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Some regularities of diamond phase formation at nonequilibrium transition process of C vapors with low Ti concentration into condensed state

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The mechanisms of structure formation of Ti–C system layers have been studied. The layers have been obtained at nonequilibrium process of transition of vapors with necessary component ratio into condensed state. Various levels of the condensation process nonequilibrium have been reached by exposure of the growth surface by electron streams with different intensities. Some regularities of transition of the metastable compound TiC_2 into diamond phase have been determined by complex studies of physical properties of the condensates using methods of electron diffraction analysis, Raman scattering.

Изучены механизмы структурообразования слоёв системы Ti–C, полученных при неравновесном процессе перехода паров с необходимым соотношением компонент в конденсированное состояние. Различная степень неравновесности процесса конденсации достигалась облучением ростовой поверхности потоками электронов различной интенсивности. Путем комплексного изучения физических свойств конденсатов с использованием методов электронографии, комбинационного рассеяния были установлены некоторые закономерности перехода метастабильного соединения TiC_2 в алмазную фазу.

At the hydrogen-free synthesis of α-C layers, the growth surface is exposed to ion streams, providing local compression stresses in the sites of interaction with condensate, thus facilitating the diamond phase initiation [1, 2]. In contrast to chemical deposition, such synthesis of the layers is less equilibrium, and the transition to graphite-like structure occurs as the condensation temperature (T_c) exceeds 100...200°C [3].

Due to small electron mass, the interaction of relatively weak electron streams with the growth surface does not result in local stress increase up to levels required for effective diamond-like structure formation. For this reason, aiming the partial conversion of the formed graphite-like layer into diamond-like state, a short-term influence of high-power electron stream is usually used [1], while continuous irradiation by a weaker electron stream during the condensate growth does not provide a positive result. At the same time, using nonequilibrium transition of weak C and Ti vapor streams into condensed state, it is possible to obtain the TiC_2 compound, which is metastable with respect to diamond [4]. Such a metastability reveals itself under the action of the electron beam. In this connection, the idea is offered [5] that under certain conditions, the TiC_2 may favor the diamond

phase nucleation. During the realization of this idea, diamond microcrystals were obtained presumably [5], containing small amount of Ti (up to 1 at.%). In that case, the TiC_2 influence was considered to be limited only to the initiation of diamond phase growth, while the main role in layer-to-layer crystal growth was played by the selective processes occurring at extremely nonequilibrium transition of matter into condensed state. However, in this case, one should not exclude the precursor role of TiC_2, i.e. Ti enriched growth surface formation, promoting the layer-to-layer crystal growth. Verification of this statement is the primary goal of the present work.

The simultaneous deposition of C and Ti in required ratios along with exposure of the growth surface to electron stream were performed using two Ti magnetron sputterers and one C sputterer. The C sputterer discharge was stabilized using the hollow cathode effect [6], as well as electric and magnetic field superposition (Fig. 1a). It is also to note that the hollow graphite cathode being sputtered served as a source not only of carbon plasma, but also of a sufficiently intense secondary electron stream. Since a fundamentally new engineering solution has been used in the C sputterer, let its main functional capabilities be considered in more detail. At first, note that if the hollow cathode effect is used without magnetic field, the discharge initiation shifts to higher working gas pressure region (P_{Ar} ~ 60 Pa), the initiation voltage being the same, while the discharge current decreases by about one order of magnitude. Besides, the magnetic field assists in focusing the electron stream onto the substrate.

Study of the sputterer voltage-current characteristics, condensate growth rate R_c and substrate heating temperature by electron stream, depending on the working gas pressure P_{Ar} reveals the following regularities. As P_{Ar} increases, the discharge current tends to saturation gradually, and voltage-current characteristics do not contain typical knees usually defining glow-to-arc discharge transition (Fig. 1b). Their absence shows that the internal part of the warming-up cathode turns in essence into a diffuse arc discharge cathode spot progressively [6]. Besides, when the sputterer power input (P_w) remains constant while P_{Ar} increases from 0.4 to 40 Pa, the growth rate R_c falls from 4.8 to 0.01 nm/s. This fall seems to be caused by the corresponding intensification of sputtered C and Ti outdiffusion [7]. The substrate heating temperature by the electron stream depends on its thermal capacity and geometry. Here, in each specific case, the increase in P_{Ar} from 0.4 to 40 Pa at a fixed C sputterer power input results in T_c reduction by about a factor of three. This is the consequence of electron beam dispersion intensification. It is possible to control the Ti concentration in

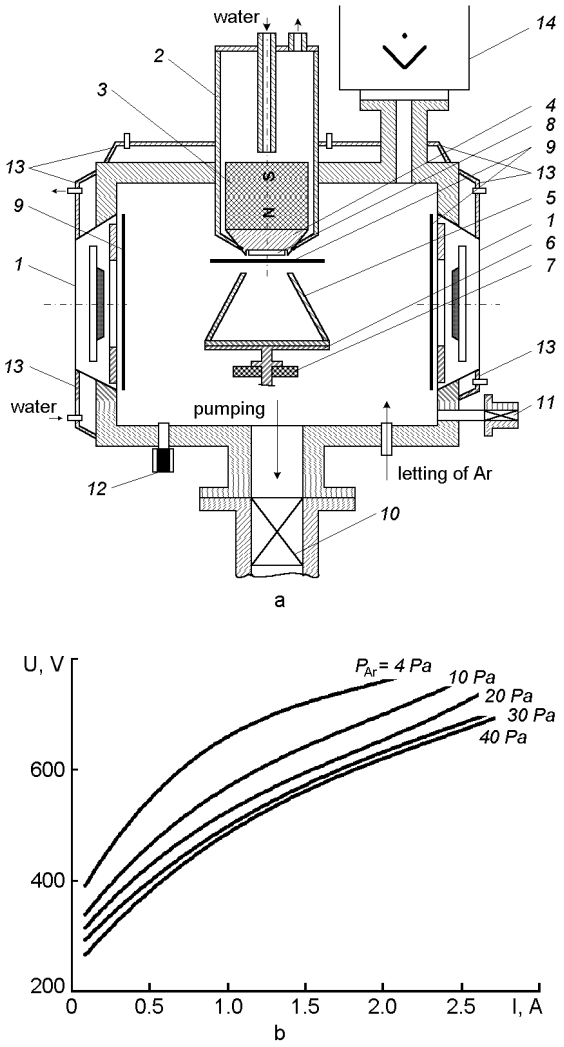

Fig. 1. The scheme of the vacuum-sputtering system (a) and voltage-current characteristics of the C sputterer at different P_{Ar} (b): 1 — Ti magnetron sputterers; 2— C sputterer anode body; 3 — the magnet; 4 — the magnetic conductor; 5 — sputtering cathode graphite body; 6 — the cathode holder; 7 — the isolator; 8 — the substrate; 9 — the flaps; 10 — the valve, joining the vacuum camera to the evacuation system; 11 — the valve, joining the vacuum camera to the rough evacuation channel; 12 — the ionization pressure sensor; 13 — the vacuum chamber water cooling; 14 — the mass-analyzer.

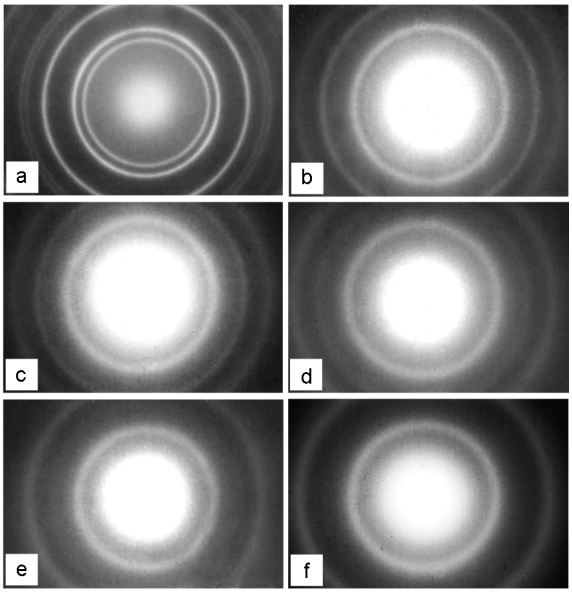

Fig. 2. The regularities of condensate phase composition changes at decrease in Ti concentration from 50 up to 30 at.% (transition from TiC (a) to TiC_2 (b)) and under the influence of the TEM electron beam (c — TiC_2 + diamond phase; d — TiC_2 + diamond phase; e — diamond phase; f — diamond phase, grown from the acetone vapors).

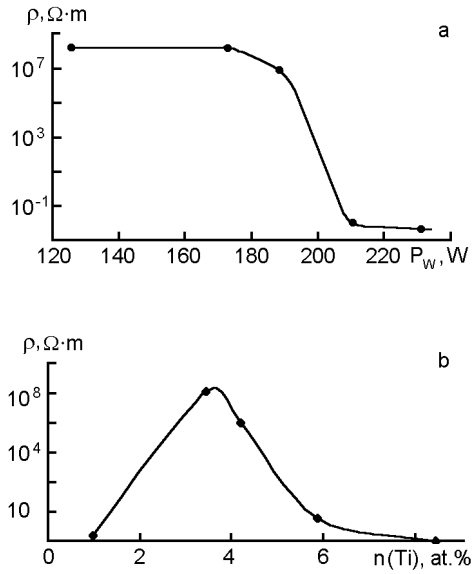

Fig. 3. The P_w dependence of ρ at P_{Ar} = 10 Pa, T_c = 220...350°C, Ti concentration ~1 at.% (a) and Ti content dependence of ρ for the condensates, obtained at P_w = 210 W, P_{Ar} = 10 Pa и T_c = 250...380°C (b).

condensates precisely by varying P_w of the magnetron sputterers while keeping other process variables constant.

At the initial stage of the experiments, the vacuum chamber was pumped out, degassed and then cut off completely of the evacuation system. Then Ar was leaked in and Ti sputterers were turned on for a long period of time (about 30 h). In that way, due to the getter properties of condensed Ti, the fine purification of Ar [8] and also decrease in Ar pressure down to the necessary value were provided. It is to note that during such purification, the graphite sputterer was connected and degassed by heating. These preparatory stages prevented any further interaction between the deposited Ti and chemically active components of residual gases, because the partial pressure of those came to only $8 \cdot 10^{-8}$ Pa [8].

The Ti–C system layers were condensed on freshly-cleaved KCl facets, Si single crystals, glass, and polished stainless steel plates free of Ti. The condensate structures were studied using scanning and transmission electron microscopy (SEM and TEM, respectively) and electron diffraction. The chemical composition was determined from characteristic X-ray emission spectra directly in the scanning electron microscope. Using the electron beam of about 1 μm in diameter, the local chemical analysis was carried out when necessary. The layer resistivity ρ was used as a parameter sensitive to diamond formation.

First, using P_{Ar} = 4 Pa and selecting Ti sputterer power input, the layers with chemical and phase compositions answering to TiC compound were deposited (Fig. 2a). Thus, the condensation conditions are effective for carbide formation, and this fact is a significant point in this work. At the further decrease in Ti sputtering intensity, the transition to formation of TiC_2 bcc lattice [4] in the condensates was provided (Fig. 2b). The subsequent Ti concentration reducing down to several at.% at other process variables fixed resulted in a gradual ρ increase up to about 10^3 Ω·m. The condensates were essentially opaque in the visible spectral range, and the regularity of phase composition change corresponded to that described in [4]. Transition to higher working gas pressures (P_{Ar} = 10 Pa) along with keeping C sputterer power input unchanged and Ti concentration up to 1 at.% favored the increase in ρ to $1.4 \cdot 10^8$ Ω·m. At the same time, the visible range transparency of the 0.4 μm thick layers grew to 70...80 %, and electron diffraction study evidenced their amorphous state. It should be noted that the microhardness of the lay-

ers remained constant being as low as about 150 kgf/mm^2. Obviously, such regularity of physical properties change at increasing P_{Ar} was due to corresponding decrease in R_c and T_c, as noted above.

Increase of C sputterer power, the flaps of Ti sputterers being shut, results in breaking-up the diamond-like state formation, as revealed by high ρ values (Fig. 3a). At the same time, the process variables of diamond-like to graphite-like state transition can be obtained. Evidently, by varying Ti concentration at these parameters, it is possible to ascertain the degree of Ti influence on the diamond formation process. In this connection, as it follows from Fig. 3b, increase in Ti concentration up to 3 at.% results in a considerable increase of ρ, thus, role of Ti as a catalyst being verified rather pronouncedly. Besides, the further increase in Ti content up to 8 at.% results in a gradual decrease of ρ by 10 orders (Fig. 3b) and also in almost full loss of the layer transparency. Analysis of the phase composition of the last experimental series condensates shows the presence of highly dispersed diamond phase and TiC_2, and a regular intensification of diamond phase reflections taking place as Ti concentration decreases. The same phase changes can be observed as the layers with Ti concentration about 3 to 5 at.% are exposed to electron beam directly in TEM (Fig. 2c, d, e). The observed $TiC_2 \rightarrow$ diamond transition can be explained as follows. The TiC_2 lattice represents a distorted fcc lattice of TiC, with additional C atoms introduced into some interstices [4]. Hence, the carbon sublattice of TiC_2 represents a strongly distorted lattice of diamond. If TiC_2 is decomposed due to electron stream action and Ti diffuses to grain boundaries and surface of the condensate, then the vacancies become shut by compressing carbon sublattice to diamond form. Such processes are evidenced to a certain extent during TEM-investigations by corresponding appearance of contrasts in condensate microstructure patterns visible as more light stripes and spots (Fig. 4a). Apparently, such sites are enriched in Ti. The dark regions of this microstructure pattern represent most likely finely dispersed diamond phase, which scatters electrons more efficiently. It is necessary to note that, as it follows from electron-diffraction analysis, accumulation of Ti between diamond inclusions is not accompanied by carbide formation. Perhaps the necessary stoichiometry is

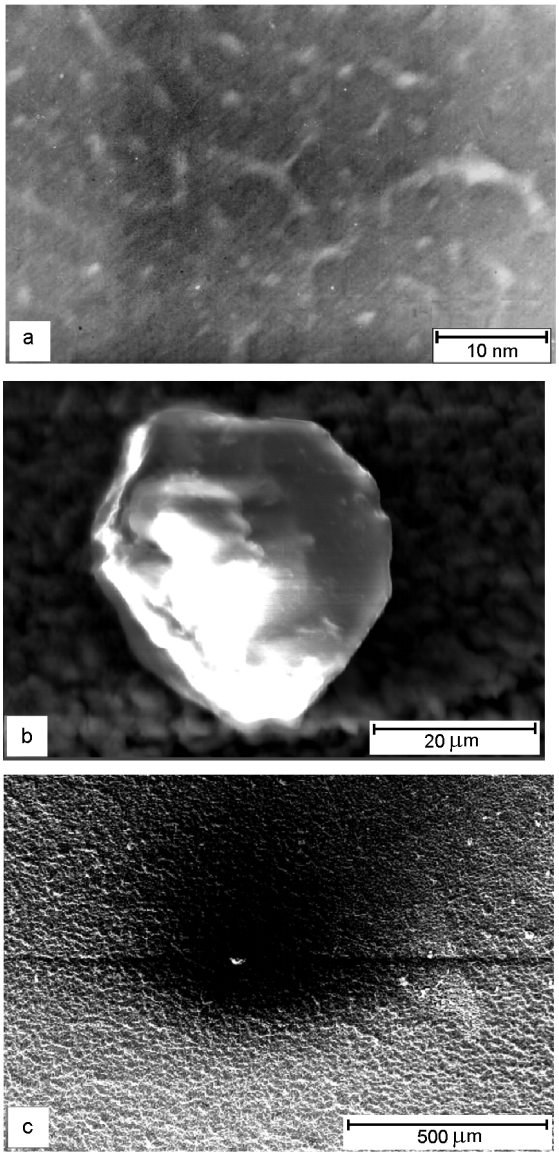

Fig. 4. The microstructure patterns of the condensates (a — after affecting by the electron beam in TEM, b и c — dielectric inclusions at large and small enlargements correspondingly).

lacking, and TiC_2 formation needs special technological conditions [4].

Using acetone vapors as the working gas and also the C sputterer proposed in this work, fully transparent dielectric layers with enhanced microhardness (about 1200 kgf/mm^2) were produced. Those layers contained finely dispersed diamond phase. The electron diffraction patterns for structures obtained by means of $TiC_2 \rightarrow$ diamond transition were compared to those obtained using acetone vapors. In spite of principal difference in approaches to layers formations, identity of the patterns was revealed

(Fig. 2e and 2f). However, as it follows from that comparison, intensity of the diffraction reflections from α-C:H is more considerable, and this fact, together with increased microhardness, points out obviously a higher content of diamond phase. An attempt to get hard layers with Ti concentration 3 to 8 at.% by their vacuum annealing at about 500°C for 4 hours did not have positive result. The microhardness remained only 150 to 200 kgf/mm^2 after annealing. All these facts, taken together, indicate a specific structural state, when possible superhard nanofragments of the substance are weakly bound to each other. Most likely, diamond nuclei, appeared due to the $TiC_2 \rightarrow$ diamond phase transition, did not get their further development. As preliminary investigation results showed, Raman spectra, sensitive to molecular state, have a complex character dependent on Ti concentration. However, for a series of samples condensed on Si and glass at Ti concentration about 3 to 5 at.%, we were succeed to ascertain the presence of clear maxima at about 1332 cm^{-1} (Fig. 5) that testifies to the presence diamond phase.

Summarizing all stated above, we can affirm that a low Ti concentration really stimulates diamond formation. The TiC_2 phase, however, acts as a precursor mainly under electron stream or other possible action upon already formed condensate. Here, it is not excluded that to intensify these precursor functions during the diamond phase growing, it is necessary to use such technological conditions that could provide continuous synthesis and decomposition of TiC_2 on the growth surface. Perhaps it is just those conditions that were realized in [5]. But to verify such assumption, it is necessary to control the Ti vapors coming onto growth surface very strongly. In [5], from the technical point of view, such a task did not seem to be attained. In this connection, to uncover the precursor role of TiC_2, the nonequilibrium mode of the matter (Ti and C) transition into condensed state was first of all increased. To that end, the C sputterer power input was elevated up to 650 W, and, respectively, the steel substrate was heated up by electron beam to temperatures near 800°C. In addition to electron stream, negative ions and condensing atoms with increased energy seem to affect the growth surface as well. All that in combination was an important prerequisite for intensification of the process nonequilibrium.

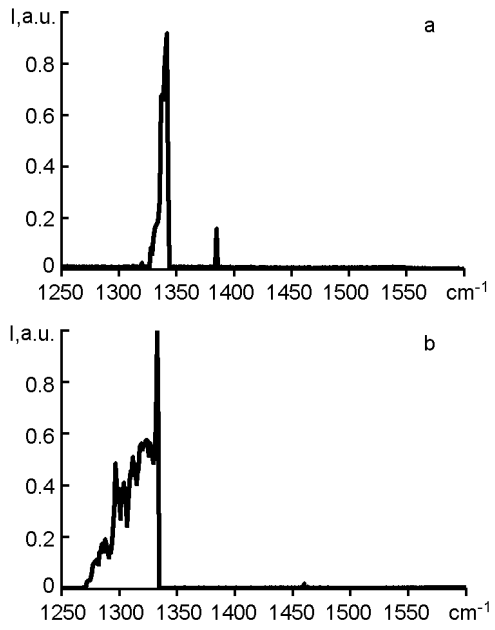

Fig. 5. Raman spectrums of the condensates, obtained on Si substrates (a) and glass (b).

As SEM analysis showed, the condensates obtained in such conditions, consisted mainly from porous graphite-like structure with rather low value of ρ and have a characteristic black color. However, in some samples, inclusions with features of crystalline faceting (Fig. 4b) and Ti content no more than 1 at.% were revealed. Besides, SEM analysis showed at low magnifications that the inclusions accumulate negative charge, thus creating dark background about them (Fig. 4c). This fact points out their dielectric properties. Gathering all mentioned above, it is possible to define these inclusions as diamond at a high probability. It should be emphasized that the formation process of such inclusions occurred under continuous coming of Ti vapors in minimum amounts to the growth surface. If Ti vapors coming was interrupted at a certain stage of the condensate formation, then further deposition did not result in formation of the dielectric inclusions. This is what let us to presume that TiC_2 performs precursor functions.

To conclude, the metastable compound TiC_2 is formed at nonequilibrium transition of C and Ti vapors taken in certain ratios into condensed state. The compound can be transformed into diamond phase under the action of electron beam. Increasing T_c to 800°C by means of more intense electron stream influence upon the growth surface, and thus increasing the condensation proc-

ess nonequilibrium, it is possible to obtain individual inclusions being presumably diamond. Perhaps their layer-to-layer growth occurs due to the precursor effect of TiC_2 compound.

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Деякі закономірності утворення алмазної фази при нерівноважному процесі переходу парів C з малим вмістом Ti у конденсований стан

В.І.Перекрестов, Ю.О.Космінська, І.Б.Янчук

Вивчено механізми структуроутворення шарів системи Ti–C, отриманих при нерівноважному процесі переходу парів з необхідним співвідношенням компонентів у конденсований стан. Різний ступінь нерівноважності процесу конденсації досягався опроміненням ростової поверхні потоками електронів різної інтенсивності. Шляхом комплексного вивчення фізичних властивостей конденсатів з використанням методів електронографії, комбінаційного розсіяння встановлено деякі закономірності переходу метастабільної сполуки TiC_2 в алмазну фазу.