

PHASE COMPOSITION AND STRUCTURE OF CONDENSATES OF LOW SUPERSATURATED Ti–C VAPORS

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The results of investigations of the interrelation between the chemical composition and the structure of Ti–C layers obtained by magnetron sputtering of composite targets are reported. The layers were deposited at low vapor supersaturations and investigated by a transmission electron microscope using electron microdiffraction method. The chemical composition was determined by calculations and energy dispersion analysis. It has been found that, at certain concentrations of C, the deposited layers consist of a new TiC₂ carbide and a diamond phase. The TiC₂ condensate has a bcc lattice with a period about 0.3 nm, being metastable with respect to diamond. A decisive role of the low supersaturation degree of vapors in the formation of porous structures (at C concentration above 70 at.%), as well as the epitaxial layers of TiC, has been shown.

TiC layers are now widely used due to their valuable mechanical properties and chemical stability [1–3]. Moreover, our experiments have shown that the condensates of the Ti–C system with the carbon concentration over 3–5% (here and further an atomic concentration is indicated) have a high stability of electrophysical properties even beyond the homogeneity region of TiC_{1–x} ($0 \leq x \leq 0.43$), which is a necessary condition for their application as Ohmic contacts [3].

Of special interest is the fact that C atoms which are not chemically connected to Ti (free carbon), due to the ability of creating various valence bonds (*SP*³-, *SP*²-, and *SP*-hybridizations), are able to make up different correspondent allotropic compounds, e.g., diamond or graphite. So, above the upper limit of the TiC_{1–x} homogeneity region, i.e. at the C concentration greater than 50%, different eutectic states and even new compounds can appear in condensates depending on a technological conditions of deposition. In this connection, attention should be paid to the condensation of superweak vapor streams of the relevant chemical composition in a highly purified inert environment. For example, in contrast to condensates of strongly supersaturated vapors [4,5], previous investigations showed that when depositing weakly oversaturated carbon-titanium vapors with certain concentrations, a

diamond phase has been synthesized and a new carbide TiC₂ has been discovered [6].

Therefore, film technologies make it possible to extend our ideas concerning the Ti–C system. Moreover, the synthesis of new structural modifications in condensate forms will inevitably result in the appearance of their new electrophysical characteristics. However, in order to use Ti–C films, it is necessary to develop the technological procedure of their production with preferably perfect structure and reproducible chemical composition.

From the viewpoint of what was said above, this work aims at investigating the interconnection between the chemical composition and the structure of the condensates of weakly supersaturated Ti–C vapors deposited on KCl crystal chips and on glass.

1. Experimental Procedure

The Ti–C films were obtained using the ionic sputtering of composite targets, made of Ti and C, by means of a dc magnetron system. In the weakly supersaturated vapor condensation performed with the purpose to obtain impurity-free Ti–C layers, the negative role of residual chemically active gases increases by many times. Our vacuum system made it possible to lower the partial pressure of chemically active gases down to 7×10^{-8} Pa, and to monitor their chemical compositions [7, 8].

The chemical composition of condensates was determined both by calculations on the basis of the composite target configuration and the ionic current distribution in the erosion zone [9, 10], and by energy dispersion analysis. The layers were deposited simultaneously on glass and KCl chips at temperature 350–500 °C. It should be noted that the structural manifestations of weak vapor supersaturation are sharper in condensates for elevated pressures of inert gas ($P_{Ar} = 10$ Pa) when due to the small free path length of the vapor stream molecules, their movement becomes of the diffusive type [11, 12].

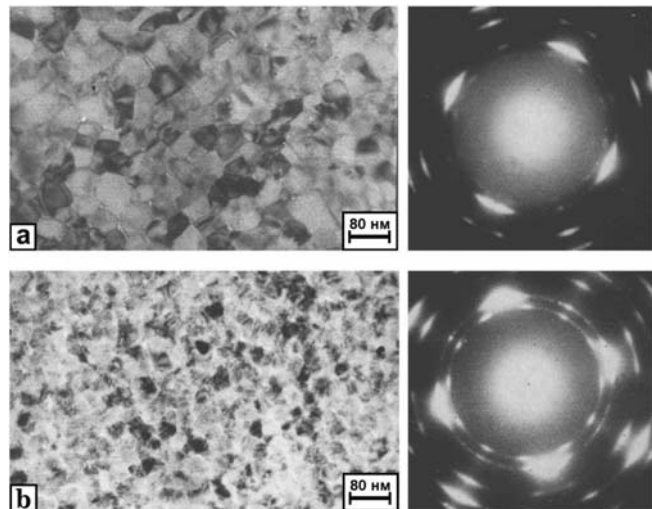


Fig. 1. Structure and phase content of the Ti-C layers in the eutectic region of $TiC_{1-x} + \alpha-Ti$ deposited at $T_{cond} \sim 500$ °C: a – C concentration $\approx 4\%$, b – 10%

The structure and the phase composition of the layers were studied with a transmission electron microscope taking advantage of electron microdiffraction. In so doing, the structure-phase analysis was carried out in layers isolated from KCl, while the chemical analysis was performed in thicker condensate specimens deposited on glass.

2. Experimental Results and their Discussion

Let us consider the regularities in structure and phase composition changes of the layers with increase of the C concentration in them. At minimal C concentrations in Ti-C layers ($\sim 4\%$), only the reflections from $\alpha-Ti$ are present on electron diffraction patterns (see Fig. 1,a). This fact evidences once more for superlow partial

pressures of chemically active gases, because otherwise, due to enhanced gettering properties of Ti, the formation of its oxides, nitrides, or hydrides is inevitable.

An analysis of interplane distances on the basis of electron diffraction patterns of $\alpha-Ti$ (see the table) and the geometry of reflex dispositions, made it possible to isolate major growth textures, where $(0335)_{\alpha-Ti} \parallel (001)_{KCl}$ and $(0001)_{\alpha-Ti} \parallel (001)_{KCl}$. In this case, the microstructure of condensates (see Fig. 1,a) is polycrystalline with the average grain size of ~ 40 nm. For the chemical composition being in the eutectic range of $TiC_{1-x} + \alpha-Ti$ with the C concentration of about 10%, the average grain size decreases to 14 nm and the grain edges become fuzzy (see Fig. 1,b). Additionally, reflexes of epitaxially oriented TiC_{1-x} appeared on electron diffraction patterns. The calculation of an electron diffraction patterns (see the Table) and the construction of relevant cross-sections of reciprocal lattices (see Fig. 2,a) confirmed the availability of the $\alpha-Ti$ growth textures determined earlier, as well as the occurrence of the TiC_{1-x} fcc-lattice with a period of about 0.432 nm with mutual orientation $(001)_{TiC_{1-x}} \parallel (001)_{KCl}$. The smearing of grain edges may be due to the carbide formation on the $\alpha-Ti$ crystal edges under condition of a gradual decrease in the C concentration in the grain edge–grain center direction. It is the grain-boundary carbidization that stabilizes, probably, the electrophysical properties of layers.

A further increase of the C concentration up to 27%, as was expected, resulted in a gradual increase in the reflex intensities of TiC_{1-x} and weakening of the diffraction maxima of $\alpha-Ti$. Moreover, microdiffraction studies showed that the microstructure contained relatively large inclusions of $\alpha-Ti$ and the diffraction maxima smeared out to more extent ones, which can be explained by the presence of a disordered intergrain

Experimental values for interplane distances and lattice types of system Ti-C condensates

<i>h k l</i> lattice type	Interplane distances, Å (table data)	4 % C,	10 %C,	27 % C,	37 % C,	43 % C,	50 % C,
		hcp	hcp+fcc	hcp+ fcc	fcc	fcc	fcc
Interplane distances, Å(exper.)							
01.0 hcp	2.56 $\alpha-Ti$	2.5	2.5	2.5			
111 fcc	2.49 TiC				2.5	2.5	
01.1 hcp	2.24 $\alpha-Ti$	2.22	2.24	2.25			
200 fcc	2.15 TiC		2.16	2.14	2.18	2.14	2.15
01.2 hcp	1.73 $\alpha-Ti$	1.73	1.73				
220 fcc	1.52 TiC			1.55	1.53	1.53	1.54
11.0 hcp	1.48 $\alpha-Ti$	1.47	1.49				
01.3 hcp	1.33 $\alpha-Ti$	1.34					
311 fcc	1.31 TiC		1.32				
02.0 hcp	1.29 $\alpha-Ti$		1.29				
11.2 hcp	1.25 $\alpha-Ti$	1.25					

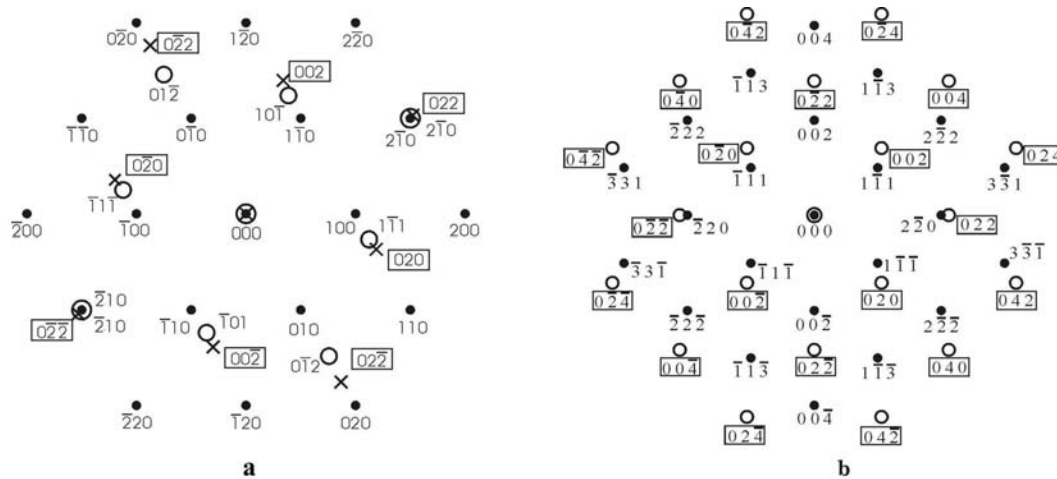


Fig. 2. Reciprocal lattice cross-sections: *a* – $\text{TiC}_{1-x} + \alpha\text{-Ti}$ with $(03\bar{3}5)_{\alpha\text{-Ti}} \parallel (001)_{\text{KCl}}$ (hollow circles), $(0001)_{\alpha\text{-Ti}} \parallel (001)_{\text{KCl}}$ (solid circles), and $(001)_{\text{TiC}_{1-x}} \parallel (001)_{\text{KCl}}$ (crosses); *b* – TiC_{1-x} with $(011)_{\text{TiC}_{1-x}} \parallel (001)_{\text{KCl}}$ (solid circles) and $(001)_{\text{TiC}_{1-x}} \parallel (001)_{\text{KCl}}$ (hollow circles)

space. Due to the presence of $\alpha\text{-Ti}$ inclusions and to the fact that the chemical composition of condensates is close to the TiC_{1-x} homogeneity region, premises for an appearance of a minor amount of free and disordered carbon on the TiC_{1-x} grain surfaces are probably created. Such a chemical nonhomogeneity, in turn, may be enhanced by an elevated contribution of the surface diffusion of adatoms to the structure formation, which is typical of the weakly supersaturated vapor condensation [8, 11, 12].

While entering the TiC_{1-x} homogeneity region, the formation of local fluctuations of the chemical composition, observed before, gradually becomes minimal, and the diffraction maxima become sharper. At the same time, when the C concentration grows to 50%, the gradual transition to the well-defined epitaxial growth and to the creation of a mosaic structure with the average grain size of about 8 nm (see Figs. 3, *a* and *b*) takes place. The phase content of condensates (see the table) corresponds completely to the state diagram of the Ti–C system [1, 2], i.e. the layers in the TiC_{1-x} homogeneity region have a fcc lattice of the NaCl type with a period of about 0.432 nm. The disappearance of local fluctuations of the chemical composition can be related to the fact that, at the condensate origination stage, no $\alpha\text{-Ti}$ crystals are created because of its lower concentration in the vapor phase. The reasons for the formation of a mosaic structure observed with an electron microscope (see Fig. 3, *b*) are most probably as follows. Since the periods of the NaCl and TiC lattices are different, the atoms of carbide islands, which are

unbounded at first, have different displacements upon their generation with respect to $(001)_{\text{KCl}}$ atoms. This circumstance inevitably results in the appearance of a dislocation structure in the areas where those islands fuse together, and the contrast from which is enhanced due to stresses appearing during the condensate cooling after its deposition as a result of high elastic characteristics of TiC_{1-x} . This conclusion is supported by the fact that the mosaic structure manifests itself in TiC layers, i.e. at maximal values of Young's modulus (about 4600 kg/mm² [1]). Thus, the stresses generated in the regions where islands fuse together enable us to visualize the mosaic structure with an electron microscope.

The identification of the electron diffraction patterns (Fig. 3, *a*) by plotting the relevant cross-sections of the reciprocal lattices (see Fig. 2, *b*) allowed us to discover the orientations of the TiC_{1-x} crystal growth, for which $(011)_{\text{TiC}_{1-x}} \parallel (001)_{\text{KCl}}$ or $(001)_{\text{TiC}_{1-x}} \parallel (001)_{\text{KCl}}$. The coincidence of the relevant electron diffraction patterns forms and the reciprocal lattice cross-sections, depicted in Figs. 2, *a* and *b*, can be obtained by superimposing, on those cross-sections, their twins azimuthally rotated by 90°, which stems from $(001)_{\text{KCl}}$ symmetry.

The investigation of a layer structure at the C concentration of above 50% confirmed, on the whole, the results of work [6]. For example, the phase content of condensates obtained under the conditions of diamond formation at a C concentration of about 70%, corresponds to the bcc lattice with a period of about 0.3 nm (see Fig. 4, *a*). In this case, the limits of chemical composition, where the TiC_2 compound is created, are

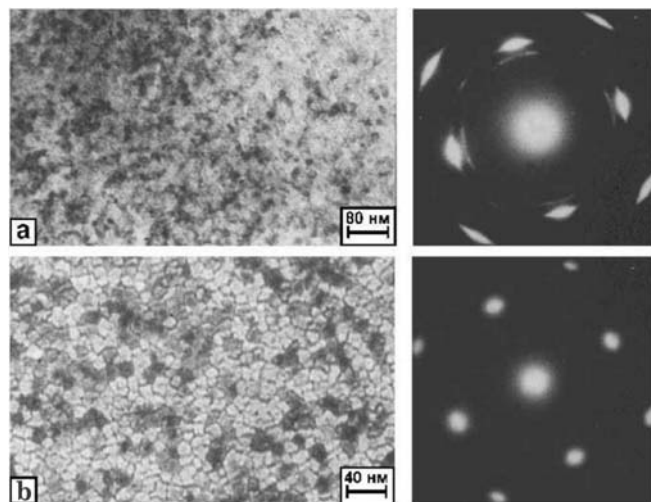


Fig. 3. Structure and phase content of the TiC_{1-x} layers deposited at $T_{\text{cond}} \sim 500$ °C on the KCl chips: *a* – C concentration $\approx 37\%$, *b* – 50%

smear out. It should be noted that the existence of carbide in the form of TiC_2 is proved evidently by the bcc-lattice [6], the correspondence of the chemical composition, the increase of microhardness discovered earlier, and the metastability of TiC_2 with respect to diamond, which, in turn, is of special interest. For example, when an electron beam irradiates TiC_2 disposed just in an electron microscope, the 200-reflexes of the bcc-lattice gradually disappear, and the 110- and 211-reflexes transform into 111- and 220-ones, respectively, of the diamond phase. This fact evidences indirectly for the validity of the TiC_2 crystal lattice construction proposed in [6]. Indeed, such a transformation is possible, if the diamond lattice, being even in a greatly deformed state (as was proposed in [6]), does exist in the TiC_2 lattice from the very beginning, because its synthesis under the action of a low-power electron beam is practically impossible. This conclusion allows us to make a suggestion that if a rather prolonged concentration profile is created in the form of a layer of the Ti–C system, where a gradual increase of the C concentration is foreseen from zero (at the layer-substrate interface) to 100% (on the outer surface of the layer), and if the generation of TiC_2 occurs in this layer under relevant conditions and concentrations, then a transition to the diamond phase is possible, i.e. TiC_2 can serve as a precursor of the diamond formation. But it should be noted that the synthesis

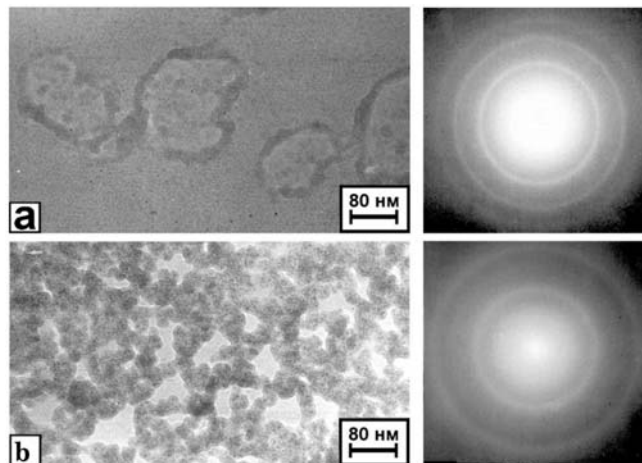


Fig. 4. Structure and phase content of the Ti–C layers at C concentration above 50% deposited at $T_{\text{cond}} \sim 500$ °C: *a* – C concentration $\approx 70\%$, *b* – 100%

of TiC_2 is a rather involved technological task by itself.

A transition to chemical compositions with the C concentration above 50% leads to an essential increase of the condensate dispersion and to the gradual decrease of the orienting action of the plane $(001)_{\text{KCl}}$. At the same time, with the increase of the C concentration, a transformation of a uniform, continuous, fine-dispersed structure into porous globular formations occurs. In this case, a sharp boundary of such a transition is observed as early as at C concentrations of about 70% (see Fig. 4, *a*). The highest porosity is observed in layers containing the diamond phase and possessing the C concentration of about 100% (see Fig. 4, *b*).

It is probable that the creation of porous structures results from the condensation of vapors with extremely low supersaturation. In this case, the origin of a condensate takes place only locally. Then the surfaces of those germs are the sites of vapor deposition under most equilibrium conditions. As a result, those growing germs acquire a bulk globular form. It should be also noted that the increase of the C concentration promotes its partial transition into the amorphous free state. It is evidenced for by the enhancement of the diffuse electron scattering (see Figs. 4, *a* and *b*) and by a substantial electrical conductivity of layers containing the diamond phase.

An increase of the vapor supersaturation by reducing the condensation temperature to 350 °C, with all other

technological parameters to be invariable, results in a general growth of the structure disorder which is mainly observed in condensates with C concentration less than 50% and manifests itself in both diminishing the grain size and increasing their mutual disorientation. At the same time, when reducing the condensation temperature down to 350 °C and increasing the C concentration from 50 to 100%, a smooth transition from TiC to amorphous C takes place with a simultaneous reduction of the orienting influence of the (001)_{KCl} plane.

The studies of the electrophysical properties of TiC epitaxial layers showed that their resistivity ρ and Hall factor R_H change in the limits $(91.26 - 92.74) \times 10^{-8}$ Ohm m and $(2.8 - 3.63) \times 10^{-10}$ m³/K, respectively, in the temperature interval 20–140 °C. Moreover, R_H is negative and the dependence $\rho(T)$ is of a metallic type with $T\rho = 1.35 \times 10^{-4}$ K⁻¹, which is by one order of magnitude less than that in single-crystal TiC [1]. The value of R_H is also substantially smaller (approximately by a factor of 3) in comparison with the relevant value of the bulk TiC [2]. All those disagreements may be due to a mosaic structure of the epitaxial layers as well as to the film form of the substance. It should be also noted that the electrophysical properties of the TiC_{1-x} films remained almost constant in 8 months. At the same time, when diminishing the C concentration from 4–6% to zero, the resistivity varies from 30% to 2–3 orders of magnitude.

One of the most interesting results of the present work is undoubtedly the formation of TiC₂ and the diamond phase. It is clear that the low vapor supersaturation affects ambiguously the structure formation of condensates. We believe that it is governed by the diffusion of adatoms, their binding energy with a growth surface, and a stronger pronounced ability to reevaporate weakly bound adatoms, with all the factors being unbrokenly interconnected. Although these factors play an important role in the process of formation of a condensate structure under any supersaturation, their influence is manifested more expressively in our case. It is well known [13] that the condensation of weakly supersaturated vapors leads to a decrease of the concentration of germ formation centers and, therefore, favors the manifestations of the decoration effect. The main reason for these manifestations consists obviously in more nonequilibrium conditions for the vapor-condensate transition. The latter results eventually in the condensation of those atoms only which made sufficiently strong chemical bonds with a substrate or a growth surface during their thermal accommodation.

In turn, the probability of formation of such bonds will increase for adatoms possessing energies at the condensation moment which are sufficient for the creation, e.g., of SP^3 -hybridized bonds. All other adatoms would be reevaporated with a large probability due to small supersaturation. Just this phenomenon became the basis for the formation of a porous globular structure, the diamond phase, and TiC₂.

In conclusion, we note that, using the condensation of weakly supersaturated carbon-titanium vapors under minimal partial pressure ($\sim 7 \times 10^{-8}$ Pa) of chemically active gases, it is possible to perform the epitaxy of a stoichiometric titanium carbide on KCl chips and to obtain a new carbide compound TiC₂ and the diamond phase. Moreover, the TiC₂ substance is metastable with respect to diamond, which is possibly a premise for obtaining the diamond phase with the use of the TiC₂ → diamond transition.

1. *Samsonov G.V., Upadkhaya G.Sh., Neshpor V.S.* Physical Properties of Carbides. — Kyiv: Naukova Dumka, 1974 (in Russian).
2. *Kiparisov S.S., Levinskii Yu.V., Petrov A.P.* Titanium Carbide: Production, Properties, and Applications. — Moscow: Metallurgia, 1987 (in Russian).
3. *Lee S.-K., Zetterling C.-M., Östling M. et al.* // Solid-State Electronics. — 2000. — **44**, N 7. — P. 1179–1186.
4. *Inoue S., Wada Y., Koterazawa K.* // Vacuum. — 2000. — **59**. — P. 735.
5. *Perekrestov V.I., Pavlov A.V., Kosminskaya Yu.A.* // Visnyk Sumskogo Derzh. Univer. — 2002. — **46**, N 13. — P. 140–150.
6. *Perekrestov V.I., Pavlov A.V.* // Pis'ma Zh. Eksp. Teor. Fiz.— 2001. — **73**, N 1. — P.17–21.
7. *Perekrestov V.I., Kravchenko S.N.* // Prib. Tekhn. Eksp. — 2002. — N 3. — P.123–126.
8. *Perekrestov V.I., Kravchenko S.N., Pavlov A.V.* // Fiz. Met. Mater. — 1999. — **88**, N 5. — P.72–77.
9. *Perekrestov V.I., Khvorost V.A., Pavlov A.V.* // Poverkhn. — 2001. — N 11. — P.30–32.
10. *Perekrestov V.I., Khvorost V.A., Pavlov A.V.* // Sverkhtverd. Mater. — 2000. — N 5. — P.10–15.
11. *Perekrestov V.I., Koropov A.V., Kravchenko S.N.* // Fiz. Tverd. Tela. — 2002. — **44**, N 6. — P.1131–1136.
12. *Perekrestov V.I., Khvorost V.A., Kravchenko S.N.* // Visnyk Sumskogo Derzh. Univer. — 2002. — **38-39**, N 5-6. — P.72–79.
13. *Thin Film Technology: Handbook* / Ed. by L. Maissel, R. Glang. — Moscow: Sov. Radio, 1977. — Vol. 2.— P. 13–55 (in Russian).

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ФАЗОВИЙ СКЛАД ТА СТРУКТУРА КОНДЕНСАТІВ
СЛАБКОПЕРЕСИЧЕНИХ ВУГЛЕЦЕВО-ТИТАНОВИХ
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Резюме

Наведено результати досліджень взаємозв'язку хімічного складу та структури шарів системи Ti-C, отриманих магнетронним розпиленням складених мішеней. Шари конденсувалися

при слабкому пересиченні парів і досліджувалися за допомогою просвічувального електронного мікроскопа (ПЕМ) з використанням методу мікродифракції електронів. Хімічний склад визначався розрахунковим методом і шляхом енергодисперсійного аналізу. Встановлено, що при відповідних концентраціях вуглецю осаджуються шари, що містять новий карбід у вигляді TiC₂ і алмазну фазу. TiC₂ має ОЦК-ґратку з періодом 0.3 нм і є метастабільною фазою відносно алмазу. Показано визначальний вплив низького ступеня пересичення парів на утворення пористих структур (при концентрації C, більшій ніж 70 ат.%), а також отримання епітаксialьних шарів TiC.