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PECULIARITIES OF ELECTROPHYSICAL PROPERTIES OF ARSENIDE GALLIUM FILMS DEPOSITED UNDER NONEQUILIBRIUM CONDITIONS

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The electrophysical and photoelectrical properties of thin films of arsenide gallium produced by the deposition on substrate of polycrystalline corundum from the ablation plasma, formed by power ions bunch, were investigated. The annealing effect in vacuum and air on the characteristics of dark and photoconduction of films was established. Chalcogenide passivation from the alcohol solution treatment effect and followed annealing in vacuum and air effect on the electrophysical characteristics and photosensitivity of films were investigated. The conditions of the thermal and chemical treatment were determined, in which the most stable properties changes were achieved. The chalcogenide passivation allows improving the films characteristics, to stabilize them and to enhance the stability of a films surface to an oxidation in air.

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Keywords: thin films, electrophysical properties, thermal and chemical treatment, oxidation in air, stability.

Introduction

The optimization of optoelectronic devices supposes a selection of semiconductor for production the functional layers and investigation of their optical and photoelectrical properties [1-5]. Arsenide gallium GaAs obtains several advantages compared with the other semiconductors [4-10]. Characteristics of alloys of the GaAs with some chemical elements promote to expand the properties of GaAs with broad abilities of its design in devices [3-5]. The radiation and annealing effect enhance the properties of GaAs for aims of devices manufacturing [4, 5, 10]. Doping an epitaxial GaAs with several kinds of elements [4, 10], the structure modification [2, 3, 5] and heterostructure formation were used, too [1-4, 10]. The nanoporous GaAs application enables enhancing device effectiveness [10].

Electrical properties of an epitaxial GaAs were investigated widely enough [1-3, 10-13]. The objective laws of the electrical properties changes after annealing [4, 6, 14-15], ion irradiation [4, 16, 17], chemical chalcogenide passivation and passivation by a thin films [4, 18-20] were established. The ion implantation enhances electrical characteristics. The films of amorphous a-GaAs deposited from RF-plasma [6, 7, 9] and by the flash-evaporation method [21] and co-evaporation elements method [14] for devices were applied. Unique film properties, connected with quantum confinement effects, promote the application of pulsed laser ablation in the producing solar cells, waveguides, optical switches and other devices [22, 23]. Deposition of the films with the use of the dense ablation plasma formed by power ions bunch enables to solve some problems of classical methods of vacuum deposition and to realize the high velocity of deposition with regulation of the films thickness, and to form the films on the considerable areas and different substrates [24, 25].

The purpose of this work is a study of the electric and photoelectric properties of GaAs films, deposited on polycrystalline corundum by pulsed ions ablation (PIA) using power ion beams and properties change after the subsequent thermal annealing in vacuum and in air and after a chemical passivation.

Result and discussion

The GaAs films were deposited on polycrystalline corundum (polycor) by using the accelerator «TEMP» [24] at the following parameters $U=200$ kV, $j=180-230$ A/cm², $t_p\sim 60$ ns,

pulses number ~ 100 , residual pressure in the work camera is 10^{-2} Pa. The target GaAs in diameter 3 cm is situated at the distance 12 cm from diode, under angle 20° relatively to normal diode plane. The substrate is situated across to target plane, the distance between the target and substrate was 9–17 cm. Average thickness of the GaAs films deposited per one pulse was 2–5 nm. The investigated films were formed at subsequent deposition of thin films. Annealing was performed in vacuum at $P \leq 10^{-2}$ Pa and in air at interval $T_{\text{an}} = 300\text{--}900$ K. Sulfide passivation was performed in saturated solution of the sodium sulfide in the ethanol during the time interval $\Delta t_{\text{treat}} = 10\text{--}60$ minutes according to [18, 19]. This procedure was performed until and after annealing in air or in vacuum. That was promoted an etching the oxide layer on a surface of deposited films directly by a passivation solution [18]. Before the thermal and chemical treatments the silver electrodes for electrical measurement were deposited on GaAs films by a thermal sputtering. The measurements of a surface dark conduction σ and a photoconduction $\Delta\sigma_{\text{ph}} = \sigma_{\text{ph}} - \sigma$ (σ_{ph} – conduction at illumination by arc lamp light) were fulfilled at the dc voltage $U = 0\text{--}300$ V within a temperature interval $T = 300\text{--}700$ K and within a spectral range $h\nu = 1.5\text{--}4.0$ eV [25].

Optical parameters of films are changed depending on deposition condition variation and differ for films, produced by using the low-resistance and semiinsulating target GaAs (resistivity $\rho_v \sim 10^{-3}$ and $\rho_v \sim 10^6$ Ohm·cm) [24, 25]. The films deposited in centre and at the optimal distance between the target and substrate possess spectral characteristics similar to target GaAs parameters and absorption coefficient $\alpha = 10^4\text{--}10^5$ cm $^{-1}$. These samples have the conduction values $\sigma = 10^{-10}\text{--}10^{-7}$ S [25]. The films, produced at edges of deposition, have values $\alpha = 10^2\text{--}10^4$ cm $^{-1}$, and their spectral parameters are proper to amorphous semiconductors [6–9, 14, 15, 22, 23]. Conduction of these films is $\sigma = 10^{-14}\text{--}10^{-11}$ S. The films were differed by falling of drop fraction portion, which was not control in this experiment. The properties difference is stipulated by change the content of a drop fraction and deviation from stoichiometric ratio respect to sputtering target GaAs [22, 24].

The nature of the J–U characteristics in the most of deposited films is linear [25]. The J–U character indicates a presence of the potential Schottky barrier in the structure Ag/GaAs [3, 25]. The current of the conduction in the case of $\sigma \leq 10^{-7}$ S and a low concentration of charge carriers are determine by the thermoionic mechanism [3, 11]. Potential Schottky barrier height for structures metal–GaAs has values $q \cdot \Phi_B = 0.8\text{--}0.9$ eV (n-type GaAs) and $0.4\text{--}0.6$ eV (p-type) for most metals [3, 11–13]. The barrier height $q \cdot \Phi_B$ was determined by extrapolation of the J–U curves to value $U = 0$ from the saturation current and from the temperature dependency of a current (the method in detail was described in [11]).

Power dependence $\Delta y_{\text{ph}} \sim y^s$ ($s = 0.8\text{--}1.0$) is realized between values y and Δy_{ph} of the films (Fig.1). That is proper to most of photosensitive semiconductors. The change of values in the wide ranges y and $\Delta y_{\text{ph}} = 10^{-16}\text{--}10^{-7}$ S is stipulated by variation of deposition conditions, such as distance between the target and substrate and the direction of deposition (Fig.1). The decrease of values y and Δy_{ph} occurs if the distance between the target and substrate increases and if deposition deflects from the centre of plasma flame. Conduction and photoconduction values of the films deposited by PIA belong to a common group with values of films deposited from plasma of RF–discharge (Fig.1) [6–9]. The higher photosensitivity was obtained in hydrogenated films of amorphous a-GaAs, that was connected with lowering the degree of structural disorder in it as a result of hydrogen effect (Fig.1, massive 3) [9].

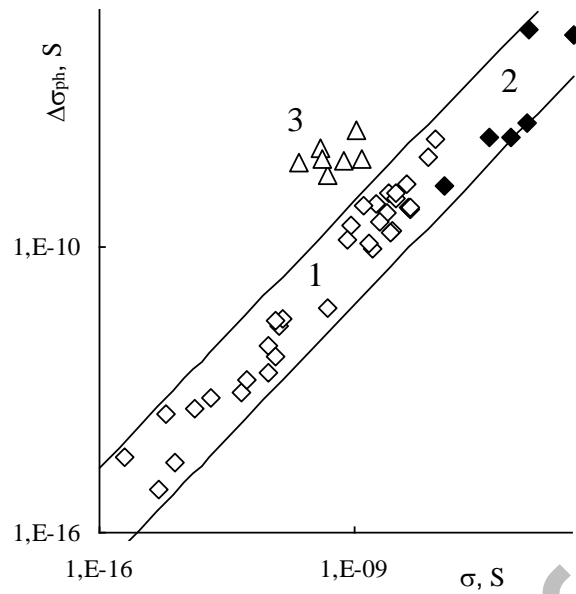


Fig.1. Dependence of the photoconduction $\Delta\sigma_{ph}=\sigma_{ph}-\sigma$ (σ_{ph} -conduction at illumination) from the dark conduction σ in GaAs films, deposited by the PIA on the polycor (1) and by the RF-discharge on the glass substrate (2) [7] and (3) [9]

The thermal annealing of the deposited films in vacuum changes the surface electronic state of GaAs owing to processes of a partial reconstruction of a near surface layer, the polycrystalline phases Ga_xO_y formation and additional structural disordering of a material and growth of a density of localized states (LS) and a bending of bands [1, 4, 16, 17, 22]. As a result, the I-U curves and barrier height $q\cdot\Phi_B$ and photosensitivity $K=(\sigma_{ph}-\sigma)/\sigma$ change considerably (Figs.2-4). The two stages occur in change of the films properties (Figs.2-4). The electrical and photoelectrical characteristics changes may occur owing to a surface cleaning from natural oxides and from absorbing gases. The decrease of thickness of double layer formed by surface and molecules of acceptor gases lowers a surface potential barrier for charge carriers [3, 12].

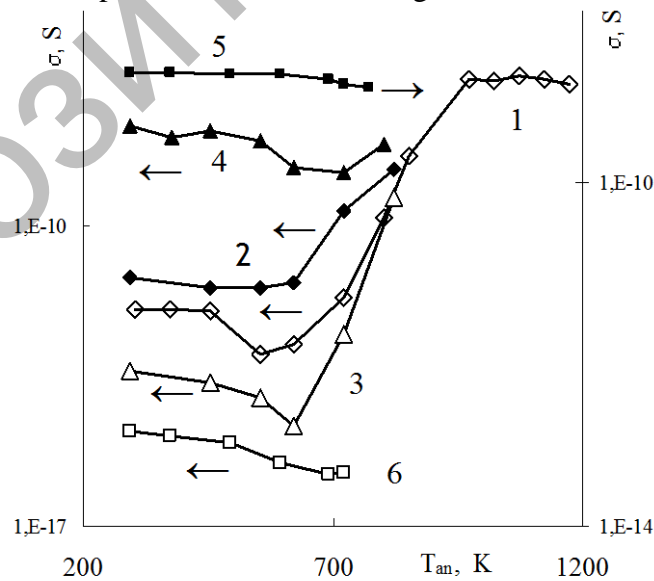


Fig.2. The annealing effect in vacuum (curves 1-4) and in air (curves 5 and 6) on conduction σ GaAs films, deposited by the PIA on the polycor (curves 1-4), and after the subsequent sulfide passivation (curves 5 and 6). The time of treatment in alcohol solution $\Delta t_{reat}=10$ (curve 5) and 30 minutes (curve 6)

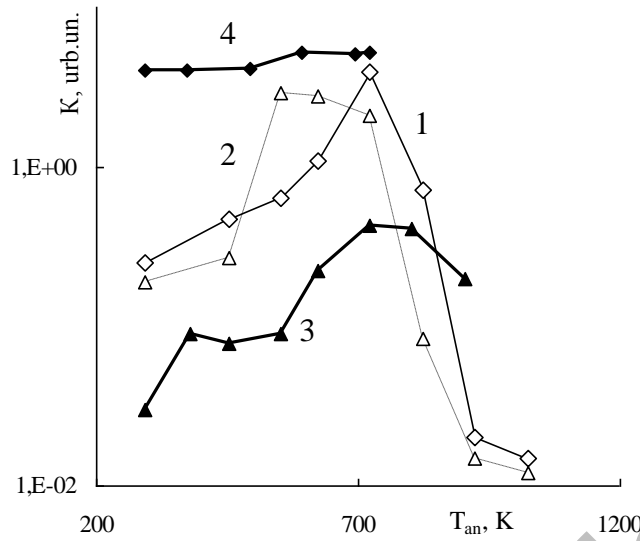


Fig.3. The annealing effect in vacuums (curves 1–3) and in air (4) on the photosensitivity $K=\Delta\sigma_{ph}/\sigma$ of films, deposited by the PIA on the polycor (curves 1–3) and after the subsequent sulfide passivation (curve 4). The time of treatment in alcohol solution $\Delta t_{treat}=30$ minutes

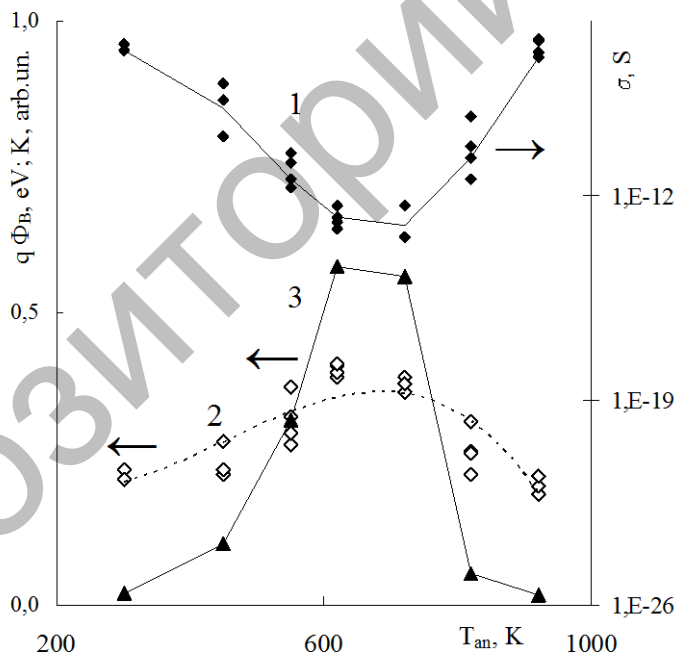


Fig.4. The annealing effect in vacuums on the conduction σ (1), on the Schottky barrier height $q\Phi_B$ (2) and on the photosensitivity K (3) of the GaAs films, deposited on polycor by the PIA by using the semiinsulating target GaAs ($\rho_v \sim 10^6$ Ohm-cm)

After annealing at the interval $T_{an}=290-750$ K conduction is decreased and K increases irrespective of a deposition conditions variation (Figs.2, 3). A last change determines an energy activation of conduction ε_σ , calculated in intervals ΔT , where $y(T)$ submit to activation law and character of dependence $\varepsilon_\sigma(T_{an})$ (table). The deposition conditions determine the interval ΔT_{an} in which photosensitivity achieved the maximum and conduction begins to increase (Figs.2-4). The

maximal photosensitivity is achieved after annealing at $T_{an}=600-800$ K and at values $\sigma=10^{-15}-10^{-9}$ S (table). In this interval of annealing the degree of disorder induced by radiation defects is diminished. The second reason is redistribution of recombination centers within the structural fragments of the films and the mechanism conduction change too [6, 17, 22, 25].

Table. The parameters of dark and photoconduction of films, deposited by PIA onto polycor, until and after annealing in vacuum, in air and after subsequent chemical sulfide passivation after deposition and annealing in vacuum

T_{an}, K	$\Delta t_{treat}, min.$	σ, S	$\Delta\sigma_{ph}, S$	$\Delta T, K$	ε_{σ}, eV	$K, arb.un.$
Annealing in vacuum						
300	30	$10^{-8}-10^{-12}$	$5 \cdot 10^{-10}-10^{-13}$	300-430	0.27-0.43	0.05-0.3
650	30	$10^{-10}-10^{-13}$	$10^{-11}-10^{-12}$	300-450	0.25-0.48	0.2-3.0
850	30	$10^{-8}-10^{-11}$	$10^{-9}-10^{-11}$	300-470	0.22-0.25	0.2-1.0
Annealing in air						
400	10	$(1-3) \cdot 10^{-15}$	$10^{-16}-3 \cdot 10^{-15}$	300-430	0.19	0.1-3.0
750	20	$10^{-15}-10^{-16}$	$(1-3) \cdot 10^{-15}$	430-680	0.41-0.45	3-8
Passivation after the deposition and the annealing in vacuum at $T_{an}=820$ K						
300	10	$(1-6) \cdot 10^{-10}$	$(0.3-2) \cdot 10^{-10}$	300-430	0.12-0.15	0.2-0.4
300	20	$10^{-10}-10^{-11}$	$(4-6) \cdot 10^{-11}$	300-430	0.11-0.23	0.4-5
300	60	$10^{-13}-10^{-15}$	$10^{-13}-10^{-14}$	300-530	0.12-0.21	2-5

The processes of recharging of the defects and of formation of the defects complexes determine the electrons exchange between localized states and the photoelectrical parameters of films. The curves $\sigma(T_{an})$ and $K(T_{an})$ are concentrated after annealing at $T_{an} \geq 900$ K that is stipulated by influence of the implanted ions into the polycor substrate (Fig.2) [25].

The annealing of deposited films in air at $T_{an}=300-720$ K change values σ and K similarly to annealing in vacuum (Fig.5).

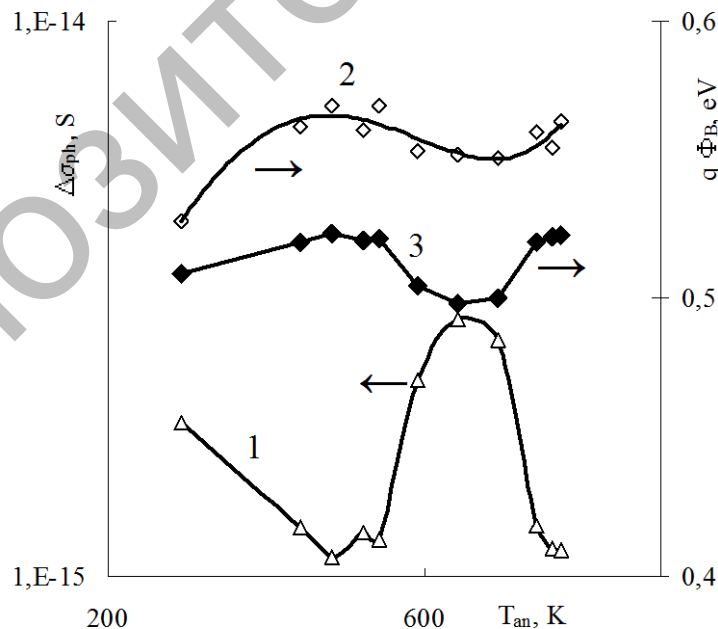


Fig.5. The annealing effect in air on the photoconduction $\Delta\sigma_{ph}$ (1) and on the Schottky barrier height $q \cdot \Phi_B$ (2, 3) for dark current (2) and photocurrent (3) in the GaAs films, deposited by PIA on the polycor and annealed in vacuum at $T_{an}=620$ K

A stabilizing effect of air annealing on I–U curves and on growth of the ε_σ are caused by the passivated effect of the air on the properties. A physical adsorption of the atmospheric gases molecules was realized on the defects, which LS was determined of the instabilities of the characteristics. The photoconduction decrease at $T_{an}=300\text{--}500\text{ K}$ was connected with the growth of the potential barrier height for the electrons excited by light (Fig.5). Increase in value $q\cdot\Phi_B$ indicates a formation of the physical absorbed layer consisting from gas molecules on the surface of the film. So the shift of a Fermi level within band gap is negligible. A maximum of photoconduction at $T_{an}=590\text{--}690\text{ K}$ corresponds to a minimum value of potential barrier height 0.55 eV in dark and 0.5 eV at illumination (Fig.5, curves 2 and 3). Decrease of values Δy_{hh} and growth of values $q\cdot\Phi_B$ at $T_{an}\geq 900\text{ K}$ and enlarge of the activation energy indicate formation of the stability forms of chemical adsorption of the gas molecules in a surface layers (table).

The sulfide passivation modifies the surface properties of GaAs films by absorbing sulfur atoms and has a chemical and an electronic character [18, 19]. The passivation allows to diminish density of the surface LS in the band gap of GaAs and to decrease the recombination velocity of charge carriers [3, 4, 18, 19]. The passivation procedure improves the characteristics and diminishes the process of oxidation of the surface which was etched by chemical treatment of material (Figs.2, 3, 6; table). Effectiveness of treatment of films after vacuum annealing is higher than in case of fresh deposited films (Fig.6, table).

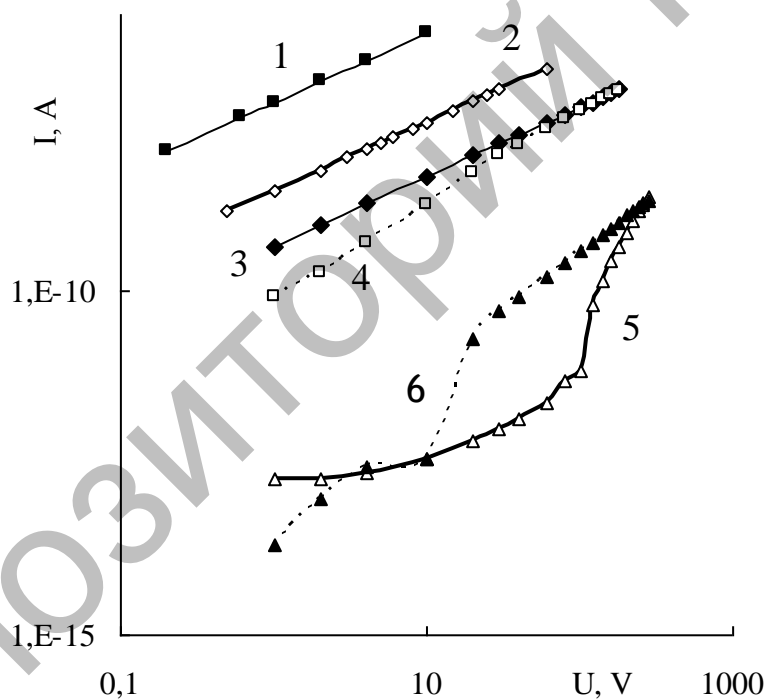


Fig.6. I–V curves of the GaAs films, deposited on the polycor by PIA, after the deposition (1), after the annealing in vacuum at $T_{an}=620\text{--}720\text{ K}$ (2) and after the subsequent chemical sulfide passivation (3-6). The time of treatment in alcohol solution $\Delta t_{\text{treat}}=10$ (3), 20 (4), 30 (5) and 50 minutes (6)

The behavior of electrical characteristics has an electronic character. The properties change is determined by boundaries formation between the films and the sulfur atom layer and surface GaAs and high concentration of defects and inclusions of the crystal phase into amorphous texture, as well.

Conclusions

The electrical and photoelectrical properties of the GaAs films, deposited by the pulsed ions ablation, are change in the wide range. The parameters of the films were determined by conditions of the deposition, the subsequent annealing and depend on the conduction of GaAs target. The stable properties occur in films having conduction 10^{-10} - 10^{-8} S after annealing in the vacuum or in the air at 600-800 K.

The change electrical characteristics correlate with change of the potential barrier height and photosensitivity. A chalcogenide passivation enhances the films parameters, stabilizes them and raises the resistance to oxidation. The optimal properties films were achieved after the vacuum annealing and subsequent sulfur passivation. The electrical and photoelectrical properties allow recommend the deposited films for application in solar cells and other optoelectronic devices.

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