Розглянуто технологічні аспекти формування тонких карбонових плівок α-C:H, особливості іонно-плазмових спектрів Q-DLTS гетероструктур α-C:H-Si та α-C:H-GaAs і визначені енергія активації, переріз захоплення і густина глибоких пасток, відповідальних за зарядовий стан. Встановлена кореляція між технологічними режимами формування плівок α-C:H і густиною пасток. Визначені технологічні методи і режими, які дозволяють отримувати структури з відносно невеликою густиною поверхневих станів (NПС)≤10^{12} см$^{-2}$, що дає можливість використання цих структур в ролі підзатворного діелектрика в GaAs-КМОН структурних ВІС

Ключові слова: комплементарні структури, гетероструктури, епітаксія, інтегральні схеми, технологічні особливості, карбонові плівки

Рассмотрены технологические аспекты формирования тонких карбоновых пленок α-C:H, особенности ионно-плазмовых спектров Q-DLTS гетероструктур α-C: H-Si и α-C:H-GaAs и определены энергия активации, сечения захвата и плотность глубоких ловушек, ответственных за зарядовое состояние. Установлена корреляция между технологическими режимами формирования пленок α-C:H и плотностью ловушек. Определены технологические методы и режимы, которые позволяют получать структуры с относительно небольшой плотностью поверхностных состояний (NПС)≤10^{12} см$^{-2}$, что позволяет использовать их в качестве подзатворного диэлектрика в GaAs-КМОП структурных БИС

Ключевые слова: комплементарные структуры, гетероструктуры, эпитаксия, интегральные схемы, технологические особенности, карбоновые пленки

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FORMATION OF CARBON FILMS AS THE SUBGATE DIELECTRIC OF GaAs MICROCIRCUITS ON Si-SUBSTRATES

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1. Introduction

The progress in the development of integrated circuits/large scale integrated circuits (ICs/LSICs) technologies on GaAs was characterized by significantly less success than provided previously [1–3]. In particular, this is due to the problems of obtaining reproducible, less-defective initial materials and structures on Schottky field and complementary metal-oxide-semiconductor (CMOS) transistors of submicron sizes with a small dispersion of the output parameters over the substrate plane.

Carbon films due to a large number of stable and metastable modifications and high activation barriers between them are promising as a subgate dielectric for GaAs-CMOS LSICs. The use of carbon films as a subgate dielectric enables to form CMOS transistors on GaAs epitaxial layers (thereafter, epilayers) with symmetric threshold voltages, which is very actual and opens a new direction for the development of the sub-micron technology of LSICs.

2. Literature review and problem statement

Silicon has always played a decisive role in the technology of ICs as the main semiconductor material. In recent years, as an alternative, semiconductor compounds such as $A^{III}B^{V}$ (for example, gallium arsenide) have been used. Since 2010, the volume of commercial products of microelectronics based on gallium arsenide has increased several times [4]. This growth trend persists until now. One of the applications of GaAs electronic devices is microwave electronics. Typical values of the diameters of the grown ingots are 100–150 mm. The commercial crystals of 200 mm in diameter have also appeared [5], but they are quite expensive.

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The decrease of geometric sizes of transistors results in a reduction of the crystal area, parasitic capacitances, LSICs energy consumption and increase of speed. In recent years, the gate length of the MOS-transistor has decreased to less than 60 nm [6]. Today, special attention is focused on the architecture of structures for the LSI of submicron range [7, 8]. It is the architecture that qualitatively expresses the issue of technology: the growth of epistructures, the formation of functional layers and circuitry [9, 10].

The dielectric layers of Al_2O_3 are promising for GaAs structures. The main way of such layers obtaining at present is the atomic layer deposition method [11, 12]. Certain successes have been achieved in the creation of a field GaAs-transistor based on MOS-structures with Al_2O_3 [12]. In parallel, works are carried out on the use of carbon-containing films, both as a dielectric, and attempts are made to create graphene-containing conductive channels of field transistors [13]. The authors [14] considered the modification of silicon oxide films by carbon and indicated significant changes in their electrical characteristics, depending on the technological conditions of obtaining.

Due to the significant influence of technological factors of obtaining on electrical properties, it is difficult to achieve stable results on large-diameter substrates. Therefore, in-depth studies of the technological aspects of carbon films obtaining from the point of view of their use as a subgate dielectric for GaAs chips on Si-substrates of large diameter remain relevant.

3. The aim and objectives of the study

The aim of the work is to develop a technology for the formation of CMOS transistor structures for LSICs on GaAs epilayers grown on silicon substrates of large diameter (>150 mm).

To achieve this aim, the following objectives were accomplished:

– to develop a technology for the formation of carbon films by deposition from a carbon target;

– to develop the technology of low-temperature epitaxy of GaAs layers on silicon substrates using excimer lasers, where germanium film acts as a buffer layer between Si and GaAs;

– to form CMOS-transistors on GaAs epilayers with symmetric threshold voltages using carbon films as a subgate dielectric.

4. Methods of ion-plasma deposition of carbon films as insulating layers of a subgate dielectric

The α-C:H films were formed by depositing from the directional ion-plasma streams of particles of the “Radical” type and by magnetron sputtering of the carbon film (graphite target) in different environments with the supply of an additional potential to the substrate holder. The main parameters of the deposition processes for the directed flow technology are: the energy of particles 0.5–6 keV, ion current density 0.5–1.7 mA/cm^2, the power emitted on the Si-substrate 100–800 W. These parameters for magnetron sputtering are equal, respectively, to: 0.1–0.5 keV, 0.1–10 mA/cm^2, 1–100 W.

If during the deposition from directed ion-plasma streams, the interaction of particles in the stream can be neglected, then during magnetron deposition it is necessary to take into account the collective interaction of particles, which is comparable to the distance of the source-substrate of the device [15].

Carbon films were obtained by depositing from directed streams formed from vapors of cyclohexane (S_6H_{12}), propane (C_3H_8), toluene (C_7H_8), acetylene C_2H_2 and by magnetron sputtering of a graphite target in argon, cyclohexane C_6H1_2 and their mixtures at different power applied to the Si-substrate [16]. GaAs, sitall (S-50), quartz (SiO_2), leuco sapphire (Al_2O_3), optical glass (K-8) were also used as substrates.

The measurement of the film density, the study of the atomic and electronic structure of the films were carried out by auger spectroscopy [17–19]. The estimation of the size of graphite clusters was carried out by comparing the position of the maximum of the π-subzone with the data of photoelectron spectroscopy and π-states of carbon molecules, which consist of different numbers of C and H atoms.

The choice of initial environments was also due to the hybridization of bonds in molecular carbon: sp^3 in C_6H_{12} and C_3H_8, sp^2 in C_7H_8, sp in C_2H_2, its structure and composition, because this determines the effect of hydrogen on the structure of the carbon film.

The density of electron states in the valence band, obtained on the basis of the spectral auger-peak forms allows estimating clearly the sp^3:sp^2-ratio as hybridized bonds in the amorphous α-C: H carbon film.

Fig. 1 shows the density of electron states for carbon films obtained from C_6H_{12}, C_7H8, C_2H_2.The photoelectron spectra of C_6H_{12}, C_7H_8, C_2H_2 molecules, which indicate different structures, are presented for comparison.

According to research results, carbon films obtained from cyclohexane C_6H_{12} and toluene C_7H_8 contain diamond and graphite phases in the ratio of 7 and 90 %, respectively, and in the carbon films obtained from acetylene C_2H_2, the carbon phase is less than 55 %. The maximum content of the diamond phase is achieved at an accelerating voltage of 2.9–3.1 kV.

The study of the kinetics of the carbon film formation showed that the deposition rate of the films obtained by depositing from the selected compounds is substantially nonmonotonic. Maximum growth rates, density and specific resistance of carbon films are given in Table 1.

Table 1

Parameters of carbon films, deposited from different compounds of ion-plasma streams

No.	Initial compound	Ratio of atoms C:H	Type of hybridization	Deposition rate, nm/s	Density, g/cm^3	Specific resistance, Ω·cm
1	C_6H_{12}	1:2	sp^3	0.17	2.8	$7\cdot10^7 – 2\cdot10^{11}$
2	C_3H_8	3:8	sp^3	0.15	2.6	$2\cdot10^6 – 6\cdot10^8$
3	C_7H_8	7:8	sp^2	0.19	1.9	$2\cdot10^4 – 7\cdot10^7$
4	C_2H_2	1:1	sp	0.12	1.8	$3\cdot10^3 – 5\cdot10^4$

The dependence of the conductivity of amorphous carbon α-C:H films on the magnitude of the accelerating voltage showed a fundamental difference in the effect of low-energy streams on the electrical conductivity of the films obtained from the compounds of cyclohexane (C_6H_{12}), toluene (C_7H_8), and acetylene (C_2H_2).

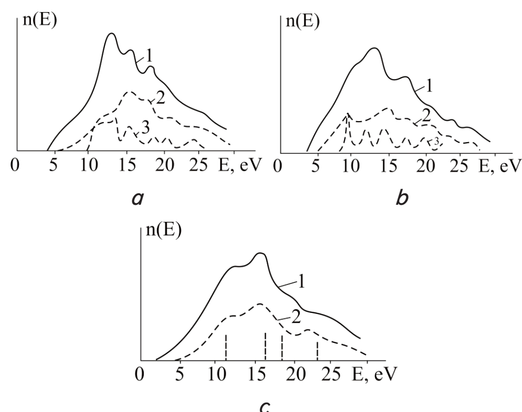

Fig. 1. Electron structure of carbon films, deposited from vapors of C_6H_{12} (*a*), C_7H_8 (*b*), and C_2H_2 (*c*). The state density of graphite (1) and non-graphite (2) components, photoelectron spectra (3)

An increase in the accelerating voltage for particles forming a carbon film up to 2.5 kV or a decrease to 0.3 kV lead to an increase in the proportion of graphite dielectric properties, and, conversely, contributes to the growth of specific resistance. This fact suggests that the electrical conductivity of carbon films is determined by the contribution of the graphite component (based on sp^3-bonding), the degree of cluster disorder and the size of the clusters themselves. The lower the energy of the maximum of the density of states in the π-zone, the larger the size of the π-cluster, i. e. fragmentation of the structure based on sp^3-hybridization takes place.

For films made in C_6H_{12} vapors, the reduction of the accelerating voltage U_{acc} affects the position of the maximum of the π-zone (Fig. 2): $E(\pi_{max})$=9 eV for U_{acc}=3 kV, $E(\pi_{max})$=9.5 eV for U_{acc}=8 kV. Thus, the reduction of the graphite cluster size leads to a significant increase in the specific resistance to 10^{11} Ω·cm and activation energy from 0.4 to 1 eV.

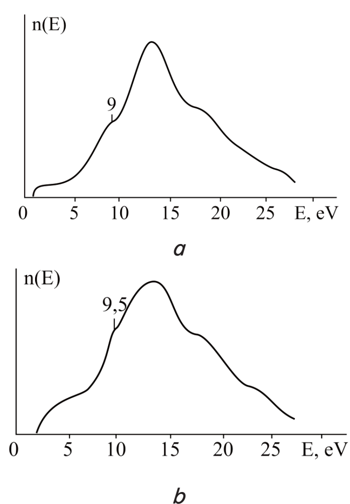

Fig. 2. Electron structure of amorphous α-C:H films of 100 Å in thickness formed from C_6H_{12} at U_{acc}=3 kV (*a*) and U_{acc}=8 kV (*b*)

α-C:H carbon films, obtained by C_7H_8 decomposition in the ionic source and containing mainly the graphite phase change their conductivity to a lesser degree at the change of the accelerating voltage. At the same time, the maximum of the π-subband within ±0.4 eV does not change its position and is fixed by the value of 9 eV for U_{acc}=1 kV and 9.5 eV for U_{acc}=2 kV.

The studies have shown that α-C:H carbon films obtained from carbohydrates are amorphous and heterophasic. The properties of such carbon films depend not only on the predominant type of short-range ordering, but also on the structure of the graphite component. This structure determines the electronic states in the slit of mobility (localized states) and electrophysical properties in conditions of hopping conductivity.

The particle energy and ion current density, as well as the type of the resulting carbon compound, affect the dominant type of short-range ordering and the structure of the graphite component.

The effect of the particle energy change from 0.3 to 0.5 kV and ion current density from 0.5 to 1.7 mA/cm^2 on the type of short-range ordering, formation kinetics and composition of the films were considered in [17–19]. In this case, α-C:H carbon films were obtained from directed sources of particles of the "Radical" type, formed from carbohydrate layers using ion current. The change in the ion energy and the ion current density are determined by the magnitude of the accelerating voltage and the discharge current.

Relevant data on the π-electronic system of films from C_6H_{12}, which allow determining the size of graphite clusters by the presence and characteristics of CH-bonds, are given in Table 2.

Table 2

The effect of formation modes on the size of clusters of α-C:H films

No.	Accelerating voltage, kV	π-band position, eV	Presence and characteristics of CH-bonds, eV	Number of cluster rings
1	4.0	7±0.5	CH 16.5 21.5	>4
2	3.0	7.5±0.5	CH 15 18	>3
3	0.8	9±0.5	CH_2 16.5 19	>1

There is a decrease in the size of graphite clusters, an increase in the H_2 content and the activation energy of conductivity, when the accelerating voltage decreases. Under such conditions, the removal of hydrogen from the molecule is less effective. At the same time, the growth rate and density of the films decrease to 0.005 nm/s and 1.8 g/cm^3 respectively, while the specific resistance increases.

The values of the electrical conductivity of α-C:H films obtained by deposition from directed ion-plasma streams formed from C_6H_{12} vapors are given in Table 3.

The use of a magnetron discharge for obtaining amorphous α-C:H films gives a wider ability to control the process of carbon films forming. This can significantly increase the process efficiency by increasing the ion stream density and improve the uniformity of the films in thickness on the large diameters of the substrates (>150 mm). The use of different gas environments for the same target makes it possible to form carbon films with a specific resistance of up to 10^9 Ω·cm.

Table 3

The effect of formation modes of ion-plasma streams and magnetron sputtering on the electrical conductivity of α-C:H films

No.	Method of α-C:H film formation	Initial gas	Accelerating voltage, V	Power on substrate, W	Specific resistance, Ω·cm	Activation energy of conductivit, eV	Temperature range, °C
1	Deposition from ion-plasma streams	C_6H_{12} C_6H_{12} C_6H_{12} C_6H_{12} C_6H_{12}	4000 3000 2000 1000 800	800 600 400 200 160	10^5 10^5 $5{\cdot}10^5$ $8{\cdot}10^5$ 10^{10}	0.84 0.41 0.32 0.41 0.42	180÷200 90÷100 90÷200 50÷70 50÷100 180÷280
2	Magnetron sputtering of graphite target (puriss. spec.)	C_6H_{12} C_6H_{12} C_6H_{12} Ar Ar Ar Si_2H_6	300 200 50 50 250 300 400	60 40 10 5 15 20 30	$7{\cdot}10^7$ $6{\cdot}10^8$ $2{\cdot}10^9$ 0.5 0.6 1.1 1.2	2.3 0.86 1.1 0 0 0 0	–85÷40 –85÷40 –180÷150 –180÷150 –180÷150 –180÷150

Films, formed with the use of argon as a working gas, exhibit metal conductivity. Their specific resistance is less than 1 Ω·cm and is practically constant in the temperature range –180÷+200 °C. In the case of cyclohexane use, carbon α-C:H films have a thermally activated mechanism, and the specific resistance value is up to $2{\cdot}10^9$ Ω·cm.

The electronic structure of α-C:H films indicates graphite phase composition (up to 90 %). The difference in the nature and magnitude of the conductivity of the films, depending on the formation conditions, is very well correlated with the size of graphite clusters. The shift of the π-subband maximum is about 8 eV for the films obtained by sputtering of the graphite target in Ar and 9 eV for the ones formed in Ar+ C_6H_{12} (1:3), indicating a decrease in the size of the graphite clusters.

Thus, the application of the magnetron sputtering of the graphite target (puriss. spec.) in C_6H_{12} will significantly increase the deposition rate at the size of graphite clusters and film properties that are characteristic for deposition from directed ion-plasma flows. This makes it possible to significantly reduce the power emitted on the substrate, which is especially important for a large-diameter substrate (≥150 mm).

The research, the results of which were recorded using the test electrophysical diagnostics (Fig. 3), showed that the deposition of amorphous α-C: H film led to an increase in the capacity of test structures (TS) over the whole voltage range (curves 1 and 2, respectively). Such results are related to the expansion of the TS area in the presence of a deposited film, which is essentially semi-insulating one. The calculated change in the voltage of flat bands (U_{FT}) of the MOS-structure after the deposition of the protective α-C: H film was 0.3 V, which is a very good indicator when comparing these films with protective coatings for the Si-technology, such as Si_3N_4, Al_2O_3, Ta_2O_5. The estimation of the protective properties of carbon films was also carried out on the basis of the analysis of the change in the capacitance C_{inv} of TS, depending on the time of exposure by a constant voltage, which exceeds the inversion voltage. These changes relate to the redistribution of charge on the surface due to their boundary migration. Accumulation of charge on the surface of the upper metal electrode of the MOS-structure can lead to the expansion of the area of the inversion region, and, accordingly, to an increase in the capacity of the structure.

Thus, the rate of change of C_{inv} upon exposure of the MOS-structure under the bias will characterize the protective and stabilizing properties of the carbon α-C:H films deposited on the gallium arsenide surface. The studies have shown that $C_{inv(t)}$ significantly depends on the mode of carbon film obtaining. $C_{inv(t)}$ dependence was constant and didn't change with prolonged exposure in the conditions of high humidity (90 %) and high temperature (125 °C) for optimal regimes using the deposition method from C_6H_{12} with the simultaneous introduction of electrons into the ion-plasma stream. This behaviour characterizes the carbon films as an excellent protective coating, in contrast to films such as phosphorus silicate glass (PSG), Al_2O_3, SiO_2, Ta_2O_5, which in these test regimes gave a significant increase in C_{inv} in the range of 70–80 %.

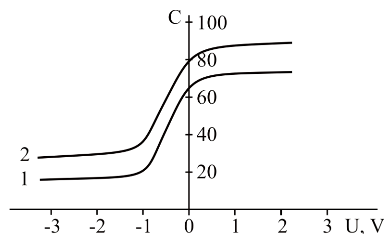

Fig. 3. Volt-farad characteristics of MOS-transistors TS before (1) and after (2) deposition of the protective α-C:H carbon film at a frequency 10 kHz

Thus, the change in the hybridization type of the initial state by changing the C:H ratio in the gas molecule and the effect on the film properties showed that the carbon films formed from the vapors of compounds with sp^3-hybridization of the bond (C_6H_{12}) provide the maximum deposition rate of the mass of the substance with the highest value of specific resistance (10^9 Ом·cm).

The change in particle energy during the carbon film formation affects in a different way the electronic structure and properties of α-C:H films obtained from compounds with different types of bond hybridization in the initial material. Thus, the reduction of particle energy from 2.5–0.3 keV for films deposited from C_6H_{12} results in a sharp increase of the graphite component (from 35 to 92 %) and an increase in specific resistance from 10^5 to 10^{11} Ω·cm in the case of cluster size reduction. The reduction of particle energy during deposition of α-C:H films from C_7H_8 leads to an increase in specific resistance from 10^5 to 10^8 Ω·cm; the contents of the graphite component and the size of the clusters do not change. For α-C:H films deposited from C_2H_2, when the particle energy was reduced, no change in specific resistance was practically observed.

The use of magnetron sputtering of the graphite target (puriss. spec.) in the C_6H_{12} atmosphere can significantly increase the deposition rate of carbon film at the size of graphite clusters and the properties of amorphous films characteristic for deposition from directed ion-plasma streams at low particle energies, but with a significant reduction in the power allocated on the substrate (silicon or arsenide gallium).

The estimation of the protective and stabilizing properties of carbon α-C:H films by changing the capacitance of test structures of MOS-transistors as electrophysical diagnostics showed that these properties of carbon films formed by magnetron deposition considerably exceed the protective and stabilizing properties of coatings such as Si_3N_4, SiO_xN_y, SiO_2, Al_2O_3, PSG, Ta_2O_5. Such films can be used as a subgate dielectric for arsenide-gallium CMOS structures of LSICs formed on large-diameter substrates, which makes arsenide technology competitive with silicon one.

5. Carbon films as a subgate dielectric when forming submicron structures on GaAs epilayers

The methods of formation and properties of carbon films with high hardness, chemical inertness and high thermo- and radiation resistance were considered above. Such films can be used as wear-resistant, masking, passivating coatings in the technology of ICs manufacturing both on Si and GaAs substrates. Today, the possibility of carbon films using as a subgate dielectric in promising super high-speed MOS-devices based on $A^{III}V^{V}$ semiconductors, as well as the main material in multilayered structures with quantum wells in resonance tunneling diodes and a subgate insulator for GaAs-transistors, is intensively investigated.

α-C:H films, as discussed above, were obtained by depositing from directed ion-plasma streams of hydrocarbon vapors (cyclohexane, toluene, acetylene) and magnetron deposition in plasma of hydrocarbons. The particle energy during α-C:H films formation was 0.1–0.6 keV, the thickness of the films varied in the range of 30–300 nm. Also, pre-treatment of substrates with argon ions with an energy of 1–2 keV for 10–30 s was carried out.

The deposition of α-C:H films was carried out on silicon substrates (SHB-80 (100)) and n-GaAs substrates of 0.3–0.5 mm in thickness. The ohmic contact to the substrates was performed by burning of In-electrode, and to α-C:H films – by thermal spraying of Ni or Al layers in a vacuum. In addition, α-C:H carbon films were deposited directly on glass substrates, where low-ohmic tin oxide layer (SnO_2) was as an electrode.

The study of the carbon films stability was carried out using the method of charge deep level transient spectroscopy Q-DLTS [17]. The automated measuring system allowed the formation of Q-DLTS spectra when using both the temperature-free scan and scan in a time window, as well as measuring the kinetics of photodetection in a mode close to idle. In other words, spectra were viewed which made it possible to estimate both the temperature and time drift of the charge state of the interphase boundary, which is important for the formation of the threshold voltage.

The kinetics of photo-emf for the heterostructure (HS) α-C:H-GaAs with $|V_{ph}|\approx|\phi_s|$ is shown in Fig. 4. The intensity of the pulsed illumination was $\geq 10^{22}$ quanta/cm·s, which was sufficient for the saturation of the photo-emf. The analysis of $V_{ph}(t)$ dependence for this and other heterostructures (AlGaAs – α-C:H) shows the formation of the convergence of the zone bends in semiconductor materials of HS at the boundary with the α-C:H layer regardless of the type of substrate and the mode of application of the carbon film layer. This is due to the presence of traps for the main carriers of bend on the heterointerface in all investigated samples.

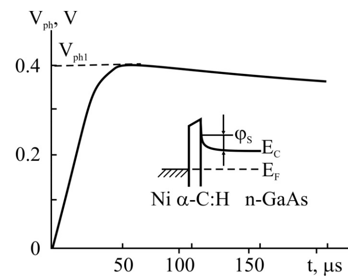

Fig. 4. The kinetics of photo-emf for the α-C:H – GaAs heterostructure at $|V_{ph}|\approx|\phi_s|$ (inset – zone diagram of the heterostructure)

The spectrum of the HS (inset in Fig. 4) was obtained at room temperature using a scan in the time window $\Delta t=2t$, where t is the time from the beginning of the discharge (relaxation) to the charge after switching the sample from the source of the bias voltage U_{bias} in the measured circuit. Q-DLTS spectra were obtained for all voltages U_{bias} used at various temperatures, amplitudes and duration of enrichment pulses. Data analysis showed that the traps, located at the heterointerface and in the volume of the carbon layer, give the predominant contribution to the spectra. There are two peaks A and B in all the spectra (Fig. 5), associated with an increase in the density of traps with ionization energy E_t=0.30 eV and a capture cross section $\sigma_n=3\cdot10^{-18}$ cm^2. These peaks are in Q-DLTS spectra for all HS on semiconductor Si and GaAs substrates and may be due to traps located in the α-C: H carbon layer near the heterointerface at a distance no more than 50 nm. The change in the thickness of α-C:H layer from 30 to 300 nm has a rather weak effect on Q-DLTS spectra. Peak A was not detected in the spectra of semiconductor substrates based on Si and GaAs (without α-C:H layer). There was no peak A in the spectra of structures obtained by depositing one or several (with different energy of optical activation of conductivity) α-C:H layers on glass substrates (optical glass KO-8 of the photomask) with the SnO_2 layer as an electrode. At the same time, the integral density of recharging traps in TS was the same as in HS on semiconductor substrates and essentially depended on the modes of carbon film formation.

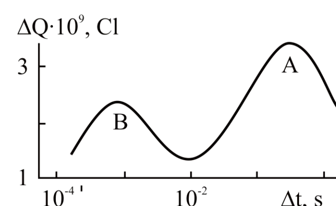

Fig. 5. Q-DLTS spectrum of the α-C:H-Si heterostructure (peak A is related to the recharging of traps with the ionization energy of 0.35 eV; peak B – with the ionization energy of 0.5 eV)

The research of dependence of the density of traps of the HS test samples, which are responsible for the accumulation

of ions A and B in the spectrum (Fig. 5), on the time t of treatment of Si or GaAs substrates by argon ions was performed. An increase in time t (10–60 s) leads to a decrease in the density of traps from 10^{12} to 10^{11} cm^{-2} in the region of peak A (by an order of magnitude) and approximately the same magnitude in the mode of the investigated spectral region (from 0.2 to 1 eV). Peak B is smaller, and the peak A decreases by an order of magnitude and more.

Annealing of the HS in a vacuum (10^{-6} mm Hg) at T=450 K decreases also the order of the density of traps on the interphase boundary. The values of the density of traps N_a with ionization energy corresponding to peak A in Q-DLTS spectra before and after annealing for TS on p-Si, n-GaAs, and n-AlGaAs substrates are given in Table 4.

Table 4

Effect of annealing on the density of traps A on the interphase boundary on p-Si, n-GaAs, n-AlGaAs substrates

No.	Sample and substrate	Annealing temperature, K	Density of traps N_a, cm^{-2}	
			before annealing	after annealing
1	α-C:H – n-GaAs	425	$3{\cdot}10^{11}$	$5{\cdot}10^{10}$
2	α-C:H – GaAs – a-GaAs	450	$2{\cdot}10^{12}$	$4{\cdot}10^{10}$
3	α-C:H – n-AlGaAs	430	$2.5{\cdot}10^{12}$	$2{\cdot}10^{10}$
4	α-C:H – p-Si	370	10^{12}	$5.6{\cdot}10^{11}$
5	α-C:H – p-Si	450	10^{12}	$8{\cdot}10^{10}$
6	α-C:H – n-Si	430	$2{\cdot}10^{12}$	$5.6{\cdot}10^{10}$

The conditions and method of α-C:H carbon films forming determine the significant effect on the density of traps on the interphase boundary. For example, a decrease in the density of traps, which have an activation energy of 0.36 eV corresponding to peak A to (1–5)$\cdot 10^{10}$ cm^{-2} is possible. This indicates that the search for the technology and modes of formation of α-C:H carbon films was carried out. In particular, we have found technological regimes for the formation of HS that allow us to change the density of traps in a wide range of energy and to obtain structures with a relatively small trap density. This is essentially a necessary and sufficient condition for using of α-C:H carbon films as a subgate dielectric in sub-micron CMOS LSICs on gallium arsenide. The technology allows the formation of super-fast LSICs on silicon substrates, on which the epitaxial arsenide-gallium layers are grown.

6. Results discussion and practical realization of sub-micron technologies of CMOS LSICs on GaAs

To reduce the cost of LSICs structures, a technology for the formation of GaAs-structures on silicon substrates with a diameter >150 mm was developed. This technology allows using the whole set of special technology equipment of silicon technology [20]. Here, instead of GaAs-substrates, epitaxial layers are used which significantly reduce the cost of gallium [21], which in nature is only ≤10–4 %. In addition, gallium arsenide has a thermal conductivity of almost an order of magnitude smaller than monosilicon, which limits the power of sub-micron structures on GaAs.

Therefore, the basis of this technology is atomic layer epitaxy (ALE) on GaAs using an excimer laser KrF, which provides the deposition of only one monolayer during one growth cycle at a temperature T=500±25 °C. In addition, the epitaxial growth of layers on GaAs (AlGaAs) completely excludes the presence of isoconcentric impurities of oxygen and carbon from the films, which negatively affects the charge state of the interphase boundary. This process is also unique in this regard, which allows forming a buffer layer with one to two germanium monolayers between a silicon substrate and an epitaxial GaAs-layer to equalize a constant silicon lattice to gallium arsenide.

ALE of gallium arsenide using an excimer laser makes the process low-temperature due to the efficient decomposition of reagents by photochemical reactions.

Monolayers of semiconductor compounds can be grown by the method of plasma-photochemical deposition from the layers of organometallic compounds at temperatures >650 °C. The ALE method, in which the deposition stimulated by radiation by an excimer (KrF) laser greatly increases the epitaxial growth with decreasing temperature. Theoretically, it is believed that there are two mechanisms for influencing on ALE in photo-radiation by a laser: the first one is to increase the decomposition of the Ga- and Ge-containing absorbents due to the transition of photo-carriers to the surface of the substrate; the second one is a significant increase in the decomposition of reagents due to the absorption of photons by absorbent. The effect of photo irradiation on the epitaxial growth increases significantly with a decrease in wavelength (up to 248 nm). In both cases, it is necessary to eliminate or reduce the phenomenon of photolysis of initial materials in the gas phase.

The low-temperature method of epitaxial growth of GaAs-layers on silicon substrates is developed. The equipment for such layers growth is shown in Fig. 6.

Trimethygallium (TMG), trimethylaluminium (TMAl), AsH_3 (10 % in H_2) are used as gaseous sources and H_2 as a carrier gas with a dew point of not higher than –72 °C. The reactor is a vertical stainless steel pipe, which is designed to suppress the convection of the gas stream.

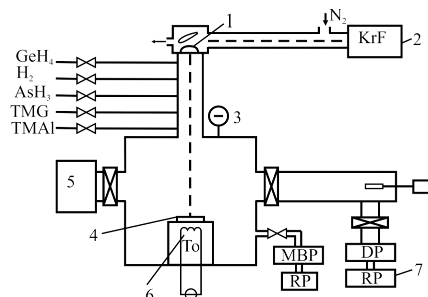

Fig. 6. The scheme of equipment for the growth of GaAs epilayers using an excimer laser: 1 — window, 2 — excimer laser, 3 — vacuum gauge; 4 — substrate (Si or GaAs); 5 — cryopump; 6 — heater with thermal resistance; 7 — backing vacuum and diffusion pumps, cryomolecular pump

The carbon resistive heater provides the thermal mode of the substrate (Si or GaAs). Mono-Si substrates (SHB-80 (100)) were treated in peroxide-ammonia and peroxide-salt mixtures. Then, the epitaxy of germanium from GeH_4 (20 % in H_2) to form a buffer monolayer for equalizing the lattice constants of mono-Si and GaAs was carried out on these substrates at T=480–520 °C. Here organometallic compounds $Ga(CH_3)_3$, $Ga(C_2H_5)_3$, $Al(CH_3)_3$, $As(CH_3)_3$ are used.

Si-substrates were heated at T=600±20 °C in the hydrogen stream before the start of the epitaxial growth. TMG and AsH3 were alternately fed to the GaAs growth surface. Such gas streams were interrupted by hydrogen to prevent the movement of gases in the gas stream.

TMG and AsH_3 were alternately delivered to the GaAs growth surface. Such gas streams were interrupted by hydrogen to prevent the movement of gases in the gas stream.

One technological cycle consists of a sequence of four gas pulses when growing GaAs, i. e. AsH_3, H_2, TMG, H_2. The duration of each pulse was seconds (3–10 s), the flow rate of AsH_3 – 25 cm^3/min. A fifth gas cycle is also possible, when it is necessary to dope the film by a donor or acceptor impurity. For example, the n-type donor impurity from monosilane (SiH_4 in H_2, 10 %), where gas compounds Si, S, Se are the donor impurities, and Be, Cd, Te – acceptor ones. All these impurities should be represented as compounds with hydrogen with a dew point of –72 °C and a purity of 10^{-4} %.

After etching of SiO_2-mask, the height of the step was measured on the Si-substrate using the MII-11 interferometer (angle measurement error was <1 %).

Epitaxial films usually didn't deposit on SiO_2. In addition, the developed epitaxial process removes all oxides and increases the purity of epilayers by an order of magnitude. One should pay attention to the second unique feature of ALE, which is that the simple replacement of an excimer KrF laser (248 nm) with ArF one (193 nm) allows increasing the power of such an equipment almost 1.5–2 times and reducing the temperature of growth to 470 °C.

Six growth cycles were realised in the experiment of the atomic layer epitaxial process of deposition of mono-GaAs-layers. The rate of growth per cycle was determined by dividing the height of the step by the number of cycles. It was found that monoatomic growth was achieved in a rather narrow temperature range close to 500 °C. This fact suggests that Ga-containing absorbents give stable Ga-As-bonds during the growth deposition of GaAs at higher temperatures.

When researching the dependence of the growth rate on the TMG flow rate for the thermal process, it was found that TMG is absorbed and decomposed intensively on arsenic atoms. This is the novelty of the epitaxial process using an excimer laser.

Fig. 7 shows the change in the growth rate of epilayer per cycle as a function of the deposition temperature at laser irradiation. The growth rate of TMG was 1.85 cm^3/min, and AsH_3 – 25.5 cm^3/min.

Monolayer growth is achieved in a wider temperature range (470÷530 °C) compared to thermal growth during irradiation by KrF laser (Fig. 7, curve 3). The effect of laser irradiation on the expansion of the temperature range can be explained by the following processes: 1 – increase in temperature; 2 – collision of such reactive particles as gallium atoms during TMG photolysis in the gas phase; 3 – decomposition of Ga-containing absorbents in photochemical reactions.

If the laser irradiation causes an increase in the temperature of the Si-substrate, then the start of the decrease in the growth rate should occur at a temperature below 500 °C. The temperature range of the monolayer formation expands not only in the region of lower temperatures, but also in the region of higher temperatures under the action of laser excimer radiation. This fact indicates the effect of laser irradiation on the growth of the substrate temperature.

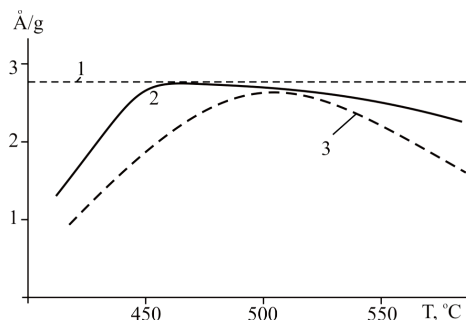

Fig. 7. The deposition rate of GaAs-epilayers at ALE using photoactivation by an excimer laser as a function of temperature (1 — monolayer, 2 — growth during irradiation, 3 — growth without irradiation)

The cross section of the absorption spectrum of TMG on the length of the excimer laser KrF (248 nm) or ArF (193 nm) is approximately $1\cdot10^{-18}$ cm or $1\cdot10^{-16}$ cm, respectively. Although these quantities are rather small, there is a probability that the photolysis of TMG in the gas phase increases with the expansion of the temperature range of the monolayer growth. This reaction is amplified with a decrease in the wavelength of the excimer laser to λ=193 nm, i. e. monolayer growth is already achieved at T=500 °C during laser irradiation of the gas stream. This result indicates that monolayer growth is also achieved at T<500 °C during irradiation by an excimer laser. This result shows that reactive particles in the gas phase are not created by laser irradiation. Accordingly, the observed effect of laser irradiation is due to a significant increase of decomposition of Ga-containing absorbents on the surface with arsenic atoms. It turned out that such a photochemical process is similar to the process that provides the activation of implanted impurities, so-called photoannealing.

Thus, the original complete self-limiting monolayer growth of GaAs-films was obtained by the ALE method. The temperature range of monolayer growth is formed in the temperature range of 470–530 °C (or 450–550 °C) when irradiated with an excimer laser KrF (or ArF). Therefore, the effect of laser irradiation is due to the significant increase in decomposition of Ga-containing absorbents due to active photochemical reactions and effective heating of Si-substrates. As a result, there are no isoconcentric impurities of oxygen and carbon in the GaAs epitaxial film. The latter fact creates the basis for a significant decrease in the charge state at the interphase boundary.

Consider the aspects of the formation of a complementary structure on MOS-GaAs transistors with induced channels, which have a self-aligned structure. Such structure is formed on a weakly alloyed Si-substrate (1) of p-type (KHB-80) (Fig. 8).

The main layers of this transistor are as follows: 2, 3 – drain-source regions of the n-channel MOS transistor; 4, 8 – self-aligned carbon gate; 5 – n-type pocket; 6, 7 – drain-source regions of the p-channel MOS-transistor; 9, 10 – layer doped with acceptors; 11 – local isolation by multicharge boron ions (B^{++}); 12 – contact to the n-type pocket; 13 – protective layer SiO_2 or Si_3N_4; 14 – metal contacts to the drain-source regions of MOS-transistors; 15 – lateral insulating GaAs layer, doped by boron or chromium (interlayer insulation).

As shown above, a buffer germanium monolayer is formed between the Si-substrate and GaAs-epilayer to equalize lat-

tice constants of silicon and gallium arsenide. Let us give a brief description of this structure.

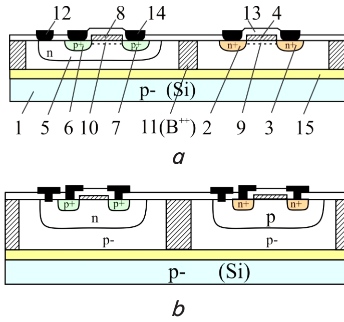

Fig. 8. Structure of CMOS-GaAs transistors with the n-type pocket (*a*) and GaAs-MOS transistors with p-pockets of n- and p-types (*b*) on the Si substrate

A transistor with the p-type channel is placed in a special n-pocket (as is done in silicon technology) of 1.5–2 μm in depth, which is formed by multicharge silicon implantation in two stages (Si^{++} and Si^{+++}) with subsequent drive-in to reduce the concentration (to 10^{17} cm^{-3}) of donors near the surface. It consists of p^+-type drain-source regions (6, 7); self-aligned carbon gate (8), covered by the SiO_2 or S_3N_4 dielectric (13); layer doped by acceptors (10), forming the value of the threshold voltage U_{Tp}; metal AuGe contacts (12, 14).

The negative threshold voltage in the absence of layer 10 is quite significant in absolute value due to the effect of positive surface charge that prevents the p-type channel formation, as well as high concentration of donors in the n-type pocket. A significant decrease in the threshold voltage is closely related to the doping dose of layer 10, i. e. U_{Tp} fitting: $|\Delta U_{Tp}|=qU_{bias\,p}C_g$ (where $U_{bias\,p}$ – the bias voltage of the subgate region doped by acceptors; C_g – specific capacity of the subgate region).

The equality of absolute values of threshold voltages of complementary transistors is optimal for CMOS-LSICs. Since the doping of the channel by acceptors increases U_{Tn} and decreases U_{Tp} ($|U_{Tp}|>U_{Tn}$), layers 9 and 10 can be formed by performing one operation of ion fitting by selecting the dose of multicharge implantation to fulfill the condition $|U_{Tp}|=U_{Tn}$ with a supply of voltage levels in the range of 0.5±0.05 V.

Several transistors with p-type channels placed in the same pocket are separated by local isolation made by multicharge implantation of oxygen or boron (O^{++}, B^{++}). The region of n-pocket 5 has a separate output, which connects to the positive terminal of the supply during the LSIC working. Retrograde doping by multicharge ions (Be^{++} and Te^{++}) is provided for low ohmic contact obtaining. The ohmic contact to the p-type Si-substrate is connected to the negative terminal of the supply.

The area occupied by the structure of one transistor in the complementary pair is larger than in the structure of the same type of n-channel transistors. This is due to the presence of the pocket with outputs to it. When pockets are formed, impurities are also distributed in the lateral direction at a certain distance, which is determined by the processes of ionic doping and diffusion, which increases its size. The distance between the p–n junctions of the pocket-substrate and the p–n junction of the nearest n-channel MOS transistor (for example, between regions 2 and 5 in Fig. 8) should be greater than the sum of the thicknesses of the depleted layers of these junctions, so that there is no closure of 2 and 5 regions. Since the substrate is low-doped, the thickness of the depleted layers of these p–n junctions is sufficiently large (~1.5–2 μm at $N_a=10^{15}$ cm^{-3} and the voltage at junctions about 3-5 V). In addition, n-channel MOS-transistors need to be removed from the edge of the pocket so that there is no so-called thyristor effect that causes the closure between layers 7 and 2 as a result of the inclusion of the horizontal thyristor p–n–p–n structure formed in the regions 7, 5, 1, 2. CMOS-structures of LSICs in p-pockets are formed, which is a dual structure to the CMOS-structure with the n-pocket, are formed similarly. The phenomenon of thyristor effect can be removed completely, using CMOS-structures with two pockets (p- and n-types).

The structure in Fig. 8, *a* is characterized by relatively large capacities between the pocket and the drain-source regions of the p-channel transistor because of the high concentration of impurities in the pocket compared to the substrate. This disadvantage is also eliminated in the CMOS-structure with pockets of both types (Fig. 8, *b*). Pockets formed in the GaAs-layer of the p-type with very low concentration of donors (10^{14} cm^{-3}) already have the same and low concentration of impurities (less than 10^{16} cm^{-3}), which is given by multicharge implantation, and provide very small capacities of p–n junctions. Local isolation between the elements is carried out by multicharge implantation of boron (B^{++}) or oxygen (O^{++}), and lateral isolation is formed in the process of epitaxial growth of p-GaAs-layers during doping of boron or chromium, giving a semi-insulating layer. All these increase the speed of such structures almost by an order of magnitude with a significant reduction in transient processes.

As we see in Fig. 8, *b*, the originality of such a technology for the formation of CMOS arsenide-gallium structures of LSICs on silicon substrates are:

1. The use of low-temperature laser epitaxy on excimer lasers allows the formation of high-quality layers of buffer, insulation and epitaxial processes in a single technological cycle that does not allow the presence of isoconcentric impurities of oxygen and carbon. This is a guarantee of significant reduction of the charge state to the level of 10^{10} cm^{-2} at the interphase boundary, which allows forming CMOS structures on GaAs analogically with silicon technology.

2. Multicharge implantation of retrograde drain-source regions, as well as local and interlayer isolation, allows forming highly stable concentric profiles, in which there are no interdiffusion displacements, providing the minimum design norms of design and technological constraints.

3. The operations of subgate dielectric forming by magnetron deposition of carbon films, low-temperature epitaxy on excimer lasers of GaAs-epilayers, and multicharge implantation of retrograde drain-source regions create the basis for the production of CMOS high-speed LSICs on GaAs-epilayers formed on Si-substrates of large diameter.

7. Conclusions

1. The unique technology for the formation of a carbon film as a subgate dielectric for CMOS-transistors on epitaxial layers of gallium arsenide grown on silicon substrates of large diameter (≥150 mm) was developed. The high stability of electrophysical parameters of the α-C:H carbon film is achieved by magnetron sputtering of the graphite target

in the plasma of cyclohexane and argon while rotating the magnetic field in a magnetron and cooling of the magnetron by deionized water.

2. The experimental equipment of low-temperature gas-phase laser epitaxy based on the UNES-2PKV device was designed, which allows forming doped and non-doped layers of gallium arsenide and a buffer layer of germanium to equalize the lattice constants of germanium and gallium arsenide. The low temperature of the epitaxy (470–530 °C) provides the formation of the highly stable charge state of the interphase boundary due to the absence of isoconcentric impurities of oxygen and carbon. This is confirmed by complex investigations of epitaxial layers formed by atomic layer epitaxy with excimer (KrF or ArF) laser using charge deep level transient spectroscopy Q-DLTS.

3. The technology of multicharge ion implantation and photon annealing was developed for the formation of retrograde drain-source regions with a small contact resistance of local and lateral isolation using multicharge implantation of boron (B^{++}) or oxygen (O^{++}) with the provision of high insulating properties of the formed layers. The unique property of multicharge implantation in the formation of n- and p-pockets for the formation of CMOS-transistors on gallium arsenide was researched and the small doses of multicharge implantation for the fine fitting of threshold voltages of n- and p-channel transistors to their symmetry and level $U_{Tp}(U_{Tn})$=0.5±0.05 V are determined.

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