Translated from *Uspekhi Khimii*, **49**, 1671-1686 (1980) U.D.C. 621.793.1:547,1'13

The Formation of Inorganic Coatings in the Decomposition of Organometallic Compounds

G.A.Domrachev and O.N.Suvorova

The present status of the methods for producing inorganic coatings from the vapour phase by the decomposition of organometallic compounds (OMC) is considered critically and systematically. The methods are classified in terms of physicochemical features and the physical procedures involved. The efficiencies of various methods for the preparation of coatings from the vapour phase in the thermal decomposition of OMC and the possibilities of their employment for a specific alteration of the properties of the coatings obtained are compared. Patent data on various procedures and devices used in the formation of inorganic coatings from the vapour phase in the decomposition of OMC are widely used.
The bibliography includes 96 references.

CONTENTS

I. Introduction 810
II. Chemical features of the use of organometallic compounds for the preparation of coatings from the vapour phase 810
III. The use of the physicochemical characteristics of the decomposition of organometallic compounds for the deposition of coatings 811
IV. Physical characteristics of the methods for the deposition of coatings from the vapour phase 816

I. INTRODUCTION

There exist numerous patents and other publications on the deposition of inorganic coatings from the vapour phase in the thermal decomposition of organometallic compounds (OMC) and metal carbonyls. In the USSR a group of investigators and technologists led by Academician G.A.Razuvaev is concerned with systematic studies and technological development of these processes.[1] Razuvaev showed an interest in the isolation of metals from organometallic compounds in thermal reactions as early as the 1920s.[2] These studies subsequently served as a basis for research by Razuvaev and his students into the thermal decomposition and photodecomposition of OMC in solution and then in the vapour phase; these studies have been surveyed in a monograph[1].

However, the literature contains no systematic review of the existing methods for the deposition of inorganic coatings from the vapour phase on decomposition of OMC; in the present review an attempt is made at such a systematic account.

II. CHEMICAL FEATURES OF THE USE OF ORGANOMETALLIC COMPOUNDS FOR THE PREPARATION OF COATINGS FROM THE VAPOUR PHASE

The use of OMC for processes where their intermediate formation transfers a metal to the substrate makes it possible to carry out the deposition at low temperatures and to increase the concentration of the working compound as a result of the lower decomposition temperature of the OMC and their higher vapour pressure at low temperatures[1]. The fundamental mechanism of the deposition of films from the vapour phase in the thermal decomposition of OMC can be formulated as follows:

$$R_nM\ (\text{solid or liq.}) \xrightarrow{t^\circ} R_nM\ (\text{gas}),$$
$$R_nM\ (\text{gas}) \xrightarrow[\text{support}]{t^\circ} R_nM\ (\text{ads.}),$$
$$R_nM\ (\text{ads.}) \xrightarrow{t^\circ} M\ (\text{solid})/\text{support} + n\,R\ (\text{ads.}),$$
$$n\,R\ (\text{ads.}) \xrightarrow{t^\circ} n\,R\ (\text{gas}).$$

These stages of the process determine its chemical nature and constitute the basis for the development of methods of deposition of coatings. In order to select the deposition procedure and to carry out the latter in a specific technological scheme, it is necessary to analyse in detail each stage of the process.

In the preparation of a multicomponent coating, for example a binary coating, a mixture of the necessary number of OMC of different metals, for example two, or a mixture of the OMC of one metal and the hydride of another element, is used[3-7]:

$$MR_n + M'R'_m \rightarrow M{-}M' + n\,R + mR',$$
$$Me_3Ga + AsH_3 \rightarrow GaAs + 3CH_4,$$
$$Me_4Pb + Me_2Te \rightarrow PbTe + x\,C_nH_m,$$
$$Me_3Ga + AsMe_3 \rightarrow GaAs + x\,C_nH_m.$$

It has been established that the intermediates in the joint decomposition of two OMC are, as in the case of Me_3Ga and Me_3As, oligomeric and polymeric fragments containing the $(R{-}Ga{-}As)_x$ group[6]; these fragments cannot catalyse the subsequent decomposition of the OMC mixture.

Hence it follows that, for the decomposition of binary compounds and OMC, one can employ the thermal decomposition of molecular complexes of OMC of the type $Me_3Ga.AsMe_3$ or organobimetallic compounds containing covalent M–M or M–E bonds[8]:

$$R_nM{-}M'R_m\ (\text{solid or liq.}) \xrightarrow{t^\circ} R_nM{-}M'R_m\ (\text{gas}) \xrightarrow[t^\circ]{\text{support}} \rightarrow (n+m)\,R\ (\text{gas}) + M{-}M'\ (\text{solid})/\text{support} + m\,R\ (\text{gas}).$$

Adsorption and desorption processes can also be involved in this scheme. In the general case the formation of a two-component system on the surface requires that the reaction between the metals liberated or the decomposition reaction must proceed via the formation of intermediate compounds containing the M–M′ bond[7].

Bearing in mind the high efficiency of the metal transfer to the support with the aid of OMC, one can also employ the metal transport reaction with the aid of organic radicals or ligands. The best known classical example of a transport

reaction with participation of free radicals is provided by the method of Paneth mirrors[9]:

$$R_nM\ (gas) \xrightarrow{t^\circ} M(solid) + n\,R\ (gas) \xrightarrow{+M'_l(solid)} R_mM\ (gas) \rightarrow \xrightarrow[t^\circ]{support} \rightarrow M'_l(solid)/support + m\,R\ (gas).$$

Free radicals, generated by the thermolysis of readily available OMC, for example Me_2Hg, behave as transporting agents for the transfer of solid metal through the gas phase to the region of higher temperatures; the support on which the metal film is formed by the thermal dissociation of the OMC formed is placed in this region. Such processes include the transport of nickel by carbon monoxide as a result of the reversibility of the reaction[10,11]:

$$Ni(solid) + 4CO \rightleftarrows Ni(CO)_4 \rightleftarrows Ni(solid)/support + 4CO.$$

Here carbon monoxide functions as the metal-transporting ligand. A metallic alloy, for example MM', can be transported similarly[12]:

$$MM'(solid) + (n+m)\,R\ (gas) \rightleftarrows \begin{cases} \rightarrow R_nM{-}M'R_m\ (gas) \\ \rightarrow R_nM\ (gas) + R_mM'\ (gas) \end{cases} \xrightarrow{t^\circ} MM'(solid) + (n+m)R\ (gas).$$

Combinations of these methods for the transport of metal are also possible.

However, a common feature of all these procedures is a high volatility of the OMC, a low decomposition temperature of the OMC with liberation of the metal, the obligatory presence of organic OMC decomposition products and sometimes their strong influence on the process, the possibility of the adsorption and secondary reactions of the OMC decomposition products, and a comparatively high vapour pressure of the organic OMC decomposition products at the deposition temperatures.

Although the first two factors are favourable from the standpoint of the use of OMC for the formation of coatings, the negative influence of the decomposition products can sometimes abolish altogether the positive effect. For the successful realisation of the OMC thermal decomposition processes, it is therefore necessary to employ special procedures for the deposition of coatings from the vapour phase in which the harmful effects of the decomposition products are diminished or eliminated with the aid of mass and heat transfer phenomena and mechanical and chemical methods.

The chemical features of the procedures for the deposition of coatings are determined by the composition and structure of the OMC and by the addition of various chemical reagents. In terms of the composition of the gas–vapour phase for the coating, the methods can be classified as follows:

(1) methods using an individual OMC;

(2) methods using a mixture of individual OMC;

(3) methods using an individual OMC mixed with the hydrides of other elements or with readily decomposed inorganic metal compounds;

(4) methods using individual OMC or their mixture in an atmosphere of a reactive gas [reducing to the metals (H_2),[13,14] oxidising (O_2),[13] etc.], which improves the elemental and phase compositions of the coatings;

(5) methods using OMC in mixtures with additives which serve as energy transferring agents or with "quenching agents" for the excited states (for example, iodine[15,16], amines[17–19], ammonia[15,20], diolefins[21,22], ferrocene[23], and other OMC[24–27]);

(6) methods using OMC in mixtures with added decomposition catalysts (halogen derivatives[28], sulphur derivatives[29] for the decomposition of bisarenechromium, transition metals for aluminium hydride complexes[30], and transition metal salts for metallocenes[31,32]);

(7) methods using OMC in a mixture with added active hydrogen atom donors in radical reactions (glycols for the decomposition of copper acetylacetonate[33,34], hydrogenated aromatic compounds of the type of dihydrobiphenyl, tetralin, cyclohexadiene, and cyclohexene[1], amines[35], etc.);

(8) methods using OMC in a mixture with added surfactants, which are adsorbed more strongly than the decomposition products, but less so than the OMC themselves and are displaced by the latter from the surface—for example, ferrocene in the decomposition of tri-isobutylaluminium[36];

(9) methods using OMC in the presence of added reactive gases (H_2S, H_2Te, NH_3, CO_2, etc.) and vapours (H_2O), which modify the elemental and phase compositions of the coating[1].

The above methods make it possible to obtain a wide variety of coatings whose composition corresponds to both pure metals, binary alloys, or semiconductor compounds and to pure oxides, carbides, nitrides, sulphides, etc. Furthermore it is possible to obtain mixed coatings of the type of carboxides[37], carbonitrides[38], etc.

The content of impurities in the phase composition of coatings can be regulated both by the chemical procedures enumerated above and by physicochemical and purely physical methods.

III. THE USE OF THE PHYSICOCHEMICAL CHARACTERISTICS OF THE DECOMPOSITION OF ORGANOMETALLIC COMPOUNDS FOR THE DEPOSITION OF COATINGS

There are many ways of depositing films and coatings from the vapour phase of OMC in their thermal decomposition; numerous devices and different types of apparatus have been developed, embodying various methods for deposition from the vapour phase.

The methods of deposition of coatings from the vapour phase can be classified in terms of the principal process parameters. The methods can differ in terms of (1) the procedure used to generate the vapour phase, (2) the pressure of the reaction mixture in the decomposition zone, (3) the state of the article being coated in the reactor, (4) the method used to heat the article being coated, and (5) the state of the principal units of the reactor.

1. Methods for the Generation of the Vapour Phase of the OMC

The methods for the deposition of coatings from the vapour phase in the decomposition of OMC differ in the procedure used to generate the vapour phase, which can be significantly non-equilibrium, or can be in equilibrium with the condensed OMC phase. Depending on this factor, when different procedures are used to generate the vapour phase, it is possible to attain markedly different maximum rates of deposition, which depend on the degree of supersaturation of the vapour phase by the metal, which is determined in its turn by the concentration of the OMC in the vapour.

Deposition from a non-equilibrium vapour phase can be carried out under both static and dynamic conditions. In the former case the process is usually performed with a deficiency

of OMC in a closed volume where the OMC vaporises completely and forms an unsaturated vapour, which is not in equilibrium with the condensed phase (since the latter is absent). The decomposition of the OMC under such conditions proceeds as a rule at low temperatures in the kinetic region, the aim being to obtain coatings with controllable physical properties (for example, the preparation of films for measuring devices).[39]

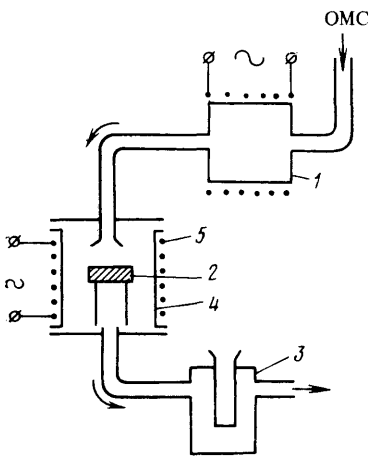


Figure 1. Deposition of coatings from a non-equilibrium vapour phase under dynamic conditions established in an autonomous evaporator: 1) evaporator; 2) support; 3) trap; 4) reactor; 5) heater.

The deposition of coatings from a non-equilibrium vapour phase under dynamic conditions is most frequently used. The equilibrium vapour phase generated by the evaporation of the condensed (liquid or solid) OMC phase is transported via pipes to the heated article to be coated, which is located in the reaction chamber. In the absence of a condensed phase in the pipes and under the conditions of high temperatures near the article to be coated and its dilution by the vapours of the decomposition products, the initially saturated OMC equilibrium vapour phase becomes unsaturated with respect to the OMC and is no longer in equilibrium with the OMC condensed phase. The state of this vapour phase, i.e. the degree of its deviation from the state of saturation with respect to the OMC and its state of equilibrium, is difficult to estimate and control. As a result of the decomposition of the OMC, the state of the vapour phase changes still further due to constant dilution by the decomposition products. For the practical employment of such a non-equilibrium vapour phase, one therefore creates dynamic conditions and uniform fluxes of the vapour phase near the surface of the article to be coated. Under such conditions, it is possible to attain reproducible rates of deposition of the coating.

However, owing to the unsaturation and the non-equilibrium nature of the OMC vapour phase, it is impossible to achieve high rates of deposition of coatings. The devices most frequently employed in this case are provided with autonomous evaporators located outside the limits of the reaction chamber used for the deposition[10,40-43] (Fig.1). The principles of the operation of the evaporator can be extremely varied, but usually one employs closed or flow compartments ("stills") and bubbling devices[44].

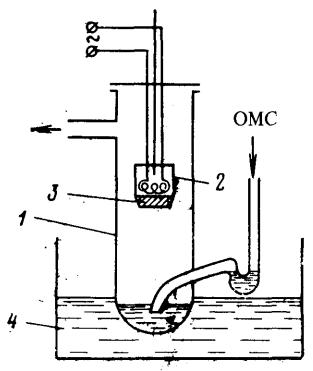


Figure 2. Deposition of coatings from an equilibrium vapour phase generated under static conditions: 1) reactor; 2) heater; 3) support; 4) thermostat.

The deposition of coatings from the vapour phase in equilibrium with the condensed (solid or liquid) OMC phase is a more effective process. Here it is possible to establish higher concentrations of the OMC in the vapour phase; since the vapour phase is in a state of dynamic equilibrium with the condensed phase, the vapour is enriched in the organometallic component when the latter is consumed in the deposition process. The process can be carried out under static or dynamic conditions such that the condensed (usually liquid) OMC phase in equilibrium with the vapour phase can exist. Under static conditions, the equilibrium OMC vapour phase is generated by the evaporation of the solid or liquid OMC within the reaction chamber. The location of the OMC condensed phase being evaporated can be below the article to be coated[45,46] or above it[47] (Figs.2 and 3). Furthermore, it has been suggested[46] that the condensed (solid) phase be placed around the article to be coated (Fig.4).

Under conditions where the condensed phase is located below the article to be coated, the deposition process takes place under least favourable conditions. This is because, in the course of the formation of the OMC decomposition products and the increase of their pressure, the partial pressure of the OMC diminishes and conditions for the supersaturation of the OMC vapour are frequently created, which is accompanied by the formation of aerosol particles of the condensed phase ("dew point"). These particles of the condensed OMC phase precipitate and the overall OMC concentration in the vapour phase diminishes. The additional vaporisation of this part of the OMC as a result of the heat radiated from the superheated (relative to the vapour temperature) support cannot occur owing to the negative temperature gradient in the direction of the fall of the particles. When this method is used, one usually observes a "peak" rate of deposition of the coating[48,49] at the initial instant of the coating process. In other words, the rate of formation of the coating initially increases to a maximum and then falls approximately by two orders of magnitude in consequence of

the decrease of the effective concentration of the OMC in the vapour phase[49].

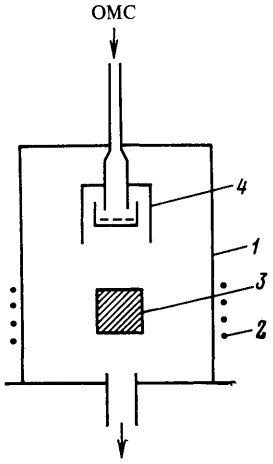


Figure 3. Deposition of coatings from a vapour phase in equilibrium with a static liquid OMC phase located below the article: 1) reactor; 2) heater; 3) support; 4) evaporator.

If the condensed OMC phase in equilibrium with the vapour phase is located on the particle to be coated and the outlet for the removal of the decomposition products ("evacuation") is placed below, then more favourable conditions are created for increasing the OMC concentration in the vapour phase[47]. Even under the "dew point" conditions, where part of the OMC condenses on increasing the pressure of the decomposition products and is precipitated in the form of liquid and solid particles, the OMC concentration in the vapour phase increases as a result of the re-evaporation of these particles as they fall freely downwards under the conditions of a positive temperature gradient towards the article to be coated, which is placed below the vaporisation zone.

We may note that the case under consideration, where the condensed OMC phase in equilibrium with the vapour phase is located above the article to be coated, cannot be classified as purely static: although the main bulk of the condensed phase is in a static state, the condensed OMC particles are in a state of dynamic equilibrium with the vapour. The use of a vertical temperature gradient (the temperature above the article is higher than under it) makes it possible to set up a pressure gradient which gives rise to a flux of particles and vapour along the surface of the article to be coated and this converts the procedure from one involving a static condensed phase in equilibrium with the vapour into a method with dynamic vapour and condensed phases in a flux[47]. Such conditions ensure higher rates of deposition of coatings than under static and dynamic conditions from a non-equilibrium vapour and under conditions of a static condensed phase located below the article to be coated and involved in equilibrium with the vapour phase.

The methods in which the condensed phase is placed around the article to be coated are a logical conclusion of the development of procedures for deposition from an equilibrium vapour phase in the presence of a static condensed OMC phase[46].

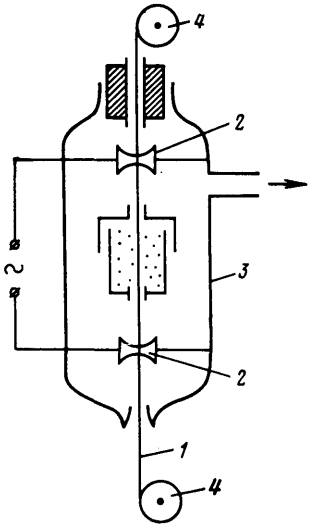


Figure 4. Deposition of coatings from an equilibrium vapour phase with a translational movement of the article: 1) filament (wire) to be coated; 2) electrical terminals; 3) reactor; 4) drums for rewinding the wire.

This method is usually applied when an article of small area is to be coated (for example, when a heated filament is drawn through a channel in a compressed substance undergoing decomposition[46]). The vaporisation of the substance being decomposed takes place as a result of its being heated by the heat emitted from the filament being coated. This method[46] makes it possible to generate a vapour phase in equilibrium with the static condensed phase.

However, in the presence of a quasi-closed reaction space bounded by the condensed OMC phase and when the area to be coated is large, the atmosphere may be supersaturated by the decomposition products, which leads to the appearance of stagnant zones, a decrease of the rate of deposition of the coating, and its contamination as a result of increased adsorption of secondary reaction products (carbon, oxides, carbides, resins, etc.). The method is then actually converted into a procedure in which coatings are deposited from a vapour phase in equilibrium with a static condensed phase under static (or quasi-static) conditions relative to the dynamics of the vapour phase. The first two instances ensure, in contrast to the last, the dynamics of the vapour phase in equilibrium with the condensed phase, although the mass fluxes established in the first case decrease the concentration of the OMC in the vapour near the substrate, while in the second the OMC concentration is actually increased in the descending vapour streams.

The use of methods involving the generation of a vapour phase in equilibrium with the condensed phase directly in the reactor for the deposition of coatings, in contrast to the procedures described above in which a non-equilibrium vapour phase is used, makes it possible to prepare coatings using involatile OMC with low vapour pressures and low decomposition temperatures. The introduction of the condensed OMC phase directly into the reactor creates conditions for the molecular distillation of involatile OMC[50] and significantly extends the scope of the deposition method under consideration compared with the previous procedures using a non-equilibrium vapour, the transport of which is relatively ineffective for involatile substances.

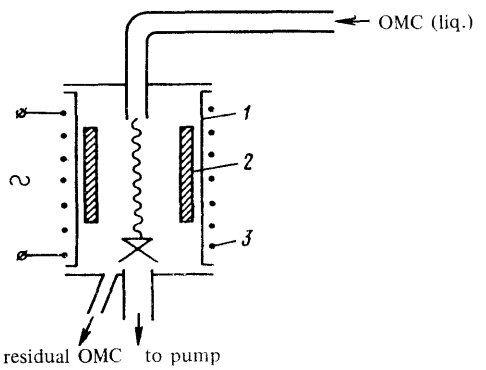


Figure 5. Deposition of coatings from an equilibrium vapour phase generated under dynamic conditions: 1) reactor; 2) support; 3) heater.

By analogy with this situation, which is observed in distillation processes, methods for the generation of a dynamic vapour phase in equilibrium with a moving liquid phase, are the most effective and have the greatest range of applications. One of the effective methods for the generation of the vapour phase in the deposition process which have been suggested[51–57] involves the use of a falling film of liquid OMC, its solution, or its suspension in a suitable solvent (Fig.5). The method permits a continuous and effective generation of the vapour phase in equilibrium with a moving spontaneous stream of the liquid phase (by analogy with all the advantages of film distillation—see Krel[50], p.301). The most important advantages of film vaporisation are that there is no need to heat thick layers of liquid for effective vaporisation[58], as happens in vaporisation from a still. This provides considerable possibilities for the employment of a wide range of involatile and readily decomposed OMC for the deposition of coatings.

The deposition of coatings by this procedure[51–57] on the surface of the heated article takes place with a continuous flow of liquid containing the OMC (liquid compound, solution, or suspension taken separately or in an appropriate combination) along the treated surface under the influence of gravitational force. As a result of the vaporisation of the liquid under the influence of the heat emitted from the article, the concentration of the vapour of the working OMC in equilibrium with its condensed phase is ensured. As the liquid moves along the surface of the article being coated, it is heated to higher temperatures, which promotes a more vigorous vaporisation of the substance being decomposed and leads to an increase of its concentration in the vapour phase and hence to an increase in the rate of deposition of the coating. An increased concentration of the vapour of the OMC being decomposed is also promoted by the fact that the particles of the condensed phase formed as a result of the condensation of the vapour, as the pressure of the decomposition products increases, migrate under the influence of gravitational force along the surface of the article being coated and are heated and revaporised as when deposition occurs from a static equilibrium vapour phase and the condensed OMC phase is located above the article to be coated.

Thus, over the entire pathway traversed by the liquid being decomposed, the saturated OMC vapour is in equilibrium with it. This leads to an appreciable increase of the steady-state OMC concentration in the vapour phase during the deposition of the coating and ensures high rates of formation of the latter; furthermore, this ensures the formation of more homogeneous coatings, with respect to thickness and chemical composition, owing to the smaller changes in the relative concentrations in the OMC vapour.

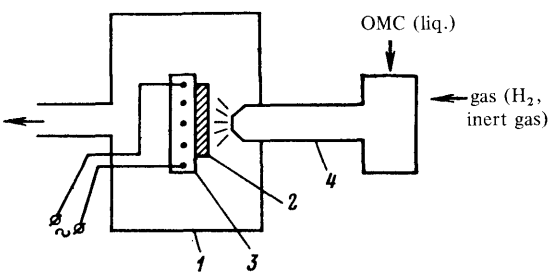


Figure 6. Deposition of coatings from an equilibrium vapour phase under dynamic atomisation conditions: 1) reactor; 2) support; 3) heater; 4) atomiser nozzle.

In this way it is possible to achieve rates of deposition of coatings of approximately 1–2 mm h^{-1} (or >10–20 μm min^{-1}), which is 10–100 times greater than the usual rates of deposition from the vapour phase by the methods already described. This procedure is most effective in the following cases: for the formation of thick coatings, particularly for the internal surfaces of hollow articles; when it is necessary to achieve a continuous process; when the rate of deposition of the coating is the rate-limiting stage of the process (when the process is automated). The method proposed in a number of patents[51–57] can be applied both for a freely falling liquid film (this is desirable for long articles and surfaces) and when the working liquid containing the OMC flows via the guiding surface under the influence of gravitational force and then along the surface to be coated starting from its upper section. The distance between the guiding surface and the

surface to be coated must ensure the heating and vaporisation of the moving liquid as a result of the thermal emission from the heated article. If heating (thermostatting) of the guiding surface is used to ensure uniform vaporisation of the liquid, then the minimum distance between the guiding and coated surfaces is determined by the distance over which there is no premature "ebullition" of the falling liquid film (before the attainment of the lower end of the article) due to heating of the liquid by the heat emitted from the article regardless of the thermostatting. The rate of vaporisation can be regulated either by altering the distance between the surfaces or by altering the rate of the free fall of the liquid along the guiding surface by changing the inclination, roughness, and relief of the latter.

The list of the available methods for the deposition of coatings from a vapour phase in equilibrium with a dynamic condensed phase is logically completed by the method involving the enforced movement of the condensed phase at the required rates. It consists in the atomisation or sputtering of the liquid phase onto the surface to be coated with thermal conditions in the heated article such that vaporisation of the condensed dispersed particles near the surface to be coated is ensured[59-61] (Fig.6). When nickel carbonyl is used, this method makes it possible to obtain coatings having a smooth surface with a thickness of several hundredths of a centimetre in the course of several seconds[59].

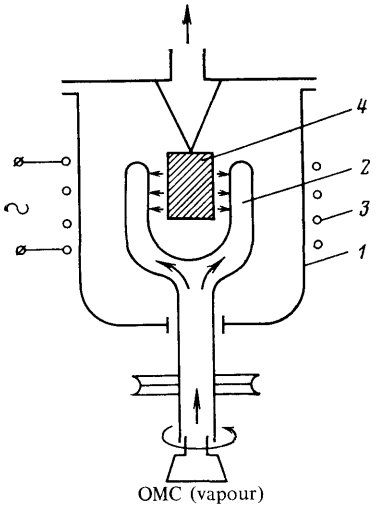


Figure 7. Deposition of coatings from a non-equilibrium vapour phase by the rotation of the vapour inlet: 1) reactor; 2) vapour inlet; 3) induction heating; 4) article.

However, despite the considerable gain in the rate of deposition of coatings compared with other methods, the atomisation procedure is relatively inapplicable to the preparation of coatings from the vapour phase using compounds having low vapour pressures. For such substances, it reduces to the preparation of coatings from the liquid phase and in many instances suffers from all the disadvantages of this procedure (contamination of the surface and bulk of the coating, difficulties when it is necessary to obtain crystalline coatings, and inhomogeneity of the coating with respect to thickness on articles of complex shape).

An interesting version of the method employing a non-equilibrium vapour phase transported along the surface of the article to be coated and gradually enriched in the decomposition products has been proposed in a patent[62]; in this method an increased rate of deposition from a vapour depleted in the working substance is achieved by establishing a temperature gradient throughout the entire extent of the article, which increases toward the end of the latter. However, this method is effective only in the kinetic region and for very large fluxes and is recommended for epitaxial processes.

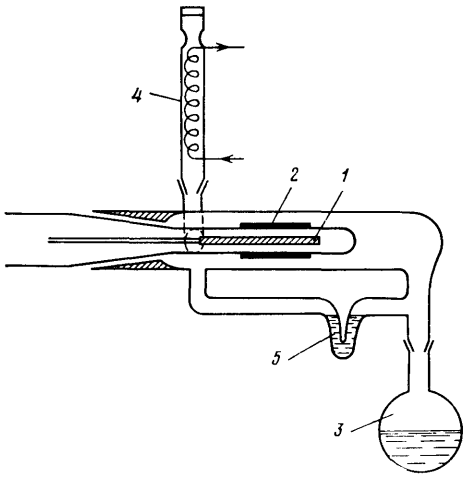


Figure 8. Method of deposition of coatings from the vapour phase in solvent vapour[1,44]: 1) support; 2) heater; 3) evaporator; 4) reflux condenser; 5) hydraulic seal.

One of the modifications of the method of deposition from a non-equilibrium vapour phase, which ensures the formation of a homogeneous coating, involves the establishment of a dynamic non-equilibrium vapour phase, proposed in a patent[63], around the article by mechanical means—by rotating a multichannel inlet supplying the vapour (Fig.7).

2. The Influence of Pressure on the Characteristics of the Deposition Process

It is possible to distinguish methods in which coatings are obtained (1) at atmospheric or elevated pressures of the test substance without a gaseous diluent, (2) at atmospheric or elevated overall pressures in the presence of a gaseous diluent, a carrier gas (usually nitrogen, inert gases, etc.), or the vapour of an inert solvent[64-66] (Fig.8), (3) at a

reduced pressure in the absence of a carrier gas, (4) at a reduced pressure in the presence of a carrier gas, a gaseous diluent, or the vapour of an inert solvent, and (5) in a high vacuum under molecular beam conditions in the absence of a gaseous diluent.

The methods used at atmospheric or elevated pressures have advantages over the remaining procedures in the sense that they make it possible to generate large mass fluxes of the test substance in the vicinity of the support to be coated, which leads to an increase in the diffusional limit to the rate of deposition of the coating and an expansion of the temperature range of the kinetic region.

However, together with this positive effect, a marked adsorption of the OMC decomposition product on the surface of the coating is observed at elevated and atmospheric pressures. For reactive coatings and decomposition products, such adsorption can promote secondary reactions leading to the formation of carbides, oxides, and similar compounds, which are in many instances undesirable. Furthermore, since the vapour pressure of the majority of OMC reaches 1 atm above their decomposition temperatures, the low thermal stability of the OMC restricts the upper limit of the OMC concentration in the gas phase and hence the rate of deposition of coatings at elevated and atmospheric pressures. On the other hand, high flow rates of the carrier gas in many cases preclude the formation of sufficiently homogeneous coatings (this is an advantage of the method of deposition of coatings from the vapour phase), leading to the appearance of a "shadow effect" due to the geometrical factors of the reactor and the support. The limiting case of this process is sputtering from an atomiser[67].

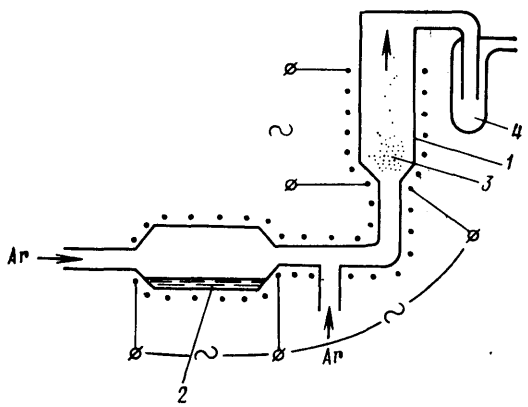


Figure 9. Deposition of coatings from a non-equilibrium vapour phase with an outside evaporator under the conditions of a fluidised bed consisting of the powdered specimen to be coated; 1) reactor; 2) evaporator; 3) specimen; 4) trap.

The use of reduced pressures makes it possible to obtain coatings with purer compositions owing to the decreased influence of adsorption by the products of decomposition and secondary reactions. However, the rates of deposition decrease owing to the decrease of the OMC concentration in the gas phase. In principle, similar rates of deposition can be attained in a stream of carrier gas at atmospheric pressure and in the absence of carrier gas at a reduced pressure. The difference between the rates of desorption of the decomposition products *in vacuo* and in an atmosphere of the carrier gas at elevated pressure may be altered. This sometimes leads to a significant difference between the impurity contents in the coatings (for example, 10% C in chromium deposited in a carrier gas and 2–3% C in chromium deposited *in vacuo* at the same temperatures[40]).

The homogeneity of the coatings obtained at reduced pressures is as a rule high. The deposition of coatings under molecular beam conditions[68] has the advantage that it makes it possible to increase the purity of the coating, but the rate of deposition is then reduced and a "shadow effect" appears when coatings are deposited onto articles of complex shape.

IV. PHYSICAL CHARACTERISTICS OF THE METHODS FOR THE DEPOSITION OF COATINGS FROM THE VAPOUR PHASE

1. Methods Differing in the State of the Article to be Coated in a Reactor

The state of the article to be coated can be determined both by its material and shape as well as its movement. The surface to be coated can be the outer or inner surface of the article or part of it, and the article can consist of a compact or porous solid body. For articles of small size, coatings can be obtained on a large number of the latter in a single cycle or with each article subjected consecutively to a single cycle. The formation of coatings on powders and friable materials requires specific deposition procedures.

Depending on the material of the substrate (the surface of the article), the methods of deposition of coatings differ mainly as regards the method and rates of heating of the surface and the employment of various chemical systems.

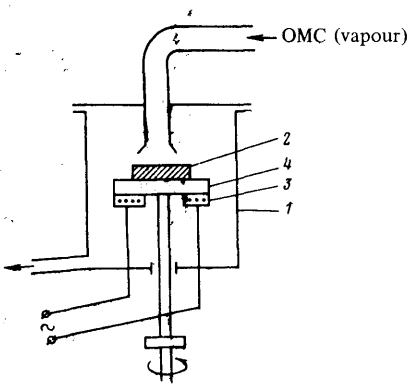


Figure 10. Deposition of coatings from a non-equilibrium vapour phase with rotation of the article: 1) reactor; 2) support; 3) heater; 4) rotating table.

A number of procedures for the deposition of coatings from the vapour phase differ by the type of movement of the article being coated in the reactor. The article to be coated may be stationary or have a wide variety of different types of movement: oscillatory movement—vibration or ultrasonic oscillations[69], a fluidised bed[10,44,70–72] (Fig.9) for the coating of powders, rotation of the article[73,74] (Fig.10), and translational movement of the article or a programmed movement[46,75–78]. A combination of different types of movement is frequently employed.

2. Methods of Heating of the Article to be Coated

The methods for the deposition of coatings from the vapour phase using OMC can differ by the method whereby energy is supplied to the article being coated. It has been suggested that different forms of energetic influences be used: thermal, light (ultraviolet and infrared irradiation[1]), laser beam[75,79-81], electron and ion impacts[82-85], and different forms of electric discharges and plasmas[84,86-88].

In methods with thermal heating of the articles to be coated, both direct heating (by an electric current[48], by a high frequency current[48], and by an electric heater built into the article[48]) and indirect heating (by the infrared irradiation of an external resistive heater[1] and by the absorption of visible and infrared radiation by the support[48]) are used.

There exist methods for the preliminary heating of the support and for carrying out the deposition process on a cooled support[89,90]. The latter is used to prepare thin films on articles with a low thermal conductivity. Despite the fact that the deposition takes place at a continuously decreasing temperature, these processes are used both in laboratory practice and in industry[77,91,92]. The possibility of employing such conditions arises partly from the fact that the process takes place at high temperatures in the diffusion region, where it depends only slightly on temperature. The coating process is highly technological and can be fully automated[92]; this being particularly suitable for the coating of dielectrics.

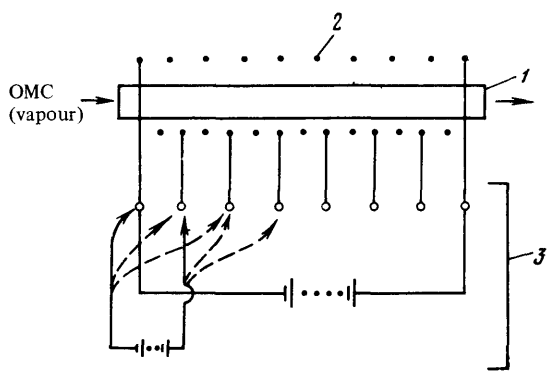


Figure 11. Zone coating of the inner surfaces of tubes from a non-equilibrium vapour phase: 1) reactor (tube); 2) electric heater; 3) switch for the maintenance of the temperature of the tube above the vaporisation temperature of the OMC and for the maintenance of the temperature of a narrow mobile zone equal to the deposition temperature of the coating.

The use of a laser beam for the local heating of the surface of the support[93,94] gives rise to extensive technological possibilities for the preparation of shaped coatings from the vapour phase[75,80,81]. The deposition process with local heating of the support by laser radiation is determined by a number of fundamental factors: the optical properties of the material of the support (high absorption coefficient and low reflection coefficient for the radiation at the wavelength of the laser emission); the thermophysical properties of the material of the support (low thermal conductivity and high melting point); the energy density of the laser beam and the duration of its action on a single site on the support (low energy density and short duration of pulses with a high repetition frequency); the rate of the chemical reaction and of mass transfer, which determine the rate of deposition.

For high local energy densities of the laser beam, a high thermal conductivity of the material of the support, a long duration of the local action, and an autocatalytic mechanism of the thermal decomposition of the OMC, the limits of the deposition of the coating undergo "temperature-dependent spreading". For high absorption coefficients of the radiation in the material of the support, there is a possibility of local fusion of parts of the support. The minimum "temperature-dependent spreading" of the limits of the coating will occur on supports with a low thermal conductivity and with a maximum absorption coefficient for the radiation. In this case the thinnest possible surface layer of the material of the support is heated and, owing to the low thermal conductivity, the energy relaxation along the surface is also minimal. The energy of the laser beam used for the local deposition of coatings from the vapour phase must therefore be optimal to avoid the breakdown of the surface of the support and to reduce the "temperature-dependent spreading" of the limits of the coating. To ensure the maximum possible rate of deposition, it is useful to employ the maximum possible concentration of the saturated OMC vapour by adjusting the temperature of the working chamber and the rate of evacuation. The temperature of the working chamber can be raised to values lower by 50–100 °C than the temperature of the coating deposition process to avoid the autocatalytic deposition of the coating over the entire surface of the support after the onset of deposition.

With a favourable combination of all four factors enumerated above, the local shaped coatings obtained possess the most satisfactory qualities.

3. Methods Differing by the State of the Fundamental Units of the Reactor

In order to obtain high-quality homogeneous coatings on articles made of different materials and of different complexity of shape and on long articles, particularly at sites which are relatively inaccessible (internal surfaces, cavities, etc.), and for the protection of friable, fibrous, and other materials, the technological features of the method and the device must be analysed.

Procedures have been developed for the deposition of coatings using different states of the fundamental units of the reactor (the evaporator, the heating of the decomposition zone, and the guiding devices for the supply of the given substance). It is possible to distinguish methods with a stationary arrangement of the units of the reactor[44], methods involving the rotation of the guiding devices for the introduction of the working substance[51-57,59,73] and the rotation of the heater together with the decomposition zone, and methods employing a translational movement of the heater or the heating zone[73,95] (Fig.11).

Depending on the purpose of the coating, a particular method of deposition and method of transferring the metal to the support (chemical transfer or a combination of several methods) are used. By virtue of the wide range of possibilities for the deposition of coatings from the vapour phase and the highly technological nature of the deposition process, coatings are extremely promising as regards their industrial applications. This is particularly important when it is possible to set up a waste-free manufacture of coatings where decomposition products such as aromatic hydrocarbons formed in the decomposition of bisarene derivatives of transition metals can be reused for the direct synthesis of OMC from

atomised metals by cocondensation[96]. This combination of "synthesis–decomposition" processes constitutes a virtually closed manufacturing cycle, which requires only the expenditure of energy and the metal and makes it possible to apply the given metal to articles of complex shape ("transfer" of the metal).

REFERENCES

1. G.A.Razuvaev, B.G.Gribov, G.A.Domrachev, and B.A.Salamatin, "Metalloorganicheskie Soedineniya v Elektronike" (Organometallic Compounds in Electronics), Izd.Nauka, Moscow, 1972.
2. V.N.Ipat'ev, G.A.Razuvaev, and I.F.Bogdanov, Zhur.Russ.Fiz.-Khim.Obshch., **61**, 1971 (1929).
3. H.M.Manasevit, J.Electrochem.Soc., **118**, 647 (1971).
4. US P.3 244 554 (1966); Chem.Abs., **64**, 17213 (1966).
5. L.S.Garba, N.I.Dychkova, and L.A.Ivanyutin, Electronnaya Tekhnika, Ser.6, 66 (1974).
6. D.J.Schlyer and M.A.Ring, J.Organometal.Chem., **114**, 9 (1976).
7. H.M.Manasevit and W.J.Simpson, J.Electrochem. Soc., **122**, 444 (1975).
8. US P.4141778 (1979).
9. F.Paneth and W.Hofeditz, Ber., **62b**, 1335 (1929).
10. V.G.Syrkin, "Khimiya i Tekhnologiya Karbonil'nykh Materialov" (The Chemistry and Technology of Carbonyl Materials), Izd.Khimiya, Moscow, 1972.
11. A.L.Kipnis, N.V.Kul'kova, and N.F.Mikhailova, Kinetika i Kataliz, **17**, 472 (1976).
12. "The Physics and Chemistry of II–VI Compounds" (Translation from English Edited by S.A.Medvedev), Izd.Mir, Moscow, 1970, p.83.
13. C.F.Powell, L.E.Campbell, and B.W.Gonsen, "Vapor-Plating", John Wiley, New York, 1955.
14. US P.3356527 (1967).
15. B.V.Zhuk, G.A.Domrachev, and A.M.Ob'edkov, Symposium, "Khimiya Elementoorganicheskikh Soedinenii" (The Chemistry of Organoelemental Compounds), Gorky, 1977, No.5, p.64.
16. W.K.Duerksen and M.Tamres, J.Amer.Chem.Soc., **90**, 1379 (1968).
17. R.H.Young, D.Brewer, R.Kayser, R.Martin, D.Feriozi, and R.A.Keller, Canad.J.Chem., **52**, 2889 (1974).
18. R.H.Young and R.L.Martin, J.Amer.Chem.Soc., **94**, 5183 (1973).
19. N.Nakashima and N.Mataga, Int.J.Chem.Kinet., **5**, 833 (1973).
20. B.V.Zhuk, G.A.Domrachev, and A.M.Ob'edkov, Izv.Akad.Nauk SSSR, Ser.Khim., 1201 (1977).
21. L.M.Stephenson, D.G.Written, G.F.Vesley, and G.S.Hammond, J.Amer.Chem.Soc., **88**, 3665 (1966).
22. A.N.Terenin, "Fotonika Molekul Krasitelei i Rodstvennykh Soedinenii" (Photonics of the Molecules of Dyes and Related Compounds), Izd.Nauka, Leningrad, 1967.
23. R.G.Brown and D.Phillips, J.Amer.Chem. Soc., **96**, 4784 (1974).
24. A.Farmilo and F.Wilkinson, Chem.Phys.Letters, **34**, 575 (1975).
25. D.Husain and J.G.F.Littler, Int.J.Chem.Kinet., 6, 61 (1974).
26. M.Bigwood and S.Boul, Chem.Comm., 529 (1974).
27. J.Grotwold and E.A.Lissy, Chem.Comm., 1367 (1961).
28. C.R.Bock and E.A.Koerner Von Gustorfin, "Advances in Photochemistry", Vol.10 (Edited by J.N.Pitts, Jr., V.S.Hammond, and K.Vollnick), John Wiley, New York, 1977, p.221.
29. US P.3203827 (1965).
30. US P.3372055 (1968); Chem.Abs., **68**, 98220 (1968).
31. Yu.A.Kaplin, L.S.Chernyshova, G.V.Belysheva, and I.F.Solov'ev, Izv.Vys.Ucheb.Zaved., Khim.i Khim.Tekhnol., **20**, 944 (1977).
32. Yu.A.Kaplin, G.V.Belysheva, T.V.Guseva, L.S.Chernysheva, and I.F.Solov'ev, Izv.Vys.Ucheb. Zaved., Khim.i Khim.Tekhnol., **20**, 771 (1977).
33. Yu.A.Kaplin, G.A.Domrachev, T.P.Starostin, G.V.Belysheva, V.S.Khabarova, and N.P.Merkulova, USSR P.496605 (1974); Byul.Izobret., No.47 (1976).
34. Yu.A.Ryukhin, G.A.Fokin, V.I.Nosach, and L.G.Molokanova, "Tezisy Dokladov II Vsesoyuznogo Soveshchaniya po MOS dlya Polucheniya Metallicheskikh i Okisnykh Pokrytii (Gor'kii)" [Abstracts of Reports at the IInd All-Union Conference on Organometallic Compounds for the Preparation of Metallic and Oxide Coatings (Gorky)], Izd.Nauka, Moscow, 1977, p.44.
35. K.G.Kochetikhina, G.A.Domrachev, and G.A.Razuvaev, Zhur.Org.Khim., **40**, 327 (1970).
36. B.V.Zhuk, V.K.Khamylov, B.A.Nesterov, G.A.Domrachev, and N.K.Zaglumonina, Dokl.Akad. Nauk SSSR, **223**, 862 (1977).
37. B.V.Zhuk, G.A.Domrachev, and N.M.Semenov, "V Vsesoyuznoe Soveshchanie 'Fizicheskie i Matematicheskie Metody v Koordinatsionnoi Khimii', Kishinev, 1974" (The Vth All-Union Conference 'Physical and Mathematical Methods in Coordination Chemistry', Kishinev, 1974), p.160.
38. G.A.Domrachev, V.A.Varyukhin, V.V.Kutyreva, O.N.Suvorova, and B.A.Nesterov, Izv.Akad.Nauk SSSR, Neorg.Materialy, **15**, 1692 (1979).
39. G.V.Almazov and V.A.Varyukhin, "Tezisy Dokladov II Vsesoyuznogo Soveshchaniya po MOS dlya Polucheniya Metallicheskikh i Okisnykh Pokrytii (Gor'kii)" [Abstracts of Reports at the IInd All-Union Conference on Organometallic Compounds for the Preparation of Metallic and Oxide Coatings (Gorky)], Izd.Nauka, Moscow, 1977, p.92.
40. G.G.Devyatykh, S.M.Vlasov, and S.M.Mazavim, Izv.Akad.Nauk SSSR, Ser.Metally, 2, 87 (1974).
41. A.G.Tumanov and K.I.Portnoi (Editors), "Tugoplavkie Metally v Mashinostroenii" (Refractory Metals in Machine Construction), Izd.Mashinostroenie, Moscow, 1967.
42. V.E.Ivanov, E.P.Nechiporenko, V.M.Krivoruchko, and V.V.Sagalovich, "Kristallizatsiya Tugoplavkikh Metallov iz Gazovoi Fazy" (Crystallisation of Refractory Metals from the Gas Phase), Atomizdat, Moscow, 1974.
43. G.G.Petukhov, A.S.Luzin, and I.N.Skuridina, Zashchita Metallov, 6, 722 (1973).
44. C.F.Powell, J.H.Oxley, and J.M.Blocher (Editors), "Vapor Deposition" (Translated into Russian), Atomizdat, Moscow, 1970.
45. I.I.Artuyushenko and G.V.Zemskov, Fizika i Khimiya Obrabotki Materialov, **3**, 34 (1971).
46. BRD P.533644 (1931).
47. V.A.Kostenkov, G.A.Domrachev, B.V.Zhuk, and V.N.Krasheninnikov, USSR P.598964 (1978); Byul. Izobret., No.11 (1978).
48. J.E.Knap, B.Pesetsky, and F.Hill, Plating, **53**, 772 (1966).
49. G.A.Domrachev, G.A.Razuvaev, V.V.Mel'nikov, and K.K.Fukin, Dokl.Akad.Nauk SSSR, **184**, 395 (1969).

50. E.Krell, "Handbuch der Laboratoruims–Destillation" (Translated into Russian), Inostr.Lit., Moscow, 1960, p.306.
51. US P.3729335 (1973).
52. B.P.1306784 (1973).
53. Canadian P.935336 (1973).
54. Swedish P.359322 (1973).
55. French P.2090384 (1976).
56. BRD P.2124400 (1975).
57. Japanese P.804958 (1975).
58. C.J.Heckmann, E.Krell, and H.Stage, Chem.Techn., 2, 252 (1950).
59. Canadian P.519674 (1955).
60. US P.3702780 (1972).
61. B.P.1325564 (1970).
62. B.P.2700365 (1955).
63. B.P.1073524 (1967).
64. French P.1406882 (1974).
65. US P.3316121 (1967); Chem.Abs., **67**, 37172 (1967).
66. BRD P.1521105.
67. E.V.Antoshin, "Gazotermicheskoe Napylenie Pokrytii (Gas-Thermal Sputtering of Coatings), Izd. Mashinostroenie, Moscow, 1974.
68. O.A.Kuznetsov, T.N.Sergievskaya, and V.A.Tolomasov, Tezisy Dokladov II Vsesoyuznogo Soveshchaniya po MOS dlya Polucheniya Metallicheskikh i Okisnykh Pokrytii (Gor'kii)" [Abstracts of Reports at the IInd All-Union Conference on Organometallic Compounds for the Preparation of Metallic and Oxide Coatings (Gorky)], Izd.Nauka, Moscow, 1977, p.92.
69. V.G.Syrkin, A.A.Uel'skii et al., USSR P.301379 (1966); Byul.Izobret., No.14 (1972).
70. B.P.1010063 (1965).
71. US P.3253944 (1966).
72. US P.3247014 (1966).
73. US P.2763576 (1956).
74. DDR P.1072723 (1973).
75. US P.3364087 (1968); Chem.Abs., **68**, 63746 (1968).
76. BRD P.1196466 (1965); Chem.Abs., **63**, 12850 (1965).
77. K.I.Martyushov and Yu.V.Zaitsev, "Tekhnologiya Proizvodstva Rezistorov" (The Technology of the Manufacture of Resistors), Izd.Vysshaya Shkola, Moscow, 1972, p.107.
78. US P.3075858 (1963).
79. W.M.Shaub and S.H.Bauer, Int.J.Chem.Kinet., 7, 509 (1975).
80. French P.1536496 (1968).
81. French P.1468426 (1966).
82. B.A.Vishnyakov and K.A.Osipov, "Elektronnoluchevoi Metod Polucheniya Tonkikh Plenok iz Khimicheskikh Soedinenii" (The Electron Beam Method for the Preparation of Thin Films from Chemical Compounds), Izd.Nauka, Moscow, 1970.
83. V.V.Demin, Z.Yu.Gotra, and M.D.Matviikiv, "Progressivnye Metody Proizvodstva Mikroskhem" (Advanced Methods for the Manufacture of Microcircuits), Izd.Kamenyar, Lvov, 1973.
84. K.A.Osipov and G.E.Folmanis, "Osazhdenie Plenok iz Nizkotemperaturnoi Plazmy i Ionnykh Puchkov" (Deposition of Films from Low-Temperature Plasma and Ionic Beams), Izd.Nauka, Moscow, 1973.
85. G.A.Efremenko, Candidate's Thesis, Moscow State University, Moscow, 1975.
86. A.A.Babad-Zakhryapin and G.D.Kuznetsov, "Khimiko-Tekhnologicheskaya Obrabotka v Tleyushchem Razryade" (Chemical-Technological Treatment in a Glow Discharge), Atomizdat, Moscow, 1975.
87. L.S.Polak, A.A.Ovsyannikov, D.I.Slovetskii, and F.B.Vurzel', "Teoreticheskaya i Prikladnaya Plazmokhimiya" (Theoretical and Applied Plasma Chemistry), Izd.Nauka, Moscow, 1975, p.277.
88. US P.3243363 (1966); Chem.Abs., **64**, 18662 (1966).
89. BRD P.1196466 (1966).
90. US P.3240623 (1966).
91. K.I.Martyushov and Yu.V.Zaitsev, "Rezistory" (Resistors), Izd.Energiya, Moscow–Leningrad, 1966, p.66.
92. N.Ya.Pratusevich and I.F.Solov'ev, "Tezisy Dokladov II Vsesoyuznogo Soveshchaniya po MOS dlya Polucheniya Metallicheskikh i Okisnykh Pokrytii (Gor'kii)" [Abstracts of Reports at the IInd All-Union Conference on Organometallic Compounds for the Preparation of Metallic and Oxide Coatings (Gorky)], Izd.Nauka, Moscow, 1977, p.7.
93. J.P.Reiser [Tentative spelling (Ed. of Translation)] (Editor), "The Effect of Laser Radiation" (Translated into Russian), Izd.Mir, Moscow, 1978.
94. J.Rady [Tentative spelling (Ed. of Translation)] "The Effect of Intense Laser Radiation" (Translated into Russian), Izd.Mir, Moscow, 1974.
95. US P.3294575 (1966).
96. G.A.Domrachev and V.D.Zinov'ev, Uspekhi Khim., **47**, 679 (1978) [Russ.Chem.Rev., No.4 (1978)].

Institute of Chemistry,
USSR Academy of Sciences,
Gorky