The latter can create the centers of recombination and scattering in the band gap of gallium antimony. Therefore, the active formation of ZnO in process of diffusion makes it possible to decrease the quantity of these oxides that are harmful for optoelectronic devices, and

the presence of thick anodized films on the GaSb surface reinforces this effect.

Conclusion

Using high-resolution PES with application of the synchrotron radiation, the structures were studied for photovoltaic converters obtained by zinc diffusion into GaSb through the films of natural and anode oxides. The quantitative analysis of Zn $2p$ -spectra showed that the method to develop such a film determines the quantity of zinc atoms embedded into the sample, and that practically all atoms of the impurity form a compound with oxygen in the near-surface area. From the analysis of Sb and Ga $3d$ -spectra and O $1s$ - and $2s$ -spectra, the conclusions were made on the phase composition of oxide films. In particular, it was shown that the anode treatment makes it possible to eliminate the Sb-Sb bonds, and the diffusion of zinc — to considerably decrease the antimony content. At the same time the introduction of zinc and method of oxide layer growth will practically not impact the compounds of gallium atoms. The obtained data confirm the useful

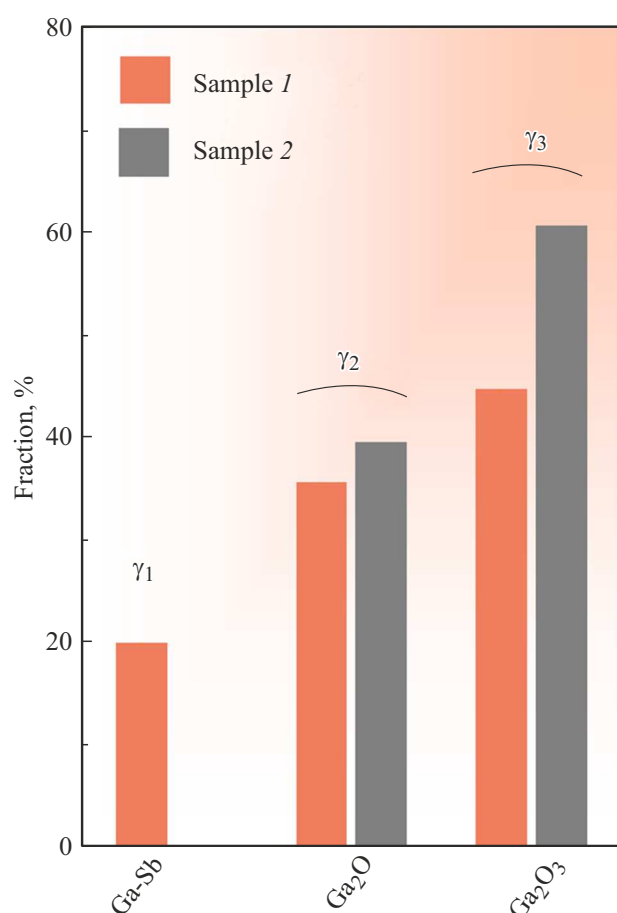


Figure 6. Same as in Fig. 4, but for Ga 3d-spectra.

role of anode treatment of GaSb substrates and explain the important aspects in zinc introduction into such structures, which should be taken into account when developing semiconductor technology. Seemingly, such trends are applicable to other A_3B_5 semiconductors, which opens new opportunities for the improvement of the characteristics of a wide class of optoelectronic devices. Besides, the given results demonstrate a high potential of the PES method using synchrotron radiation for the diagnostics of the device structures.

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Conflict of interest

The authors declare no conflict of interest.

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