# Physics and Technology of Heterosystems with Films of Germanium and Germanium with Gallium

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Thin films of germanium and germanium with 1.05 % gallium are prepared by thermal deposition in vacuum on gallium arsenide substrates. The thickness of the films was 1  $\mu$ m, the thickness of the substrates was 300  $\mu$ m, the growth rate of the films was 1.75 Å/s. The studies were carried out by methods of profilography of the film surface, absorption spectroscopy and electroreflectance of light. In the films and at the interface, the band gap, the spectral broadening parameters, the energy relaxation time of the light-excited charge carriers, and the mechanical stresses were determined. The additional germanium-gallium interface boundary has been identified. The tensile stresses 6.8  $\cdot 10^8$  Pa on it were greater than the compressive stresses 2.6  $\cdot 10^8$  Pa at the film-substrate interface.

**Keywords:** Heteroepitaxy, Internal mechanical stresses, Absorption and electroreflectance, Band structure, Electronic parameters of the films and substrate.

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# 1. INTRODUCTION

Physical properties of heterosystems are not the sum or averaging of the properties of the film and the substrate. They acquire new properties, because mechanical stresses and additional electronic states appear on the film-substrate interface. This changes the band structure of the film and substrates, their electronic and optical properties.

Ge/GaAs heterosystems are used in electronic and sensing technology for the production of photodetectors, temperature and deformation sensors, as well as magnetic field ones [1, 2]. Germanium films on gallium arsenide are also used to create resistance thermometers that cover the temperature measurement range from 0.03 to 500 K, and for creation of bolometers [2]. Improvement of the existing and creation of new types of sensors based on Ge/GaAs heterostructure require the development of new technologies for their manufacture. The physical properties of fullerenes C<sub>60</sub> and fullerenes with the addition of metals (Ti, Cu) on glass and silicon substrates were investigated in [3] by methods of profilography of film surfaces, atomic force microscopy, spectroscopy of absorption and electroreflectance of light. The films were obtained by thermal evaporation of metal and fullerenes simultaneously from various sources of evaporation. In heterosystems with metal-fullerene films, two interfaces were found: film-metal and filmsubstrate. They had different parameters of band structure and a different sign of mechanical stress. At the metal-fullerene interface they were stretching, and at the film-substrate interface, compressive stresses occurred, less tensile stresses. The purpose of our work was to create and study heterosystems with germanium films and the addition of 1.05 % gallium, the determination of their band structure, mechanical stresses and electronic parameters.

# 2. EXPERIMENTAL

#### 2.1 Production of Heterosystems

Germanium films on GaAs (100) substrates were produced in a VUP-5M vacuum unit by thermal evaporation in a vacuum of  $10^{-4}$  Pa with a growth rate of 1.75 Å/s. Their thickness was 1 micron, the thickness of the substrate was 300 microns. The thickness of the films was chosen from the considerations that the mechanical stresses in them first decreased with increasing film thickness and did not change after a thickness of 1 µm (Fig. 1). Composite germanium films with 1.05 % gallium were obtained under the same conditions as the germanium film.

But before deposition, the Ga + Ge mixture was annealed for 15 min at 500 °C. After the shutter was closed, the following annealing was performed at 500 °C for 30 min. The termoprobe showed the *p*-type conductivity of the films in both cases.



Fig. 1 – Dependence of the internal mechanical compressive stresses in Ge films on GaAs on the film thickness. The deposition temperature was 300  $^{\circ}\mathrm{C}$ 

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#### 2.2 Methods for the Study of Heterosystems

For the study of heterosystems, a complex of experimental methods was used: the classical spectroscopy of light absorption, the electroreflectance spectroscopy, the measurement of mechanical stresses on bending of heterosystems and on the change of the band gap width in absorption and electroreflectance spectra.

Absorption spectra of the films were measured at room temperature in the region of self-absorption edge. The band gap width in them was determined by intersection of the straight line  $k^2 = f(E)$ , where k is the absorption coefficient of light, and E is the photon energy. By the shift of absorption edge, the sign and the value of the internal mechanical stresses in the films were determined.

### 2.3 Measurement of Mechanical Stresses in Heterosystems

The sign and the value of the mechanical stresses in the films were determined from the bending profile of the heterosystems measured on the P-104 profilometer. The bending of heterosystems up corresponds to the appearance of mechanical compression stresses in films and tensile stresses in the substrates. To determine the value of stress, the Stony formula was used:

$$\sigma = \frac{Ed^2}{6(1-\nu)}Rt,\tag{1}$$

where *E*, *d*, *v* are the Young's modulus, the substrate thickness and the Poisson coefficient of substrate respectively; *t* is the film thickness, *R* is the bending radius of the heterosystem. For gallium arsenide, Young's modulus is 84.8 GPa and Poisson coefficient is v = 0.312 [4].

# 2.4 Spectroscopy of Light Absorption

From the absorption spectra of light in films, the band gap width  $E_g$  was determined by two methods: 1) at the intersection of the line  $k^2 = f(E)$  with the abscissa axis, where k is the absorption coefficient of light and E is the photon energy; 2) at the maximum of the differential absorption curve of light. Both methods gave the same value. The sign and the value of the mechanical stresses in the films were determined by shift of the band gap width of the film in relation to the band gap width of germanium single crystal ( $E_g = 0.798 \text{ eV}$ ).

#### 2.5 Electroreflectance Spectroscopy

Electroreflectance spectroscopy has significant advantages over the classical light absorption spectroscopy. It is more resolution and informative. Electroreflectance signal appears only in the area of direct transitions and disappears when removed from them. The method of electroreflectance provides information on the band structure of semiconductors, the type of surface conductivity, surface and interface perfection, their electronic parameters and mechanical stresses.

Absorption and electroreflectance spectra were measured on our make equipment on the basis of a dual monochromator DMR-4. The results of measurements were automatically output to the monitor screen during the measurement, and a specially designed program allowed determining the band gap width  $E_g$ , the type of conductivity of semiconductors and broadening parameters of the spectra.

Measurements of electroreflectance spectra were carried out in an electrolytic cell with 0.1 normal KCl water solution at room temperature, the modulating voltage did not exceed 0.3 V. The band gap width  $E_g$ , the broadening of the spectra  $\Gamma$ , the energy relaxation time of the light-exited charge carriers  $\tau = \hbar/\Gamma$  were determined by Aspens method. Parameter  $\Gamma$  characterizes the structural perfection of the surface of the film and the substrate at the interface. The value and sign of the mechanical stresses in the films and substrates at the interface were determined by shifting transition energy in the electroreflectance spectra.

# 3. EXPERIMENTAL RESULTS AND THEIR DISCUSSION

The germanium lattice parameter is a = 0.5658 nm, the gallium arsenide lattice parameter is a = 0.5654 nm. The coefficient of thermal broadening in them coincides. Therefore, in films of germanium on GaAs substrates, the mechanical stresses are always compressive. The value of the mechanical stresses in the films and at the film-substrate interface was determined from the absorption and electroreflectance spectra. For direct transitions  $E_0$  to the region above self-absorption edge, the dependence of the absorption coefficient k on the photon energy E has the form  $k^2 \sim E - E_g$ . Here  $E_g$  is the band gap width of the film. The value of  $E_g$  was determined from the intersection of the straight line  $k^2(E)$ with the abscissa (Fig. 2).

In crystals of germanium  $E_g = 0.798 \text{ eV}$ , and in the films it changes under the influence of mechanical compression stresses: it increases with the coefficient  $-17 \cdot 10^{11} \text{ eV/Pa}$ . The band gap width in the films was also determined by the maximum of the differentiated absorption curve of the light (Fig. 3). Both methods showed the same value  $E_g = 0.845 \text{ eV}$ .

Fig. 4 shows the spectral dependence of  $k^2$  for germanium film with gallium. It is seen that under the influence of the compressive stresses that arose in the heterosystem, the edge of the own absorption shifted to the region of greater energies, which is typical for het-



**Fig. 2** – Spectral dependence of  $k^2$  for germanium film on gallium arsenide in the region of  $E_0$  transition

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Fig.  $3-{\rm Determination}$  of the band gap width at the maximum of the differentiated absorption curve



Fig. 4 – Spectral dependence of  $k^2$  for germanium with gallium film

erosystems Ge/GaAs ( $E_g = 0.82 \text{ eV}$ ). Transition with energy of 0.74 eV can also be seen to the left. Its appearance can be explained by the appearance of an additional boundary between germanium and metal.

In the literature, there is no data on the change of the band gap under the influence of internal mechanical stresses in films of germanium. They were known only for crystals. Therefore, we identified them experimentally. For the  $E_0$  transition,  $dE_g/dp = 5 \cdot 10^{-11} \text{eV/Pa}$ . Stretching tension of  $5.8 \cdot 10^9$  Pa was greater than compression stresses of  $4.4 \cdot 10^9$  Pa.

Under the action of mechanical stresses in the region of  $E_0$  transition, degeneracy of light and heavy hole zones was removed and a split of the signal appeared (Fig. 5). The electroreflectance signal in this spectral region is formed by transitions of electrons from the top of the degenerate valence band into the conduction band in the center of the Brillouin zone, and the signal  $E_0 + \Delta_0$  from the split zone – into the conduction band. Here  $\Delta_0$  is the value of the spin-orbit splitting. Its value was 10 meV.

Table 1 shows the electronic parameters of the band structure of the germanium films in the region of  $E_{01}$  and  $E_{02}$  transitions.

In Fig. 6, the electroreflectance spectra of the films in the region of the  $E_1 + \Delta_1$  transition are shown. The value of the stresses in the films is  $1.4 \cdot 10^8$  Pa that coincides with the value obtained from the bending of the films by the surface profilography method. Heterosys-



**Fig. 5** – Electroreflectance spectra of the germanium film (region of  $E_0$  and  $E_0 + \Delta_0$  transitions)

 $\begin{tabular}{ll} {\bf Table 1-} Energy \ parameters \ of \ the \ band \ structure \ determined \ from \ the \ electroreflectance \ spectrum \ in \ the \ center \ of \ the \ Brillouin \ zone \end{tabular}$ 

Parameter	Type of transition			
	$E_{01}$	$E_{02}$	$E_{02} - E_{01}$	$E_0 + \Delta_0$
E, eV	0.84	0.85	0.01	1.142
Г, meV	69	67	_	66
<b>r</b> ·10 <sup>-15</sup> , s	9.5	9.8	-	9.9



**Fig. 6** – Electroreflectance spectra of the germanium films (region of  $E_1$  and  $E_1 + \Delta_1$  transitions)

**Table 2** – Transition energy, broadening parameter and energy relaxation time for transitions in the middle of the Brillouin zone

Parameter	Type of transition			
	$E_1$	$E_1 + \Delta_1$	$\Delta_1$	
E, eV	2.15	2.33	0.18	
Γ, meV	75	89		
<b>r</b> 10 <sup>−15</sup> , s	9	7.4		

tems bent the films up.

Table 2 shows the corresponding data for the  $E_1 + \Delta_1$  transitions.

In crystals and germanium films, the electroreflectance signal in the region of the  $E_1$  and  $E_1 + \Delta_1$  transitions does not split. Transitions with energies above and below the band gap of germanium appear in germanium with gallium films in the region of these transitions.

The tensile stresses in the films exceeded the compressive stresses (Fig. 7).



**Fig.** 7 – Electroreflectance spectra of the germanium with gallium films (region of  $E_1$  and  $E_1 + \Delta_1$  transitions)



**Fig. 8** – Electroreflectance spectra of the gallium arsenide substrate (region of  $E_0 + \Delta_0$  transitions)

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In (Ge+Ga)/GaAs heterosystems, the value of mechanical stresses was determined by the bending of the heterosystem, differing from the value determined by the electroreflectance method. The heterosystem bent the films down. This means the appearance of compressive stresses in the films, and tensile stresses in the substrate. Electroreflectance spectra of GaAs substrates in the region  $E_0 + \Delta_0$  transition are shown in Fig. 8. The band gap of GaAs is equal to  $E_g = 1.758$  eV. Its value, determined from electroreflectance spectra, is 1.806 eV. Thus, compression stresses and high tensile stresses appeared in the substrate.

#### 4. CONCLUSIONS

Heterosystems with thin films of germanium and germanium with 1.05% gallium were obtained by thermal evaporation in a vacuum of  $10^{-4}$  Pa. The thickness of the films was 1 micron, the thickness of the substrate was 300 microns. The experiment included a set of research methods. These are classical absorption spectroscopy, electroreflectance spectroscopy, measurement of the bending profile of heterosystems. The sign and value of the internal mechanical stresses in the films and at the interface in the substrates, the broadening parameters of the spectra and the energy relaxation time of the light-excited charge carriers were determined. The reason for the appearance of additional signals in the optical spectra of heterosystems with Ge + Ga films tensile has been established. In addition to compressive stresses, stresses of greater value arose in them, the sign and value of the bend also changed. Heterosystems bent films down.

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#### Фізика і технологія гетеросистем на основі плівок германію і германію з галієм

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Термічним осадженням у вакуумі на підкладках арсеніду галію отримані тонкі плівки германію і германію з 1,05 % галію. Товщина плівок була 1 мкм, товщина підкладок 300 мкм, швидкість росту плівок була 1,75 Å/с. Дослідження проведені методами профілографії поверхні плівок, спектроскопії поглинання і електровідбивання світла. В плівках і на межі поділу визначали ширину забороненої зони, параметри уширення спектру, час енергетичної релаксації збуджених світлом носіїв заряду і механічні напруження. Виявлено додаткову межу поділу германій-галій. Напруження розтягу на ній 6,8·10<sup>8</sup> Па були більшими напружень стиснення 2,6·10<sup>8</sup> Па на межі поділу плівка-підкладка.

Ключові слова: Гетероепітаксія, Внутрішні механічні напруження, Поглинання і електровідбивання світла, Зонна структура, Електронні параметри плівок і підкладки.