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TiB_2/GaAs and Au-TiB_2/GaAs structural transformations at short-term thermal treatment

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Abstract .The investigations of TiB_2/GaAs and Au-TiB_2/GaAs structural characteristics in dependence on technological regimes of sputtering and TiB_2-film thicknesses as well as structural relaxation processes at short-term thermal annealing were carried out. TiB_2-film on Czochralski-grown (001) GaAs substrates were prepared by the magnetron sputtering in argon atmosphere at growth velocity ~ 5 Å/s and film thicknesses ranging from 10 to 50 nm. Samples were annealed during 1 min at 400, 600 and 800 °C. By using X-ray diffraction methods, it was shown that at our experimental conditions the magnetron sputtering of titanium diboride film causes the titanium and boron solid solutions formation as well as formation of some other phases within an interface region. At short-term thermal annealing the relaxation of mechanical strains, decay of solid solutions, generation of dislocations and their propagation as well as point defects redistribution take place. The processes of structural ordering have non-monotonous temperature dependence and differ for various types of structures.

Keywords: TiB_2 film, GaAs, short-term annealing, diffusion barrier, structural defects.

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1. Introduction

The application of titanium diboride films as protective coats is widely known. It is stipulated by such their properties, as high hardness, high melting point, good thermal and electrical conductivity, resistance to chemical action. Therefore, to use them for contacts in electrical circuits, which operate at high temperatures in aggressive environments, as well as making semiconductor devices for microelectronics products, is rather perspective.

Necessity to provide of solid-state semiconductor device operation reliability and stability, particular by in microwave devices, at high temperatures and under the action of exterior electromagnetic fields requires the improvement of contact properties and causes the investigations of metal - semiconductor structures degradation processes. The state of such structure interface influences on their electrophysical and operational parameters [1]. One of the main reasons of device contact degradation is the diffusion processes near the metal-semiconductor interface, which lead to the shift of interface and increasing of its local heterogeneity. Moreover, the contacts metal - semiconductor are in an thermodynamically non-equilibrium state, and at the high temperature the relaxation processes which are impossible at the room temperatures take place. Therefore, to provide the stability of devices operation, it is necessary to remove both of these factors, and using the short-term thermal annealing and anti-diffusion layers one can develop the way for solution of these problems. The possibility of titanium diboride films application in microelectronics as barrier layers was examined [2-4]. In spite of the considerable amount of articles connected with study of TiB_2 - semiconductor contacts properties (see, for example, [5,6]), the structural aspects of relaxation processes which take place near the interface are not enough investigated.

The present paper is devoted to study of the structural characteristic transformations at short-term thermal annealing of semiconductor device structures, which were obtained using titanium diboride film.

2. Objects of investigations

Samples were obtained by magnetron sputtering in the argon atmosphere at pressure in the chamber $5\cdot10^{-3}$ torr and various currents of sputtering, the growth velocity was approximately 5 Å/s. The sputtering was carried out from separate powder targets. The metal films were sputtered on Czochralski-grown (001) GaAs substrates doped by Te up to the concentration 10^{18}cm $^{-3}$ (the thickness of substrate was 320 microns), the dislocation density was 10^3cm^{-2}. Before sputtering the film, the surface of substrate was photon cleaned by Xe-lamp irradiation. We investigated the set of samples obtained at magnetron sputtering currents 0.3 and 0.4 A, with thickness of films ranging from 10 to 50 nm. The Au-TiB_2/GaAs device structures with Au-film thickness 50 nm also were studied.

Thermal annealing was carried out by halogen lamp irradiation. Samples obtained from one plate were annealed at temperatures 400, 600 and 800°C, during one minute with approximately heating and cooling rate 30 °C/s.

3. Research techniques

Complex of X-ray diffraction methods used for the investigations was as follows: X-ray topography (in transmission and reflection geometry, Cu K_α - radiation); analysis of X-ray double crystals rocking curves and integrated intensity measurements for Bragg reflections corresponding to Cu $K_{\alpha 1}$ and Ag $K_{\alpha 1}$ - radiation (symmetric and ansymmetrical reflections), including quasi-forbidden reflections, which give information concerning point defect transformation; measurements of atomic-plane curvature radius which allow to obtain their shape and planar residual strain distribution; θ - 2θ spectra with using of Cu $K_{\alpha 1}$ - radiation for determination of interface phase composition.

4. Obtained results and discussion

The measurements of substrate atomic planes curvature radius near the contacts (the penetration deep was approximately 16 microns) indicates that all structures were concave at the metal film side, so the metal film was tensed and substrate was compressed. The level of mechanical deformation in investigated samples was estimated according to the relation $\varepsilon = t/2R$, where t is the thickness of a substrate and R is the curvature radius.

The initial structure deformation level depends on thickness of film and sputtering current. For TiB_2/GaAs structures the lowest level of deformation ($1.8\cdot10^{-5}$) was in samples with 10 nm thickness of titanium diboride films, which were obtained at the sputtering current 0.3 A (Fig.1., curve 1). Increasing the sputtering current up to 0.4 Å and, accordingly, the deposition velocity, the initial level of structure deformation increases, too (see Fig.1., curve 2). It is conditioned by more non-equilibrium state of film during the growth process at higher deposition velocity, and so the structural ordering processes are weaker. At increasing TiB_2/GaAs- film thickness up to 50 nm (the deposition current was 0.4 A), the level of mechanical deformation has increased up to $4.2\cdot10^{-5}$ (Fig. 1, curve 3). The planar distribution of mechanical strains in these samples has some propeller-shape character.

When the Au-film was sputtered on these structures (film thickness was 50 nm) the level of deformation decreased down to $1.5\cdot10^{-5}$ (Fig.1, curve 4). The Au-film was compressed and causes the tensile action on the system, which is connected with various values of lattice parameter and differences of thermal expansion coefficients for the contacted materials. The planar stress distribution becomes sinusoidal with arrangement of strain maximums along the <110> direction.

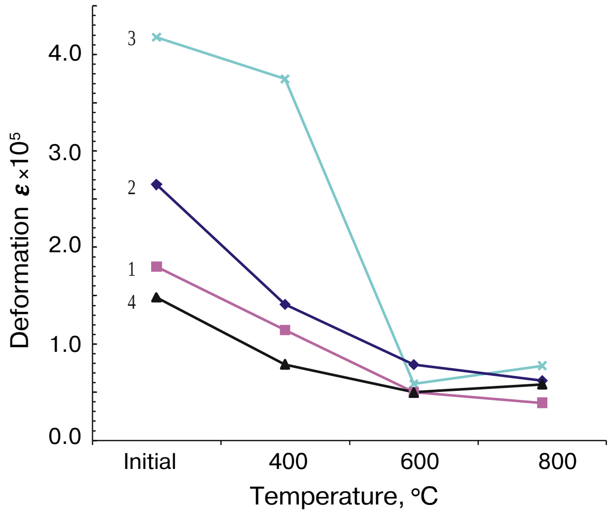

Fig.1. The changes of mechanical deformation under short-term annealing: 1- the TiB_2/GaAs structures with 10 nm film thickness obtained at 0.3 A sputtering current; 2 - the TiB_2/GaAs structures, 10 nm, 0.4 A; 3 - the TiB_2/GaAs structures, 50 nm, 0.4 A; 4 - the Au-TiB_2/GaAs structures, 50 nm for each layer, 0.4 A.

At the short-term thermal annealing, the level of mechanical deformation in all investigated structures decrease (see Fig.1.). For TiB_2/GaAs samples with thickness of TiB_2-film 10 nm the level of mechanical deformation decreases monotonously with the increase of annealing temperature. TiB_2/GaAs and Au-TiB_2/GaAs structures with thickness of TiB_2-film 50 nm have some difference that consist in non-monotonous dependence of relaxation process on the temperature of annealing. The decreasing of mechanical deformation level after annealing at the 800 °C is less then after annealing at 600°C. As in the initial state, the structures with thickness of TiB_2-film 50 nm are in more non-equilibrium state in comparison with structures having 10 nm thickness of TiB_2-film , so in the equilibrium state these systems pass through optimum temperature, at which the improvement of structural characteristics takes place. Under our experimental conditions of annealing, we observe separate stages of this relaxation process.

For structural defect characterization in transition layer of GaAs substrate, the measurements of integrated reflectivity (IR) and half-width of rocking curves (RC) for X-ray Bragg (400), (200) and (311) reflections were carried out. The character of changing of integrated reflectivity and half-width of rocking curves during the abovementioned annealing of TiB_2/GaAs structures with different thickness of TiB_2-film for 400 reflection is the same (Fig.2a, curves 1,2). At temperature of annealing 400° C we obtained the significant increasing of IR and half-width of RC in comparison with initial state of system. If we take into account that some relaxation of mechanical strains takes place, such IR and RC half-width increasing points to processes of extra defect formation, dislocations generation at this annealing temperature. At higher temperatures of annealing, the increasing of these parameters is essentially smaller and even at 800° some

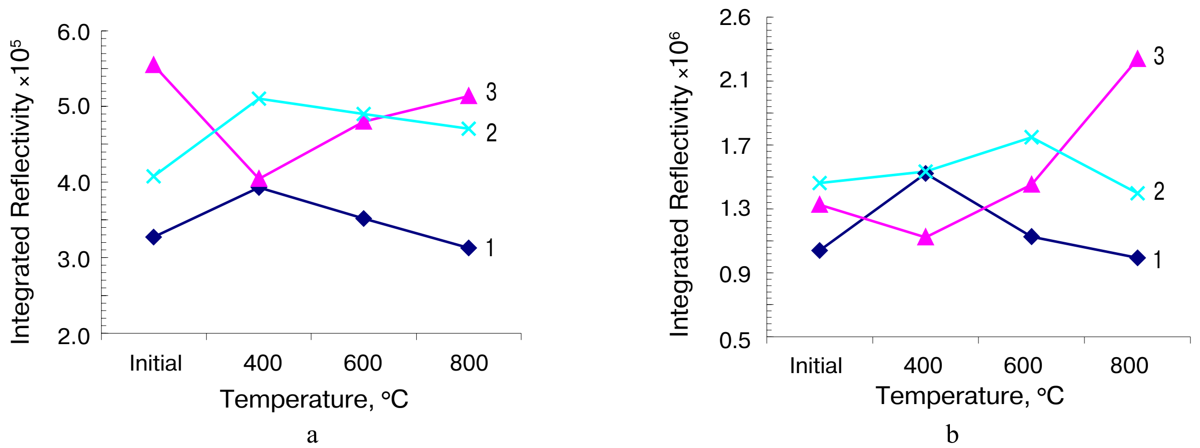

Fig.2. The IR changes under short-term annealing: (a) - (400) reflections, (b) - (200) reflections, Cu K_{a1}- irradiation. 1 - the TiB_2/GaAs structures, 10 nm, 0.4 A; 2 - the TiB_2/GaAs structures, 50 nm, 0.4 A; 3 - the Au-TiB_2/GaAs structures, 50 nm for each layer, 0.4 A.

decreasing can take place. So we observed more intensive process of strain relaxation with increasing of annealing temperature, dislocations generation with the small increases of dislocation density and at 800 °C their interaction and propagation into the depth of substrate. These results were also confirmed by X-ray topography.

The change of integrated reflectivity and half-width of rocking curves for 200 reflections with the increase of annealing temperature also has non-monotonic character but depends on thickness of the TiB_2-film (Fig.2b). For TiB_2/GaAs structures with thickness of a film 10 nm we observed the largest increase of IR after annealing at 400° C. At higher temperatures of annealing (600 and 800°C), the value of IR remains similar to the initial one. For samples TiB_2/GaAs with thickness of a film 50 nm the increase of IR after annealing at 400° C is rather small inappreciable in comparison with an initial state and it takes place at annealing temperature 600° C. At annealing temperature 800° C integrated reflectivity decreases below than that of the initial state. So far as quasi-forbidden (200) reflection is less sensitive to strains and dislocations density than structural (400) reflection, it is possible to assume that processes of point defects reorganization cause the changes of IR. Thus, the changes of integrated reflectivity and half-width of rocking curves testify that the processes of structural ordering and point defect - dislocation interaction close to the interface metal film - GaAs region take place.

For Au-TiB_2/GaAs structures the annealing at temperature 400ºC leads to some decrease of integrated reflectivity both of (400) reflection and (200) reflection (Fig. 2, a,b), at the same time the half-width of rocking curves decreases insignificantly in comparison with that of the initial state. Such behaviour of reflection parameters at given annealing temperature can be explained by some of mechanical strain relaxation process, which is accompanied with point defect transformation and without additional dislocations generation. At higher temperatures the annealing leads to more intensive relaxation of mechanical strain but with defect (dislocations) generation and point defects transformation. This process is the most considerable at annealing temperature 800ºC (Fig.2 a,b, curve 3). The Au-TiB_2/GaAs structures in the initial state were in a more equilibrium state in comparison with TiB_2/GaAs structures (Fig.1) and improvement of structural characteristics takes place at lower temperature 400° C than for TiB_2/GaAs structures.

The analysis of X-ray double crystals rocking curves from TiB_2/GaAs structures obtained at magnetron sputtering current 0.3 and 0.4A, with thickness of TiB_2-films 50 nm shows that there exist the additional peaks both for (400) and (200) reflections (Fig.3, a, b). In the case of structures with the

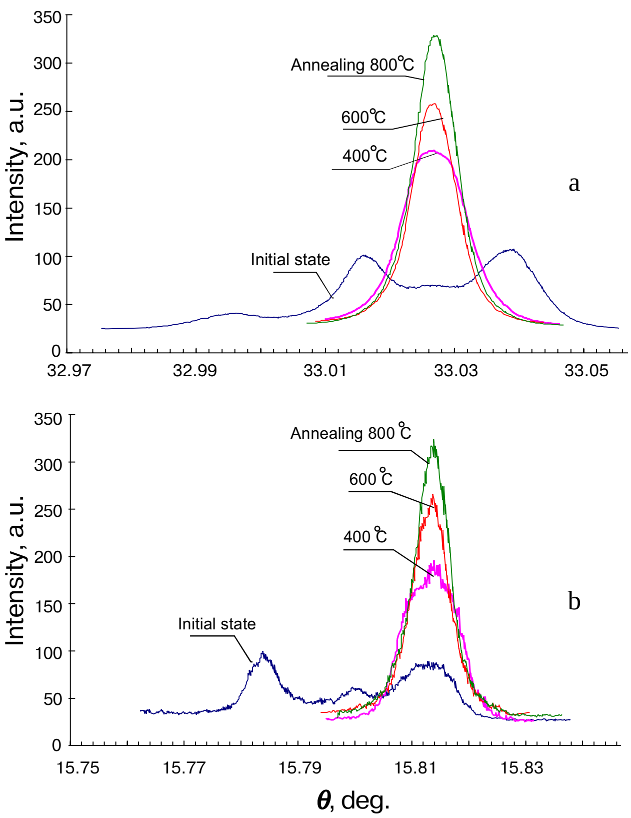

Fig.3. RC shape transformations for TiB_2/GaAs structures with 50 nm film thickness caused by annealing under various temperatures: : (a) - (400) reflections, (b) -(200) reflections, Cu $K_{\alpha1}$- irradiation.

TiB_2-film thickness 10 nm such additional peaks were not observed for any reflections. Taking into account the specificity of magnetron sputtering, it can be concluded that these peaks are connected with formation of solid solutions of Ti and B - $Ga_xTi_{1-x}As$ and $Ga_xB_{1-x}As$ withing interface region. These solid solutions should be formed in the structures with thickness of TiB_2-film 10 nm, but, probably, their amount is such small that it is impossible to reveal them by present method.

The quantitative value of x for solid solutions can be determined by additional peak positions which, give us their lattice parameter a from the relation [7,8]:

$$a = \frac{4}{\sqrt{3}}\left(r_{Ga}x + r_{dop}(1-x) + r_{As}\right),$$

where r_{Ga}, r_{As}, r_{dop} are atomic radii of gallium, arsenic and impurity, accordingly. For example, for two-layer Au-TiB_2/GaAs structures we have received the values of x from the analysis of rocking curve which are given in Table 1.

Table 1.

Solution	Lattice Parameter, nm	x	1-x
$Ga_xTi_{1-x}As$	0.566261	0.9802	0.01980
$Ga_xB_{1-x}As$	0.564994	0.9921	0.00779

After annealing at temperature 400° C the rocking curves were transformed into the Gauss curve with a considerable half-width. The annealing at temperatures 600 and 800 °C result in leads to the decrease of the rocking curve half-width. Already at the first stage of annealing at temperature 400° C the transformation of solid solutions to variable band gap structure takes place. And taking into account that the value of integrated reflectivity increases at annealing temperature 400° C, and additional peaks disappear, it is possible to conclude that besides the process of new dislocation generation the diffusion processes take place. These processes lead to considerable increasing the interface with and its heterogeneity. The processes of diffusion are more intensive at higher annealing temperatures and atoms of Ti and B are distributed more uniformly in the volume of a substrate or they can segregate in the substrate as inclusions, that was also observed by X-ray topography. In this case the structure becomes more ordered and decreasing an integrated reflectivity and a rocking curve half-width take place.

For structures Au-TiB_2/GaAs in an initial state the additional peaks on rocking curve only for asymmetrical (311) - reflection using Cu $K_{\alpha 1}$ - radiation were observed (Fig. 4). We can observe the composite shape of rocking curve on (200) - reflection using more short-wave Ag $K_{\alpha 1}$ - radiation (Fig. 5.). At annealing process these additional peaks disappear and only tails on the rocking curve remain, which indicates solid solutions dissociation. In two-layer structures we have some another situation for solid solutions formation. In an initial state of these structures the volume part of solid solutions in interface is less than in TiB_2/GaAs structures. The most probably, it is connected with the partial decay of solid solutions and partial relaxation of mechanical strains during Au-film sputtering. For this reason, we observed the increasing value of integrated reflectivity and half-width of rocking curve in such samples (i.e., improving their structural parameters) already after annealing at temperature 400°C.

The structural state of the metal film was controlled by 2θ spectra which were taken in gliding geometry (the angle of X-ray beam incidence was about 1°) and θ - 2θ spectra. The changes of θ - 2θ spectra at annealing TiB_2/GaAs structures (thickness of TiB_2 film was 50 nm) are shown in Fig.6. The given spectra are typical for another investigated structures, too. It is possible to connect the wide peaks posessing low intensity in the region of angle 10° and 20-25° with reflections from quasi-amorphous TiB_2-film. After short-term annealing at different temperatures the half-width of these peaks decreases insignificantly, so there are some transfor-

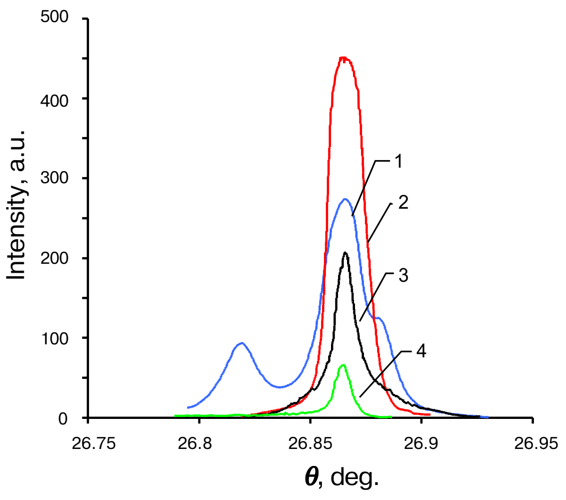

Fig. 4. RC shape transformations for Au-TiB_2/GaAs structures caused by annealing under various temperatures: (311) reflections, Cu $K_{\alpha 1}$- irradiation. 1 - initials state, 2 - 400 °C annealed, 3 - 600 °C annealed (intensity multiplied 12.5 times), 4 - 800 °C annealed (intensity multiplied 25 times).

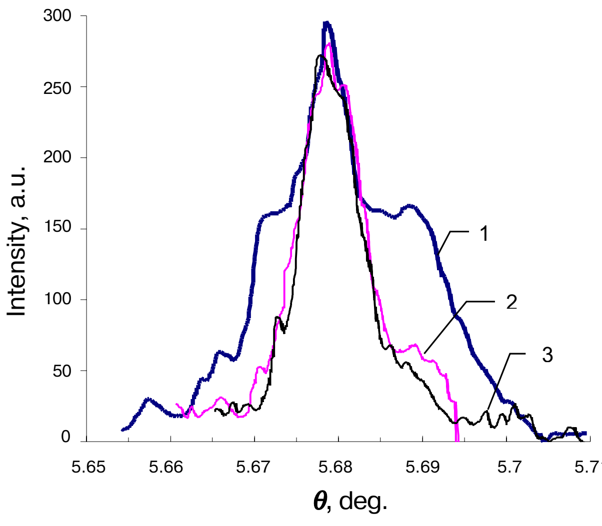

Fig. 5. RC shape transformations for Au-TiB_2/GaAs structures caused by annealing under various temperatures : (200) reflections, Ag $K_{\alpha 1}$- irradiation. 1 - initials state, 2 - 400 °C annealed, 3 - 800 °C.

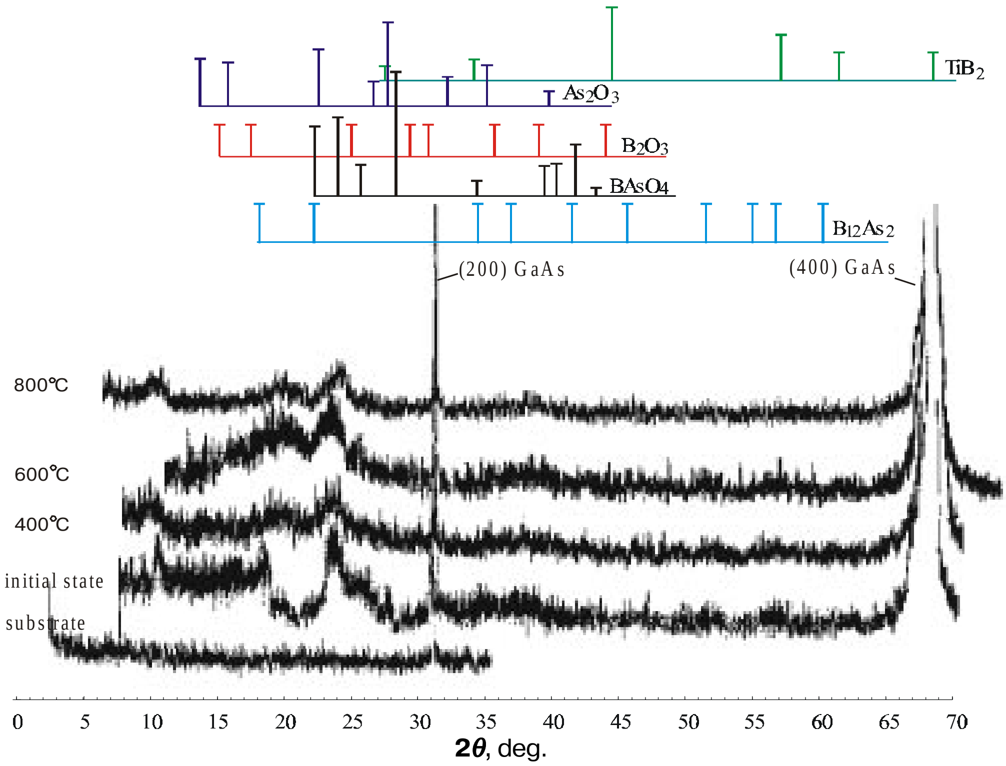

Fig. 6. X-ray diffraction spectra of TiB_2/GaAs structures with film thickness 50 nm and diffraction patterns for supposed new phases.

mations in the metal film. The size of micro grains in the film increase at annealing, but the film remains in quasi-amorphous state.

In spectra the weak wide peaks caused by the presence of small amounts of matter with other phase also take place. It is difficult to identify this matter exactly because of its extremely small amount. The most probably, this matter is of $B_{12}As_2$ composition. Taking into account that in the range of angles 10º - 45º there are wide and rather intensive peaks, it is possible to assume that peaks of reflections from quasi-amorphous TiB_2-film are also superimposed by the peaks of oxides As_2O_3, B_2O_3, $BAsO_4$, which were grown using magnetron sputtering.

Conclusions.

X- ray investigations of TiB_2/GaAs and Au-TiB_2/GaAs structures showed that at magnetron sputtering the structural characteristics of the system and interface depended on a sputtering current and a TiB_2-film thickness. At TiB_2-film sputtering we observed the formation of $Ga_xTi_{1-x}As$ and $Ga_xB_{1-x}As$ solid solutions in interface region and, probably, the additional phase of oxides and $B_{12}As_2$, too. The Au-TiB_2/GaAs structures in initial state were in a more equilibrium state, which is connected with the partial relaxation process at Au- film sputtering. Afte short-term thermal treatment, which can be used as the technological process or for modeling degradation phenomena in such systems, the structural relaxation processes take place. We observed not only the relaxation of mechanical strains, but also decay of solid solutions, dislocations generation, point defect redistribution and structure ordering in an interface region. The dependence of these processes on annealing temperature has non-monotonous character and differs for various structures. If for TiB_2/GaAs structures the improvement of structural characteristics within the interface region can be achieved at annealing temperature 600ºC, then for Au-TiB_2/GaAs structures this temperature may be about 400º C. The TiB_2 -films can be used as a diffusion barrier in microelectronic devices, but further investigation is necessary for technological process.

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References

1. Ye.F. Venger, V.V. Milenin, I.B. Ermolovich et al. / *Semicond. Phys. Quantum Electronics & Optoelectronics.* - **2**,1(1999) - p.124.
2. O. Mitterer, M. Rauter, P. Rodhammer. /*Surf. Coat. Technol.*- **41**,4(1990) - p. 351.
3. W. Herr, B. Matthes, E. Broszeit, et al. / *Mat. Sci. Eng.*- **A140**, 4 (1991) - p. 660.
4. O. Knotek, F.J. Loffler /*Hard Mater*. - **3**,1(1992) - p. 29.
5. R.A. Andrievskij, G.V. Kalinnikov, N.P. Kobelev et al. / *FTT*.- **39**, № 10(1997) - p. 1859.
6. J.Chen, J.A.Barnard / *Mat. Sci. Eng.*- **A 191**, p.233 (1995).
7. V.T. Bublik, A.N. Dubrovina. *Methods of Structure Investigations* . - M.: Vysshaya Shkola, , 1988. - 192 pp.
8. V.N. Novoselov *Physical and chemical properties of semiconductor materials.* - M.: Nauka, 1979.