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EFFEKT OF ADSORBED Ge ATOMS ON THE PHOTOEMISSION PROPERTIES OF GaAs

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ВПЛИВ НА ФОТОЕМІСІЙНІ ВЛАСТИВОСТІ МОНОКРИСТАЛІВ GaAs АДСОРБОВАНИХ АТОМІВ Ge

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A₃B₅ semiconductor compounds in the future are the most promising for further detailed consideration. In this regard, gallium arsenide is a semiconductor compound formed by elements of groups III and V of the periodic system – gallium Ga and arsenic As. Gallium arsenide and its surface properties attract much attention of researchers due to the possibility of its wide application in micro- and nanoelectronics technology. Despite numerous studies of the surface of semiconductors, many issues related to its properties and processes at the interface between two phases remain insufficiently clarified, especially in terms of the effect of the surface state on the energy spectrum of electrons in crystals. Interest in these issues is constantly growing not only from a scientific point of view, but also from a practical one, in connection with the development of semiconductor micro- and nanotechnologies. The development of its sections such as thin-layer nanoelectronics and optoelectronics, devices with MIS structures and charge coupling, cold cathodes and efficient photocathodes require an understanding of the processes in the near-surface layer of a semiconductor both with a free surface and with this free surface during the adsorption of other substances on it. This is also important for elucidating the possibility of changing the surface and near-surface properties of solids in a quite definite way. Gallium arsenide is the closest binary analog of germanium. By introducing appropriate impurities, gallium arsenide can be obtained with both n-type and p-type conductivity with different current carrier concentrations. This structure belongs to the crystallographic class of the cubic system, like germanium. Gallium arsenide and germanium crystallize in the structure of zinc blende. In view of the foregoing, it is interesting to study the influence of adsorbed germanium layers on the surface properties of gallium arsenide single crystals of various types of conductivity by photoemission method in ultrahigh vacuum. The questions of the influence of these coatings not only on the emission properties of gallium arsenide single crystals, but also the influence of these adsorbed germanium atoms on the energy structure in the near-surface region of single crystals are considered.

Key words: photoemission, quantum yield, electron energy distribution, spectral analysis, work function, electron affinity, band bending, semiconductors.

Introduction. Gallium arsenide and its surface properties attract much attention of researchers due to the possibility of its wide application in micro- and nanoelectronics.

Despite numerous studies of the surface of semiconductors, many issues related to its properties and processes at the interface between two phases are still insufficiently clarified, especially regarding the effect of surface conditions on the energy spectrum of electrons in crystals.

Formulation of the problem. Interest in these issues is constantly growing not only from a scientific point of view, but also from a practical point of view - in connection with the development of semiconductor micro- and nanoelectronics. The development of such sections of it as thin-layer nanoelectronics and optoelectronics, devices with MIS structures and charge coupling, cold cathodes and efficient photocathodes, etc. require an understanding of the processes in the near-surface layer of a semiconductor both with a free surface and with adsorption of other substances on its surface. This is also important for elucidating the possibility of changing the surface and near-surface properties of solids in the desired way.

It follows from the foregoing that the adsorption of foreign atoms on the surface of GaAs single crystals has a significant effect on photoemission. However, the influence of coatings on the properties of the surface layer of gallium arsenide and on the structure of the electron energy spectrum has not yet been sufficiently studied: it has not been clarified to what extent different coatings affect band bending and electron affinity, which is essential for elucidating a method for reducing the work function of photoelectrons. The choice of such coatings is due to the fact that various substances (metals, dielectrics, semiconductors) differ significantly in their physicochemical properties, and therefore their presence on the surface of a solid should have a different effect both

on the properties of the surface of semiconductors and on the structure of zones in the near-surface areas.

Analysis of recent research and publications. By changing the conditions on the surface, for example, by depositing foreign atoms, it is possible to influence the properties of the near-surface layer. Studies show that the adsorption of a substance on a solid substrate leads to various changes in the characteristics of the solid surface, such as the work function [1, 2], current carrier mobility in the near-surface layer [3], photoemission properties [4–6], etc. These changes occur both as a result of the appearance of an electric field layer in the layer of the near-surface volume charge, and as a result of a change in the electronic structure of a solid near the surface.

The study of the surface of solids and its influence on the physical properties of the latter is carried out by various methods: optical, slow electron diffraction, field effect, studies of the contact potential difference, electron spectroscopy, and photoemission. Each of these methods has its own advantages and disadvantages [7]. However, the advantage of the photoemission method is that it allows obtaining more information about the energy spectrum of electrons in semiconductors and, thus, makes it possible to follow the changes in this spectrum with changing surface conditions.

Especially a lot of recent work has been devoted to studying the effect of adsorption of Cs, Cs-O [8–10] on the surface properties of gallium arsenide by the photoemission method. This is due to the fact that in this case an effective emitter with a negative electron affinity is obtained [11–13]. However, most of these studies are purely practical and do not pay due attention to the elucidation of the surface properties of gallium arsenide.

The high efficiency of photoemission from p-type GaAs heavily doped with zinc ($p \approx 1 \cdot 10^{19} \text{ cm}^{-3}$) upon adsorption of Cs-O is due to the negative electron affinity that arises in this case [13], however, the high photoemission efficiency p-type GaAs samples with a much lower level of germanium doping ($p \approx 5 \cdot 10^{17} \text{ cm}^{-3}$) were also observed with the same surface treatment of Cs and O [14].

Isolation of previously unsolved parts of the general problem to which this article is devoted. It can be assumed that the high efficiency of photoemission in p-type GaAs samples doped with germanium could be due either to the effect of germanium on the bulk properties or to the special conditions formed on the surface of gallium arsenide due to the presence of germanium atoms there.

Formulation of the problem. In this regard, it is of interest to find out how the adsorption of germanium atoms affects the photoemission from samples of gallium arsenide single crystals of various types of conductivity.

Purpose of the article. Photoemission methods were used to study the effect of adsorption of germanium atoms on the properties of the near-surface layer of gallium arsenide, as well as on the structure of the energy spectrum of electrons:

a) spectral distribution of the photoemission quantum yield $Y(h\nu)$;

b) energy distribution of photoelectrons $N(E)$.

Research result. The studies were carried out in a nanometric ultra-high-vacuum photoelectron spectrometer [15] on GaAs samples (both n-type and p-type), the physical parameters of which are presented: – concentrations of current carriers, respectively, for each used n-type sample: $5 \cdot 10^{15} \text{ cm}^{-3}$, $1,24 \cdot 10^{17} \text{ cm}^{-3}$, $3,1 \cdot 10^{17} \text{ cm}^{-3}$ and p-type sample $1,4 \cdot 10^{19} \text{ cm}^{-3}$; mobility of the samples respectively: $4350 \text{ cm}^2/\text{V} \cdot \text{sec}$, $4000 \text{ cm}^2/\text{V} \cdot \text{sec}$, $3200 \text{ cm}^2/\text{V} \cdot \text{sec}$, $42,3 \text{ cm}^2/\text{V} \cdot \text{sec}$; resistivity: $1,16 \cdot 10^{-2} \text{ Ohm} \cdot \text{cm}$, $3,84 \cdot 10^{-3} \text{ Ohm} \cdot \text{cm}$, $9,47 \cdot 10^{-3} \text{ Ohm} \cdot \text{cm}$, $4,6 \cdot 10^{-3} \text{ Ohm} \cdot \text{cm}$. The orientation of the planes was controlled by the X-ray diffraction method, and the deviation from the indicated direction did not exceed 3° . For each of the four: 1n - (110); 2n - (110); 3n - (111); 4p - (110) of the investigated samples, the emitting planes were ground and chemically polished in a mixture of $1(\text{H}_2\text{O}_2):3(\text{H}_2\text{SO}_4):1(\text{H}_2\text{O})$.

All studies were carried out at different thicknesses of the germanium coating of the gallium arsenide surface under the same vacuum conditions ($p = 2 \cdot 10^{-9}$ Torr), the results obtained for all samples could be compared with each other. The thickness of the adsorbed germanium layer was determined from the deposition time from a calibrated source. The film thickness during one coating cycle was $\sim 3 \text{ \AA}$, and taking into account the size of germanium atoms (the radius of germanium atoms is $\sim 1.32 \text{ \AA}$), we can assume that the resulting film corresponds to a monolayer coating of the surface of gallium arsenide with germanium.

The deposition source was calibrated using the Tollansky interference method to measure the thicknesses of the evaporated germanium layers.

1) Spectral distribution of the quantum yield of electrons from GaAs when its surface is coated with germanium.

For all coatings, the spectral distribution of the photoemission quantum yield $Y(h\nu)$ was measured. The results of such measurements for sample 2n are shown in Fig. 1. It can be seen that the adsorption of germanium on the surface of gallium arsenide increases the quantum yield (curve 2). The maximum quantum yield is observed at coverage levels $\theta = 2$ monolayers. And when the degree of coverage is already $\theta = 3$ monolayers, the quantum yield begins to decrease.

Structural features are not observed on the curves under consideration, and no noticeable change in the long-wavelength photoemission boundary is found either.

The found value of the photoemission threshold (from the extrapolation of $Y^{1/3}$ from $h\nu$) for sample 2n was $h\nu_0 = 4.24 \text{ eV}$. Such an insignificant decrease in the photoelectronic work function cannot explain the observed increase in the quantum yield.

The relative increase in the quantum yield $(Y_{\text{Ge}} - Y)/Y$ depending on the photon energy (curves 4, Fig. 1.) differs significantly from the corresponding dependence

es in the case of GaAs surface coating with Ba and O [16] and is selective. At photon energies corresponding to interband transitions in ($h\nu = 4.6$ eV and $h\nu = 4.8$ eV), the greatest increase in the photoemission quantum yield is observed. Such dependences are observed for all studied samples of gallium arsenide coated with germanium.

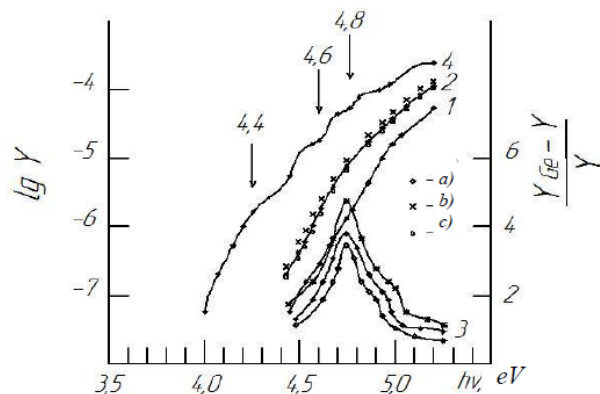


Fig. 1. Spectral distribution of the quantum yield of GaAs (sample 2n):

1 – without Ge coating; 2 – with Ge coating:
a • – 1 monolayer; b × – 2 monolayers; c ○ – 3 monolayers;
4 – spectral distribution when coated with barium
($\theta = 0.5$ monolayer); 3 – relative increase in quantum
yield upon coating

The selective relative increase in the quantum yield of photoemission $(Y_{Ge} - Y)/Y$ when the GaAs surface is coated with germanium shows that the dipole mechanism for reducing the work function in the presence of foreign atoms on the surface does not take place in this case.

When a barium layer ($\theta = 0.5$ monolayer) is deposited on germanium-coated gallium arsenide surfaces, structural features appear (curve 3, Fig. 1) at photon energy: $h\nu = 4.8$ eV; $h\nu = 4.6$ eV and $h\nu = 4.4$ eV, which, as shown [16,17], corresponds to optical transitions in GaAs. This suggests photoemission comes from gallium arsenide.

To elucidate the reason for the increase in the quantum yield $Y(h\nu)$ (curves 2, Fig. 1) upon coating the surface of gallium arsenide with Ge, experimental studies were carried out to study the energy distribution of photoelectrons in samples 2n and 4p.

2) Energy distribution of photoelectrons $N(E)$ from GaAs when its surface is coated with germanium.

The energy distribution of photoelectrons was measured for both uncoated and germanium-coated surfaces of samples 2n and 4p (Fig. 2.). It can be seen that for all degrees of coverage θ , the distributions have two maxima, one of which I corresponds to a direct interband transition in gallium arsenide ($E = 4.6$ eV) and is also observed in the energy distribution of a sample uncoated with germanium. The second maximum II for both studied samples is located at the same energy distance from maximum I. This energy distance is less than

the energy distance between the maxima in curves 4 in Fig. 1. For sample 4p, the intensity of maximum II when coated with germanium $\theta = 2$ is much higher than the intensity of maximum I. For sample 2n, the difference between the intensities of maxima I and II is much smaller.

With a change in the degree of germanium coverage θ , the intensity of maxima I and II changes: with an increase in the intensity of maximum II, the intensity of maximum I decreases. The highest intensity of maximum II is observed at $\theta = 2$ monolayers, but at $\theta = 3$ monolayers, the intensity of this maximum decreases, while the intensity of maximum I increases.

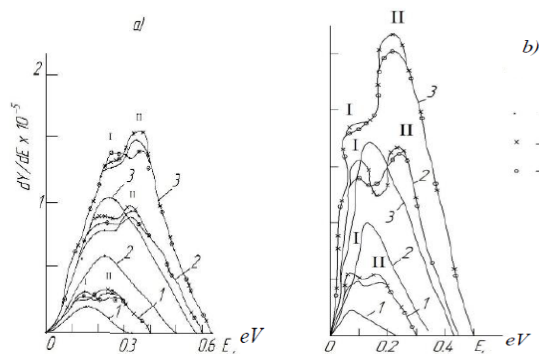


Fig. 2. Energy distributions of photoelectrons for samples 2n(a) and 3p(b). The curves were taken at different photon values $h\nu$, eV:

1 – 4.68; 2 – 4.89; 3 – 4.99 (without germanium coating),
1' – 4.68; 2' – 4.89; 3' – 4.99 (with germanium coating:
a • – 1 monolayer; b × – 2 monolayers; c ○ – 3 monolayers)

As the photon energy $h\nu$ changes, as can be seen from the presented experimental data (Fig. 2.), the maxima of I and II shift along the energy scale so that $\Delta E_{max} \neq \Delta h\nu$. This indicates that the observed electronic transitions are direct. The electronic transition energy corresponding to maximum II on the energy distribution curves is 4.7 eV. There is no transition with such an energy for GaAs.

Such a transition was not found in the study of GaAs with a reduced work function by coating with Ba [18] BaO [19], as well as in the works of other authors.

If we assume that the observed transition is due to the optical excitation of electrons in the germanium layer, then the intensity of this transition, as the degree of coverage θ of the gallium arsenide surface with germanium, should also increase. However, with an increase in the degree of coverage θ , the intensity of this electronic transition decreases, as is observed in the experiment (Figs. 2a and 2b, curves 3'b and 3'c). Therefore, there is no reason to attribute this electronic transition to germanium alone.

The authors in [20] showed the significance of the local action of the electric field on the local electronic structure of a solid. If we assume that in the case of the interaction of germanium with gallium arsenide, a similar effect of germanium atoms on the electronic struc-

ture of gallium arsenide occurs, then the additional maximum may be due to such an effect.

An analysis of the energy distributions, carried out by the method of shifting the energy distributions by the photon energy $h\nu$ (Fig. 3a and Fig. 3b), showed that adsorption of germanium atoms on the surface of gallium arsenide single crystals leads to a slight decrease in the photoelectronic work function. This decrease (Fig. 3a) for sample 2n is due to the shift of the low-energy edge of the distribution $(E_F - L_2) > (E_F - L_1)$, i.e. due to a change in the electron affinity χ . For sample 4p, there is an insignificant shift of the high-energy edge ΔH towards the Fermi level E_F , i. e. the bending of the zones slightly decreases; the low-energy edge of the L_1 distribution shifts so that $(E_F - L_2) > (E_F - L_1)$, and, consequently, for the p-type GaAs sample, the electron affinity χ decreases when germanium is adsorbed on its surface.

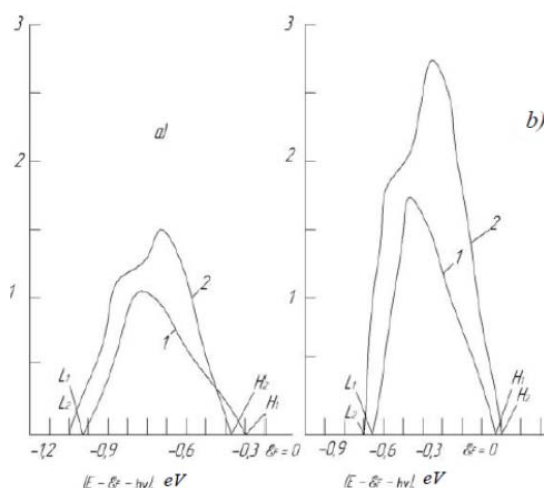


Fig. 3. Energy distributions of photoelectrons shifted by $h\nu$ from (a) 2n and (b) 4p samples. Curves 1 – without germanium coating; 2 – when coated with germanium. Photon energy $h\nu = 4.99$ eV

The energy parameters experimentally obtained for samples 2n and 4p from the spectral distributions of the quantum yield and energy distributions of photoelectrons are presented in Table 1.

It can be seen from the results presented in the table that the decrease in the photoemission threshold $h\nu_0$ and the thermionic work function ϕ_T for n-type GaAs samples upon adsorption of Ge atoms on the surface of gallium arsenide single crystals is due to a decrease in the electron affinity χ . The position of the Fermi level E_F remains almost unchanged. In a p-type GaAs sample, upon adsorption of Ge atoms on the surface of gallium

arsenide single crystals, along with a decrease in the electron affinity χ , there is an insignificant change in the bend of the bands ϕ_0 on the GaAs electron surface.

Thus, the reasons for the appearance and behavior of the second maximum on its surface of Ge atoms have not been finally revealed.

However, the observed increase in the quantum yield at photon energies $h\nu$ corresponding to direct interband transitions in GaAs (Fig. 1, curves 4) and the behavior of the maxima in the energy distributions of photoelectrons with a change in $h\nu$ and the degree of coverage θ (Figs. 2a and 2b) suggest that the interaction of germanium atoms with gallium arsenide atoms leads to a local change in the electronic structure in the semiconductor.

Conclusions.

1. A study of photoemission from GaAs samples of various types of conductivity during adsorption of germanium on its surface was carried out. The adsorption of germanium on the surface of gallium arsenide leads to an increase in the quantum yield $Y(h\nu)$ in the entire region of the studied photon energy spectrum. This increase in $Y(h\nu)$ cannot be explained by the observed decrease in the photoelectron work function ϕ_0 .

The relative increase in the quantum yield upon coating the surface in GaAs with germanium is selective. The largest relative increase in $(Y_{Ge} - Y)/Y$ is observed at the photon energy $h\nu$, which corresponds to direct transitions in GaAs in the Σ direction with an energy of 4.6 eV and the $\Gamma_{15v} \rightarrow \Gamma_{15c}$ transition with an energy of 4.8 eV.

2. In the photoelectron energy distributions, along with a maximum χ corresponding to a transition in GaAs in the Σ direction with an energy of 4.6 eV, an additional maximum with an energy of 4.7 eV is observed. This additional maximum cannot be attributed to the direct transition in GaAs, nor to the transition in Ge.

3. The change in the thermionic work function ϕ_T during the adsorption of germanium on the surface of gallium arsenide is due to a decrease in the electron affinity χ , and in the sample of p-type GaAs, an insignificant decrease in bands is observed.

4. The interaction of germanium with gallium arsenide possibly leads to a local change in the electronic structure in GaAs, which, apparently, leads to the appearance of an additional electronic transition and stimulates an increase in photoemission.

In the future, it is planned to consider this experiment in more detail using additional optical methods for studying the essence of the issue of direct electronic transitions.

Table

№ sample	$h\nu_0$, eV	ϕ_T , eV	$(E_F - E_v)_v$, eV	$(E_F - E_v)_s$, eV	χ , eV	ϕ_0 , eV
2n	4,3	4,13	1,372	0,17	2,90	1,20
2n _{Ge}	4,24	4,06		0,18	2,84	1,19
4p	4,43	4,33	- 0,032	0,10	3,03	- 0,13
4p _{Ge}	4,34	4,23		0,06	2,94	- 0,09

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Черніков М.Г., Чернікова І.Д., Чернікова О.М., Станіславова Н.А. Вплив на фотоемісійні властивості GaAs адсорбованих атомів Ge

Напівпровідникові з'єднання A_3B_5 у перспективі є найперспективнішими для подальшого докладного розгляду. У цьому відношенні арсенід галію є напівпровідниковим з'єднанням, утвореним елементами III і V груп періодичної системи – галієм Ga та миш'яком As. Арсенід га-

лію та його поверхневі властивості привертають велику увагу дослідників у зв'язку з можливістю його широкого застосування у техніці мікро- та наноелектроніки. Незважаючи на численні дослідження поверхні напівпровідників, багато питань, пов'язаних з її властивостями та процесами на межі розділу двох фаз, залишаються недостатньо з'ясованими, особливо щодо впливу стану поверхні на енергетичний спектр електронів у кристалах. Інтерес до цих питань постійно зростає не лише з наукової точки зору, але й із практичної, у зв'язку з розвитком напівпровідникової мікро- та нанотехнологій. Розробка таких її розділів, як тонкошарова наноелектроніка та оптоелектроніка, пристрої з МДП-структурами та зарядовим зв'язком, холодні катоди та ефективні фотокатоди вимагають розуміння процесів у приповерхневому шарі напівпровідника як з вільною поверхнею, так і з цією вільною поверхнею при адсорбції інших речовин на неї. Це важливо і для з'ясування можливості зміни поверхневих та приповерхневих властивостей твердих тіл цілком певним чином. Арсенід галію є найближчим бінарним аналогом германію. Введенням відповідних домішок арсенід галію може бути отриманий з провідністю як *n*-типу, так і *p*-типу з різними концентраціями носіїв струму. Структура арсеніда галію належить до кристалографічного класу кубічної системи, як і германій. Арсенід галію і германій кристалізуються в структурі цинкової обманки. З огляду на сказане вище, цікаво провести вивчення фотоемісійним методом у надвисокому вакуумі вплив адсорбованих шарів германію на поверхневі властивості монок-

ристалів арсеніду галію різного типу провідності. Також розглянуто питання впливу цих покриттів як на емісійні властивості монокристалів арсеніду галію, а й вплив цих адсорбованих атомів германію на енергетичну структуру в приповерхневій області монокристалів.

Ключові слова: фотоемісія, квантовий вихід, розподіл фотоелектронів за енергіями, робота виходу, загин зон, електронна спорідненість, напівпровідники

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