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Carbides of A^3B^5 compounds – new class materials for opto- and microelectronics

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Abstract. Discussed in this paper are options for replacing the virtual structure of SiC atoms with AlN compound. The Al_4C_3, AlNC and AlNOC compounds in vapor and solid epitaxial processes have been obtained as a result of carbothermic reduction. Analized is the role of precursors in the way of reducing the formation temperature for stable phases of aluminum oxynitrocarbide during epitaxy of aluminum nitride in the presence of carbon atoms. The dependence on preparation conditions for the aluminum single oxycarbide crystal structure has been explored. The influence of partial 2H-SiC crystal structure on the state of the single oxycarbide crystal structure was determined. The semiconductor AlNOC has been experimentally obtained.

Keywords: A^3B^5 compounds, epitaxial process, carbide compounds, binary compounds, oxycarbide aluminum, aluminum oxynitrocarbide, aluminum nitride, silicon carbide, TMA.

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1. Introduction

Prospects of development of information engineering, energy-savings and creation of alternative energy sources are related with technology of A^3B^5 semiconductor materials, in particular gallium, indium and aluminum nitride. Semiconductor properties of these compounds have been discovered by N.A. Goriunova (Book: Diamond-like semiconductor compounds. Sovetskoie Radio, Moscow, 1968, p. 268 (in Russian)) and H. Welker (Zs. Naturforsch H, 7a, p. 744; see, also Ref. [1]). They used the analogy of their electron construction with elements of the fourth group in the Mendeleev Periodic System, carbon (the diamond structure), silicon and germanium, as well as their combinations with each other inside the group IV.

N.A. Goriunova has proved the analogy of electronic construction of binary compounds for elements of the third and fifth (A^3B^5) groups in 1950. They have the diamond structure and chemical binding modification similar to the elements of the group IV. H. Welker interrogated A^3B^5 semiconductors in 1952. Thereafter, the diamond-like semiconductors joined equidistant from IV group A^2B^6 and A^1B^7 compounds that have analogical structure, electronic construction and covalent-ionic chemical bonding.

The binary, triple and more complicated atomic combinations – cations and anions that lay on both sides from the group IV (Fig. 1) and have the four-fold electron construction of outer shells, which were named as diamond-like semiconductors by N.A. Goriunova. There were comprehensively explored A^3B^5, A^2B^6 materials by the scientific analogy method in 60-ths of XX century. The laser effect invention in *p-n* junctions of GaAs and sequential development of heterolasers, LEDs, heterotransistors took place not only with binary compounds A^3B^5 employment but also their three- and multicomponent solid solutions that have been implemented in electronics. There are about half of information engineering in our days that are based on A^3B^5 semiconductors. Among them GaAs, GaN and their solid solutions are basic, exceptional multicomponent, that have been brought into electronics by N.N. Sirota and V.I. Osinsky in their previous works [1].

Silicon carbide (SiC) possesses unique electro-physical properties. But its indirect structure of Brillouin zones, high synthesis temperatures and polytypism cause high cost, which restraines the dream of the transistor inventor W. Shockley that the future of electronics is associated with silicon carbide.

Considering silicon carbide as a classical semiconductor material, that is made by two elements of the IV group in the Periodic System – carbon and silicon, one should note that each of these elements has quite completed outer shells with 4 electrons. There is a rule in semiconductor chemistry. In accordance with it atoms that has not completed shells does not form uninterrupted bonds with each other in the process of overlapping their wave functions [3]. The interruption of electrons in atoms takes place via sp^3-hybride circle of electrons in the crystal tetrahedral type lattice [1].

Further developing the analogy for A^3B^5 compounds with the elements from the fourth group, one can obtain the carbide A^3B^5, A^2B^6 compounds (Fig. 1). Among them, the replacement of the silicon atoms in the virtual structure of SiC with aluminum nitride AlN, gallium nitride, indium nitride compounds and their solid solutions of AlGaInN are of great interest.

It is possible to obtain all real as well as virtual multicomponent materials of A^3B^5, if it is necessary using the famous methods to stimulate their mutual solubility [2].

2. Preparation of A^3B^5 carbide compounds

In the latter work, proposed for the first time is a new class of materials – A^3B^5 carbide compounds, aluminum nitride carbide $(\mathrm{AlN})_x\mathrm{C}_{1-x}$ of which and their oxide derivatives have been obtained.

Recently, using the vapor-phase and solid-phase epitaxial processes we obtained Al_4C_3, AlNC and AlNOC compounds.

The full symmetry in formation of binary A^3B^5, A^2B^6 compounds and their solid compounds on both sides of the IV group axis were theoretically and experimentally explained by N.A. Goriunova and N.N. Sirota in 60-ths of the past century. Formation of binary tetrahedral and octahedral compounds takes place in accord with the same rule for electronic interaction of atoms, wherein the concentration of electrons per atom for binary cooperation is equal to four. In fact, the binary compounds are full-valence four-electron compositions [5] (Fig. 1). On the left side, the cations are situated, in which on the outer shell the orbits of three electrons are located. On the right side, the anions with 5 electrons on the outer shell are situated. For clarity only the III and V groups elements are allocated. They form the most useful tetrahedral and octahedral diamond-like compounds. There, four electrons of the III group element are added with the fifth electron of the V group element, thus forming the full-valence four-electron compounds. This rule is hold in more complex compounds like triple, quadruple and etc. phases. In triple phases like $A_{1-x-y}B_xC_y$ the third element can be donated either as cation or anion (in double cation system).

In the SiC structure, it is proposed to interchange it with electron analogs – the A^3B^5 compounds, the nearest from which in the physical and chemical properties is aluminum nitride AlN.

Triple-phase analogs of silicon with atoms (or ions) of aluminum and nitrogen presence in the reactor can be explained using the concentration triangle by replacing the silicon atoms in the virtual lattice of silicon carbide by its electron analogs of aluminum nitride and aluminum oxynitride (Fig. 2).

The aluminum carbide nitride AlNC and aluminum carbide were prepared using the trimethylaluminum $Al(CH_3)_3$ cracking method within the temperature range 500 to 1200 °C. The process was carried out on the nanotexturized sapphire with (0001) orientation, which provides the crystallographic characteristic coordination in the growth process of AlNO, AlN, AlNOC and Al_4C_3 nanolayers. This process can be spontaneous or programmable.

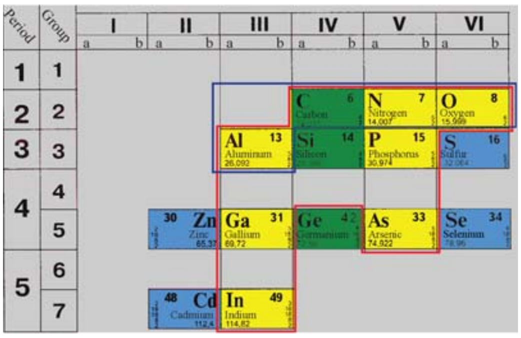


Fig. 1. Position in the Mendeleev Periodic System of A^3B^5 carbides compound, in particular, aluminum oxynitrocarbide (AlNOC).

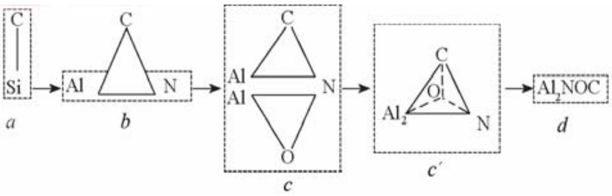


Fig. 2. Scheme of silicon carbide conversion (*a*) to AlNC (*b*), Al_2NOC (*c, d*).

It is possible to obtain the gallium carbide nitride, gallium indium carbide, phosphide indium carbide and other A^3B^5 carbide compounds. But the size of gallium, indium, phosphor atoms considerably exceeds that of silicon atoms in SiC, which embarrasses preparation of complex compounds.

The second interesting variant of the triple phase (silicon analog) is Al_2NOC that was obtained in 1956 [1]. The importance of cation-anion interaction was proved due to its stability. From all elements, only aluminum and boron form the A^3B^4 chemical compounds. An important role is played by the construction of electron shells, i.e. by the electron density. Oxycarbide aluminum Al_2OC was obtained during the Al_2O_3 and Al_4C_3 reaction near the temperature 2000 °C [1]. The lattice type – wurtzite with $a = 3.17$ Å, $c = 5.06$ Å; $c/a = 1.6$ period; pin structure; there is a superstructure [4]. It is an electronic analog of aluminum nitride that has similar lattice parameters and forms the solid solutions with AlN.

In this case, the AlO molecule acts as an analog of Si that replaces it in silicon carbide (SiC) (Fig. 2). The presence of AlN, AlNC and Al_2OC chemical compounds indicates the existence of more complex compounds of these four components that forms AlNOC as quarternary silicon carbide analog, i.e. the phase $A^3B^4C^5D^6$ (Fig. 3) is formed.

For the quadruple phase like $A_{1-x-y-z}B_xC_yD_z$ it can be three composition variants: single, double, and triple anion phases [5]. In this case, if there are aluminum, carbon, nitrogen and oxygen atoms and/or ions the most probable variant is $A^3_{1/2}B^4_xC^5_{1/2-2x}D^6_x$ phase, which corresponds to the AlNOC chemical formula with relevant concentrations of electrons per atom. In the concentration tetrahedrons (Fig. 3), each point inside tetrahedron corresponds to a definite ratio of these four elements. The faces represent triple systems, and the edges – double systems. The carbon as the IV-group element is situated in the top (Fig. 2). The analog of silicon from IV group is one phase – aluminum nitride.

There are two double phases, two triple phases and double and triple phases (Fig. 3, correspondingly) as a possible variant of analogs of IV group. More difficult is a forming variant of the system of two analogs: both systems consist of two triple phases, one system consists of two triple phases, and the second one – from double and triple phases.

The most important factor in formation of compounds is ion-covalent interaction between atoms. Delamination of the eutectic and formation of solid solutions show weak or non-covalent ionic interaction. When formation of the compound may be virtual, its implementation is determined by the energy stability of electron configurations – the minimum of free energy. An example of this configuration is sp^3-hybridization. Single oxycarbide aluminum $A1_2OC$ was first identified by the authors [3] in the study of high temperature interactions in a system of $A1_2O_3$-Al_4C_3. On the basis of single-crystal X-ray studies, single oxycarbide aluminum can be regarded as a III2/(IV,VI) – the kind of III/V compounds. This crystalline structure should be taken into account.

Al_2NOC is isoelectron to AlN, so their structural characteristics are quite close. The hexagonal crystal lattice of Al_2NOC has parameters $a = 0.317$ nm and $c = 0.506$ nm, which is 2% higher than the corresponding lattice parameters of AlN, and c/a ratio is the same. If we ignore the small difference in the positions of carbon and oxygen atoms, due to the difference in bond lengths of $\mathrm{Al-P}$, $\mathrm{Al-O}$ and $\mathrm{Al-N}$, non-metal atoms form a regular hexagonal close-packed sublattice, and atoms of metals are located in one of two sets of tetrahedral voids. In normal wurtzite-type structures, including the AlN structure, the choice of this set determines the direction of bonds along the hexagonal axis and, consequently, the polarity of the crystal. The Al atoms in Al_2NOC structure are equiprobably located in both sets of tetrahedral interstices in oxygen-nitrogen sublattice. The distance between adjacent pairs belonging to different sets is less than 0.1 nm, hence, both of these positions cannot be occupied simultaneously. The evidences of ordering their positions within a small range (about 5 nm) periodicity have been determined [4]. The short-range order structure of Al_2NOC is described by the superlattice with $a' = \sqrt{3a}$ and $c' = 2c$ parameters.

Availability of $\alpha\text{-}Al_2NOC$, $\alpha'\text{-}Al_2NOC$ and $\alpha''\text{-}Al_2NOC$ phases in the X-ray diffraction spectrum is defined by the type and state of precursors, in particular, trimethylaluminum at 1200 °C temperature.

The results of Al_2NOC X-ray researches that are present in recent works, can serve as the base for its further detailed crystalline structure.

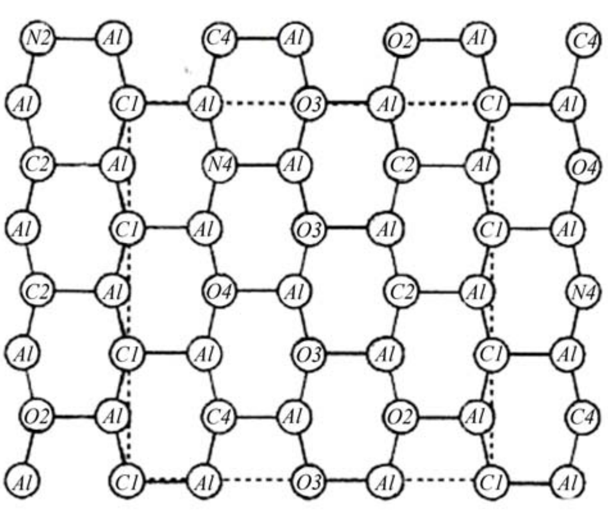


Fig. 3. Superlattice models of AlNOC: the Al atoms orderly occupy tetrahedral voids of (C,N,O) packing ((100) perspective) (Fig. 4).

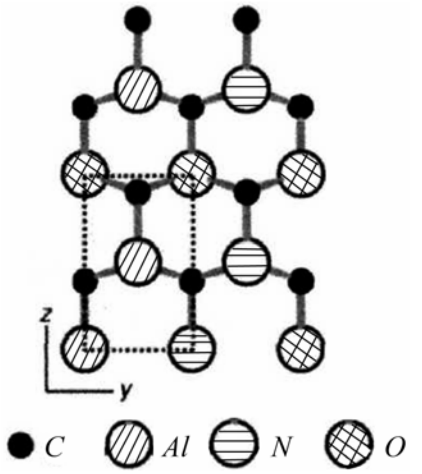


Fig. 4. The model of crystalline structure of AlNOC ((100) perspective).

Being based on investigations of order crystal-chemical transformation at carbo-thermic recovery of aluminum oxide, we can contend that α - Al_2NOC, α' - Al_2NOC and α'' - Al_2NOC are not temperature modifications, as the authors suppose, but present the metastable forms of single oxycarbide aluminum, formation of which is determined by the crystalline structure of precursors (Al_4C_3 – for α' - Al_2NOC; alumina spinel – for α'' - Al_2NOC) and processes in the structure of $A1_2NOC$ sorts.

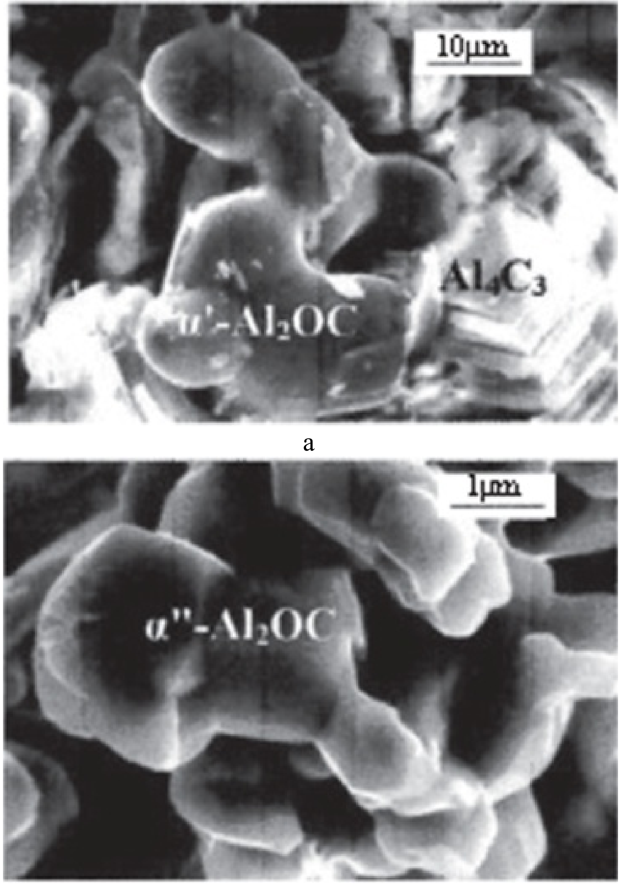
The existence of several crystalline forms of $A1_2OC$ explain discrepancies in literary data as to physical and chemical properties of this compound, in particular, concerning durability to mineral acid and base influences. This is completely confirmed by explorations of chemical stability of Al_2NOC modification. The low stability of α' - Al_2NOC to acid and base acts is determined by peculiarity of crystalline structure. Since α' - Al_2NOC is formed from the aluminum carbide and save the structure parameters – the carbide blocks $[Al_2C_2]$, we can suppose that this modification of single oxycarbide aluminum inherits the typical collection of chemical properties typical for aluminum carbide, too, in particular poor stability in acid and alkaline solutions.

It is known that single oxycarbide is characterized by relatively low temperature stability and has inclination to evaporation at high temperatures and low ambient pressure. The similar property of Al_2NOC is related with instability of its crystalline structure in a well-ordered condition. But proposed in this work is the model of Al_2NOC crystalline lattice with spatially parted structure blocks. The probability for the compound to exist with this crystalline structure is very low. The model of α - Al_2NOC structure proposed by us has not such disadvantageous, and it is more probable from this point of view. Loss of stability by single oxycarbide aluminum and, as a consequence, high degree of degeneration to gaseous components in the process of long heat treatment, is obviously caused by changing its structure in crossing to α - Al_2NOC. In the crystalline lattice of α - Al_2NOC, separate structure blocks are relatively low related with each other (see Fig. 5a).

Let us examine the crystal-chemical transformation that determines formation of oxynitrocarbide bonds of aluminum in the reactor of MOC-hydride epitaxy in the process of trimethylaluminum cracking under the low pressure 10^{-2} Pa.

Formation of the crystalline structure with crystal sizes a few micrometers or spinel faceting (micro-, nanosapphire) was shown by electron-microscopic researches. The presence of spinel phase is defined by implantation of carbon atoms into the anion sublattice of γ-Al_2O_3. The lattice parameter of $A1_2O_3$ spinel phase changes within the range 7.922 to 7.935 Å depending on the structure. The electron-microscopic images of α' - Al_2OC and α'' - Al_2OC are shown in Fig. 5.

The α'-$A1_2OC$ kernels have recast form. The crystallization of oxycarbide composition flux, which formation takes place in $A1_2O_3$-$A1_4C_3$ system, occurs [5]. The α'' - Al_2OC crystals have well pronounced facets that stem from the spinel phase. The oxide and carbon atoms in the anion sublattice form hexagonal closest packing.



a

b

Fig. 5. Electron-microscopic images of α' - Al_2OC (*a*) and α'' - Al_2OC (*b*).

Being based on results of X-ray and microprobe technique analyses, the well known data about alumina brick spinel as a clear oxide compound $A1_3O_4$ have been revised. The assumption about the oxycarbide structure of spinel phase has been grounded. The chemical formula of this formation must be presented as $xA1_2OC \cdot A1_2O_3$, where x = 0.29…0.33, or otherwise $A_{8/3+2x/3}O_{4-x}C_x$, where x = 0.32…0.36.

The structure of $\alpha''\text{-}Al_2OC$ possesses the wurtzite type. Similar to the shpinel phase structure, the statistically distributed atoms C and O form the hexagonal closest packing. The Al atoms disposed in one of two sets of tetrahedral interstice (C, O) sublattice (Fig. 5a). The parameters of elementary cell in $\alpha''\text{-}Al_2OC$ crystalline lattice are changed within the ranges: 3.11 Å < *a* < 3.14 Å; 4.95 Å < *c* < 5.00 Å.

Extending the analogy of electron construction of oxynitrocarbides with carbide silicon, the structural researches show the presence of $(Al_2OC)_{1-x} \cdot (Si_2C_2)x$ solid solutions. The SiC structure stabilizes disordered $A1_2OC$ substructures and makes this structure stable in the solid state condition.

On the base of this interpretation of experimental data, we have ascertained that the crystalline structure of precursors ($xA1_2OC \cdot A1_2O_3$ – for $A1_2OC$) and process of structural ordering for $A1_2OC$ are determined by the stable modification of $A1_2OC$.

The 2H-SiC polytype stability is defined by disordered condition of $A1_2OC$ forming $(Al_2OC)_{1-x} \cdot (Si_2C_2)x$ solid solution. The next consecution of structural transformations in the process of interaction of single oxycarbide aluminum with carbide silicon is the most probable. The beginning of interaction is related with solid solution formation based on a low concentration of SiC. The SiC locally embarrasses but, as a whole, does not exclude gradual structural stabilization and volatilization of the basic component ($A1_2OC$). Thus, formed is the solid solution of $A1_2OC$-SiC system with a definite SiC concentration necessary for stabilization of the disordered $A1_2OC$ structure that is steady in the condensed condition.

Let us consider the well known discovery of natural silicon carbide – muassant. The high contents of A1 in many attached samples give the possibility to suppose that, in the number of possible ways of muassant formation in nature, carbo-thermic recovery of aluminum silicate plays essential role. Considering the results presented in the above laboratory researches, it has to be recognized the fundamental possibility of the metastable oxycarbide compounds in $Al\text{-}Si\text{-}O\text{-}C$ system, in particular their solid solutions, to take part in formation of the Earth crust.

The first solid phase formed in the process of interaction between aluminum oxycarbide with carbon is the spinel phase. Structural characteristics of the spinel phase are rather close to those of $\gamma\text{-}A1_2O_3$. The performed evaluation has shown that the spinel phase has oxycarbide nature, and it corresponds to the formula 0.5 $A1_2OC\text{-}A1_2O_3$. Any reference to the compound of similar composition is absent in literature. The mass-spectrometric analysis of vapor above spinel phase gives the possibility to determine that this phase is vaporized incoherently. In the remaining solid fragment, one can fix only aluminum oxide (alumina). The composition of vapor is represented by A1, $A1_2O$ as well as oxycarbide and atomic oxygen. In addition, the vapor pressure of aluminum is higher than that of $A1_2O$. This phase is resistant to mineral acid and alkaline solutions. Further structural evolution during the high temperature processing of spinel phase leads to formation of $\alpha''\text{-}Al_2OC$.

Interaction of carbon with gaseous aluminum compounds leads to formation of aluminum carbide and its further interaction with the aluminum oxide to tetraoxycarbide, which leads to formation of $\alpha'\text{-}Al_2OC$.

During the annealing process (more than 1 hour), $\alpha''\text{-}Al_2OC$ and $\alpha'\text{-}Al_2OC$ are transformed into $\alpha\text{-}Al_2OC$.

The crystalline structure of these modifications of single oxycarbide aluminum belongs to the wurtzite type. In the case of $\alpha''\text{-}Al_2OC$, C and O atoms form a hexagonal densely packed structure, and aluminum atoms are located in one of two sets of tetrahedral voids in (C, O) sublattice. By contrast to $\alpha''\text{-}Al_2OC$, the crystalline structure of $\alpha'\text{-}Al_2OC$ is characterized by equal expectation of charging by Al atoms of both sets of non-metal sublattice tetrahedral voids. The atomic arrangement in non-metal sublattice in $\alpha''\text{-}Al_2OC$ and $\alpha'\text{-}Al_2OC$ structures leads to formation of $\alpha\text{-}Al_2OC$ [1]. Typically, $\alpha\text{-}Al_2OC$ is oxidized in air at 760…780 °C temperatures, which indirectly causes the range of temperatures of its formation in reactor atmosphere. This compound is experimentally unstable, which is probably caused by the difference between bond lengths of $Al\text{-}C$ and $Al\text{-}O$. The mass-spectrometric analysis of respective vapors has shown that $\alpha\text{-}Al_2OC$ evaporates congruently, the vapor is represented by A1, $A1_2O$ and, obviously, by carbon and oxygen.

Determination of the enthalpy of $\Delta_f H^0_{298}$ (Al_2OC) formation has made on the base of the null equality of free energy of $4A1_2OC = Al_4O_4C + Al_4C_3$ reaction in A point of the system $A1_2O_3\text{-}A1_4C_3$ diagram with following correction of the value obtained by bringing the temperature of $A1_2OC$ decomposition to the 1980 K value. The thermodynamic calculation of equilibrium in $A1_2O_3\text{-}Al_4C_3$ has shown that the temperature *T*(A) is very sensitive to the magnitude of $\Delta_f H^0_{298}$ (Al_2OC) formation (Fig. 6).

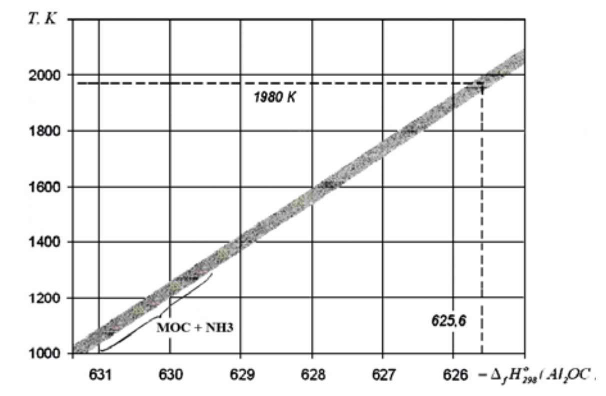


Fig. 6. The conduction of temperature and enthalpy of $-\Delta_f H^0_{298}$ decomposition of single oxycarbide aluminum Al_2OC in MOCVD reactor in the process of cracking of trimethylaluminum (TMA) by using nitrogen as the carrier gas and in the absence of ammonia and hydrogen.

In the MOCVD epitaxial reactor, on texturized and nitrized sapphire substrates in the process of cracking of trimethylaluminum (TMA), by using nitrogen as the carrier gas and in the absence of ammonia and hydrogen, the temperature of oxycarbide formation was reduced by 200-500 K in comparison with well-known in the literature [5] artificial synthesis conditions, as well as in formation of the Earth crust.

The aluminum carbide compounds have been described in this article. They were studied in detail in macro- and microcrystal chemistry of minerals. The possibility of their synthesis in the process of manufacturing LEDs, lasers, solar converters, transistors and other elements of information nanostructures gives additional degrees of freedom for the choice of technological modes that increase operational parameters of devices, for example, the efficiency of LEDs.

3. Conclusions

1. The decisive role of precursors in reducing the temperature of stable phase formation of aluminum oxynitrocarbides during the epitaxy of aluminum nitride has been established.
2. The sequence of crystal-chemical transformations that accompanies the process of aluminum oxycarbide compounds formed in the process of epitaxy of aluminum nitride when cracking the trimethylaluminum (TMA) by using nitrogen as the carrier gas and in the absence of ammonia and hydrogen has been established.
3. The dependence of the crystal structure of aluminum single oxycarbide against the formation conditions has been determined.
4. It has been ascertained that 2H-SiC silicon carbide stabilizes thermally unstable disordered state of the crystalline structure of aluminum single oxycarbide due to formation of $(Al_2OC)_{1-x} \cdot (Si_2C_2)x$ solid solutions. The latter have also increased resistance to oxidation.
5. For the first time in electronics and optoelectronics of III-nitride compounds, the aluminum oxynitrocarbides in LEDs, lasers and photodetector functional elements have been used.

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