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[3rd International Conference on Material Science, Smart Structures and Applications]

TECHNOLOGY FOR OBTAINING VO₂ FILMS FROM THE GAS PHASE DURING THERMAL DECOMPOSITION

Kh.Urinov¹, J. Urinov^a, J. Kilichov^a, M.Khadjayev^a, B.Normakhmadov^{a1}, J. Abdiyev^b

^aSamarkand branch of Tashkent University of Information Technology named after Mukhammad al-Khwarizmi,
2A Ibn Sino street, Samarkand, 140100, Uzbekistan

^b"Physics-Sun" of the Academy of Sciences of the Republic of Uzbekistan, 2b Bodomzor road street, Tashkent, 100084, Uzbekistan

Abstract

In this paper, the process of obtaining films of vanadium dioxide by the method of deposition of inorganic coatings and films from the vapor phase during the thermal decomposition of organometallic compounds (OMC) is considered. In recent years, there has been a growing interest in the practical use of OMC. This has led to the development of many devices that include various vapor deposition techniques. This technology is currently being used as the latest technology.

The design of the technological installation for pyrometric film deposition is presented and the principle of operation is given. In the course of the study, film samples were obtained and experimental work was carried out. The results obtained are presented in the form of graphs.

Keywords: Organometallic compounds, dioxide vanadium, thermal decomposition, chemical-technological process, solid metal, films.

1. Introduction

In recent years, there has been an increase in interest in the possibility of practical use of organometallic compounds to obtain I coatings and films with various methods of decomposition of MOC (thermal, photochemical, etc.)

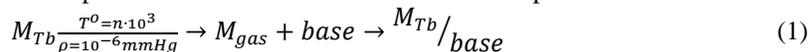
The processes of deposition of inorganic coatings and films from the vapor phase during thermal decomposition (pyrolysis) [1] of OMC are of the widest interest in connection with the possibility of obtaining coatings with a variety of useful properties: protective - corrosion, erosion, thermal, wear-resistant; electric, etc. [2,3].

As for any chemical-technological process, the process of deposition of films and coatings from the vapor phase of OMC during their thermal decomposition is characterized by the presence of many implementation options, which led to the development of numerous devices embodying various methods of vapor deposition, which can be based on various characteristics:

1. By the method of transferring the substance to the surface of the substrate;
2. By the composition and pressure of the atmosphere in the growth zone of the coating;
3. By the method of creating the vapor phase;
4. By the method of heating the product to be coated;
5. According to the condition of the article to be coated in the reactor;
6. According to the state of the main units of the reactor.

2. Main Part

All known methods of transferring metals and non-metals to the surface of a substrate to form a coating can be depicted in several sequential diagrams. The simplest of them is the scheme of vacuum evaporation of metals:

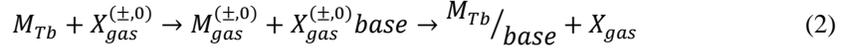


To implement this scheme, a deep vacuum and high temperature are required, since the vapor pressure of metals, especially transition metals, is low [4,5,6].

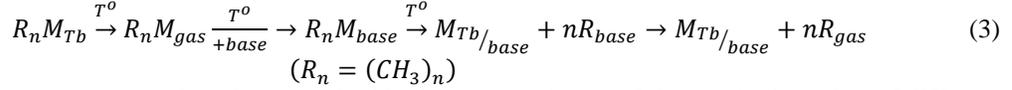
Known methods of sputtering solid metals by scattering beams of charged particles. This also includes cathodic sputtering of metals and metal transfer in an inert gas stream.

* Corresponding author. Tel.: +99-899-595-15-60.
E-mail address: urinov595@gmail.com

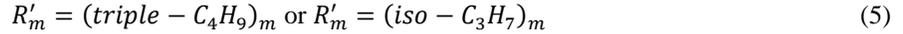
These methods can be depicted as follows:



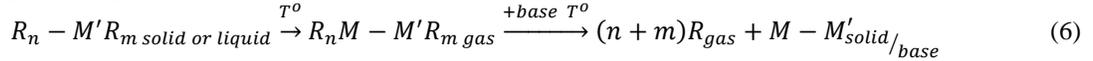
where x is an electron, ion, or neutral atom. The use of OMCs or processes of their intermediate formation for metal transfer to the substrate can significantly reduce the deposition temperature and increase the concentration of the working compound due to the lower MES decomposition temperature and higher vapor pressures at low temperatures. The basic scheme for the deposition of films from the gas phase during thermal decomposition (pyrolysis) of OMC can be written as follows:



For receiving multi-component coating, for example, bipolar, use a mixture of the required number of different metals, or a mixture Moe one metal with hydride of another element:



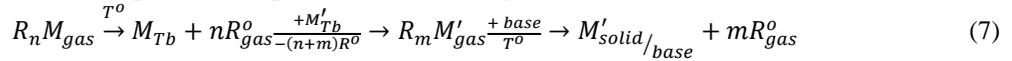
It has now been established that the intermediate products in the joint decomposition of two OMCs, as in the case of $(CH_3)_n / M$ and $(CH_3)_m / M$, are oligomeric and polymer fragments containing the $[RM-M'-R]_x$ bond, which are catalysts for further the decomposition of the mixture, Hence follows the following scheme for the deposition of binary compounds during the thermal decomposition of molecular complexes MOC of the type $(CH_3)_3MM'$ or bimetallic organic compounds containing covalent bonds M-M or M-E:



As above, this scheme may include adsorption processes. In the general case, for the formation of a two-component system on the surface, a reaction between the precipitated metal or a decomposition reaction must take place through the formation of intermediate compounds containing MM bonds [7].

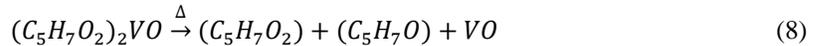
Taking into account the high efficiency of metal delivery to the substrate using GC, it is possible to use the transport reaction of metal transfer using organic radicals or ligands [8].

The most famous classical example of a transport reaction involving free radicals is the Paneth mirror method.



Free radicals generated by the thermal decomposition of readily available HC, for example, dimethyl mercury, act as a transport agent for the transfer of solid metal through the gas phase to a region of higher temperatures, where a substrate is usually located, on which a metal film is deposited due to thermal dissociation of the formed.

It belongs to such processes. transport reaction of vanadium dioxide during decomposition, for example, vanadyl bis (acetylacetonate) $((C_5H_7O_2)_2VO)$



Organic residues $(C_5H_7O_2)$ and C_5H_7O are converted further.

Common to all methods of transport of metals or oxides with the participation of OMC is their high volatility and low temperatures of decomposition reactions with the release of a metal (oxide), which is mandatory for organic decomposition products, the possibility of adsorption and secondary reactions of decomposition products, a relatively high partial pressure of organic decomposition products at temperatures deposition [9].

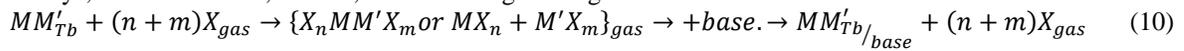
Despite the positive first two qualities, the use of OMC, subsequent negative effects of the decay products can sometimes nullify the positive effect. Therefore, for the successful implementation of the processes of thermal decomposition of OMCs, it is necessary to use special methods of deposition of coatings from the vapor phase, which, by using the phenomena of mass and heat transfer, mechanical and chemical methods, will reduce or eliminate the harmful effects of decomposition products.

3. Method

The process of transfer of a relatively non-volatile product (MTb) in the form of a volatile chemical compound (MX and gas) from the source zone to the deposition zone is called a chemical transport reaction. The sequence of the process can be depicted as follows:



n is the molar amount of gas and X is halogen (chlorine, bromine, iodine) or halo and hydrogen. A similar transport reaction can be used to transfer two or more components of a mixture. This makes it possible to obtain films of alloys, semiconductors, ferrites, etc. according to the general scheme:



In the first and second cases, the transfer is carried out due to a shift in the chemical equilibrium between the solid and gas phases in the source and deposition zones, which is set by the temperature gradient. The nature of mass - transfer is largely determined by the design features of the crystallization unit. In practice, open transport systems are used, where the material is transferred in a flow of inert gas, as well as closed systems in the form of hidden ampoules, the nature of the movement of gaseous compounds in which, depending on the total pressure, is determined by convection or diffusion. In recent years, the method of chemical transport in a small gap between the source and the substrate (sandwich method) has become widespread for the preparation of epitaxial films [10].

Like any other method, the method of chemical transport reactions has its advantages and disadvantages:

Advantages:

1. Epitaxial films can be easily obtained.
2. Easy. carry out controlled alloying and control stoichiometry.
3. Chemical etching of the substrate in the gas phase is possible directly in the setup before deposition.

Flaws:

1. The choice of substrates is limited due to the high deposition temperature.
2. It is difficult to deposit films of easily melting and sublimating substances.
3. Masking substrates is difficult.
4. The gases used in the deposition process, as well as the products of their reactions, are often highly toxic and corrosive, which requires special precautions and the subsequent removal of these substances.

Installation for pyrometric, film deposition VO₂ and VO₂: N, VO₂:S, VO₂: Cl.

Vanadium chalcogenide and alkoxy vanadium derivatives

Installation for producing films VO₂ and VO₂: N, VO₂:S, VO₂: Cl showed in fig. 1.

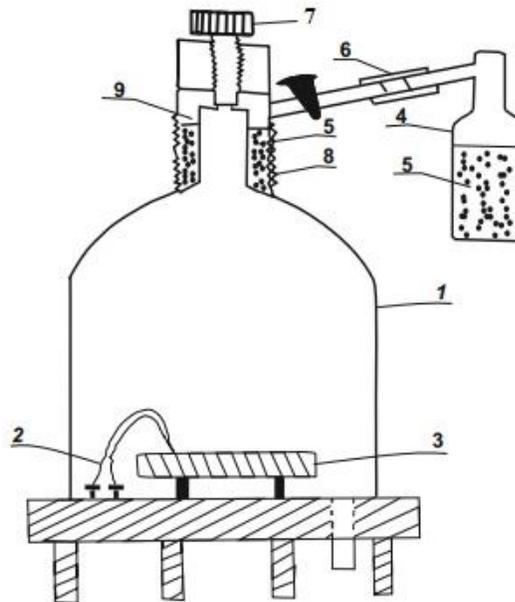
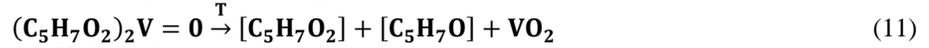


Fig. 1. Installation for producing films by pyrolysis method.

1- Air-permeable glass chamber, 2- substrates temperature thermocouple (chrome-aluminum), 3- heater located on the substrate, 4- glass ampoule, 5- alkoxy producing substance, 6- ampoule and chamber are connected by rubber hose, 7- alkoxy derivatives heated to a temperature sufficient to provide a high vapor pressure, 8- heater, 9- reserve.

Deposition of films VO_2 and VO_2 : N, VO_2 : S by pyrolysis method, films clean VO_2 and doped with sulfur, chlorine, and nitrogen were obtained by decomposition of the corresponding alkoxy derivatives in the above installation (Fig. 1). VO_2 due to the elements (N, S, C), which are contained in the original compound itself. The synthesis process is common to all films. VO_2 and VO_2 containing N, or S, and proceeds as follows: Before starting the synthesis, the air is evacuated from the chamber for five minutes. After that, the required pressure is created in the synthesis chamber and the substrate is heated to a temperature of $\sim 573 - 620$ K. Then the initial substances are heated to a certain temperature ($\sim 343 - 373$ K), which is necessary for the formation of sufficiently high vapor pressure (0.1 mm Hg) and, with the help of dry carrier gas, enters the synthesis chamber. Since the temperature of the substrates is higher temperature decomposition of the corresponding initial substances, then their decomposition occurs on the substrates and a film is formed. Detached organic residues are pumped out of the synthesis chamber and, after separation of the remaining vapors, are released into the atmosphere.

Films pure VO_2 most often obtained by decomposition bis-(acetylacetonate) vanadyl $(C_5H_7O_2)_2V=O$. The decomposition process takes place according to the following scheme:



Organic residues $C_5H_7O_2$ and C_5H_7O are further converted.

The decomposition of tris (tert-butoxy) vanadium sulfide takes place similarly $(C_4H_9O)_3V=S$. bis (tert-butoxy) vanadium bis (dimethylamide) $(C_4H_9O)_2V[N(CH_3)_2]$ and di-iso propoxy vanadium chloride, as a result of which, respectively, it is possible to obtain films VO_2 doped with sulfur, nitrogen, and chlorine. The composition and stoichiometry of the resulting films strongly depend on the oxygen pressure in the synthesis chamber, the carrier gas velocity, and the temperature of the substrates during synthesis. Therefore, during the synthesis, it is necessary to carefully control the above technological parameters. Table I lists some of the process parameters for the production of the above films.

Chemical equilibrium in the FeV_2O_4 -H-Cl system. and the deposition of films of vanadium spinels by the method of chemical transport reactions in an atmosphere of hydrogen chloride.

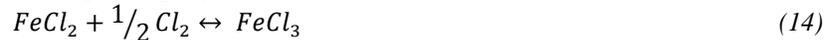
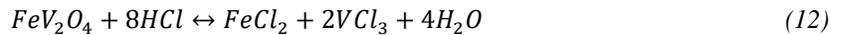
The thermodynamic features of the transfer of matter during chemical transport reactions consist primarily in the fact that the driving force of this process is the difference in the partial pressures of the components in the source and deposition zones. In the area where the transfer occurs, there is always a neutral (in the limiting case, a cross-section) located between the zones, in which the composition of the gas phase coincides with the equilibrium one. On both sides of the neutral zone, the partial pressure of each component of the gas phase differs from the equilibrium one, and the signs of deviation are opposite in the zones of the source and the substrate (under saturation at the source and saturation at the condensate). It is obvious that at not too large temperature differences between the source and the substrate, which takes place in a sandwich method, the temperature of the neutral zone can be assumed to be $1/2 (T_1 + T_2)$.

Table 1: Optimal deposition parameters films VO_2 and VO_2 doped with S and N

No.	Compound	Tisp, K (evaporation temperature)	Tp, K (substrate temperature)	Trazl, K (decomposition temperature)	Residual gas pressure, mm Hg
1	$(C_5H_7O_2)_2V$	360-380	600-650	600-640	50-70
2	$(C_4H_9O)_3S$	360-380	600-650	470-530	50-70
3	$(C_4H_9O)_2V[(CH_3)_2N]$	360-380	600-650	470-530	50-70

4. Results & Discussion

Consider spinel transfer FeV_2O_4 in the case of hydrogen chloride transport under conditions of thermodynamic equilibrium. Possible reactions in the system FeV_2O_4 -H-Cl in the temperature range 950-1350 K have the form: [11]:





where each of reactions (12) - (17) is characterized by the equation of state

$$-\Delta G_j^0 = RT \ln k.p.j. \quad (j = 1, \dots, 6) \quad (18)$$

Here is the change in the standard Gibbs energy of the reaction at temperature T;

R - universal gas constant,

Equilibrium constants of reactions k. pj are related to the fractional pressures of gaseous components Pi by the law of mass action. Obviously, these equations with unknowns do not form a complete system, and it can be supplemented with the conditions of stoichiometry of the solid phase, Fe/V = 1/2; Fe/O = 1/4, the transport agent H/Cl = 1 / and the condition for the preservation of the transport agent. In terms of partial pressures, these conditions take the form:

$$2(P_{FeCl_2} + P_{FeCl_3} + P_{Fe_2Cl_4}) = P_{VCl_2} + P_{VCl_3} \quad (19)$$

$$4(P_{FeCl_2} + P_{FeCl_3} + P_{Fe_2Cl_4}) = 2P_{O_2} + P_{H_2O} \quad (20)$$

$$\alpha = P_{HCl} + 2P_{H_2O} + 2P_{H_2} \quad (21)$$

$$\alpha = P_{HCl} + 2P_{Cl_2} + 2P_{FeCl_2} + 3P_{FeCl_3} + 4P_{Fe_2Cl_4} + 2P_{VCl_2} + 3P_{VCl_3} \quad (22)$$

$$Q_1 = X_1 X_2^2 X_3^4 X_4^{-8} \quad (23)$$

$$2(X_1 + Q_2 X_1 \sqrt{X_5} + 2Q_3 X_1^2) = Q_4 X_2 X_5^{1/2} + X_2 \quad (24)$$

$$4(X_1 + Q_2 X_1 \sqrt{X_5} + 2Q_3 X_1^2) = 2Q_5 X_3^2 X_5^2 X_4^{-4} + X_3 \quad (25)$$

$$1 = X_4 + 2X_3 + Q_6 X_4^2 X_5^{-1} \quad (26)$$

$$1 = X_4 + 2X_5 + 2X_1 + 3Q_2 X_1 \sqrt{X_5} + 4Q_3 X_1^2 + 2Q_4 X_2 X_5^{1/2} + X_2 \quad (27)$$

where $P_{FeCl_2} = 2X_1$; $P_{VCl_3} = 2X_2$; $P_{H_2O} = 2X_3$; $P_{HCl} = 2X_4$; $P_{Cl_2} = 2X_5$; $Q_1 = kp_1\alpha$; $Q_2 = kp_3\sqrt{\alpha}$; $Q_3 = kp_2\alpha$; $Q_4 = 1/kp_4\sqrt{\alpha}$; $Q_5 = kp_5^2/kp_6^2\alpha$; $Q_6 = 1/kp_5$; $Q_7 = a$.

The system of equations (23) - (27) was solved by numerical methods using iterations. The temperature dependences of the equilibrium constants were borrowed from [11,12] and were also calculated based on thermodynamic data. In fig. 2 shows the temperature dependences of the partial pressures of the gaseous components PT (T) for the cases $\alpha = 10^{-3}$ atm., $\alpha = 10^{-2}$ atm. in the temperature range 950-1350 K. Analysis of the results shows the following: I / spinel transfer is carried out mainly by gaseous chlorides FeCl₂, VCl₂, VCl₃, and O₂. The difference in the steepness of the curves of FeCl₂, VCl₂, VCl₃, and O₂ gives hope for controlling the chemical composition of the transferred compound by a small change temperature.

Based on the results obtained, let us estimate the expected spinel transfer rate in the proposal that the process is limited by gas diffusion [8].

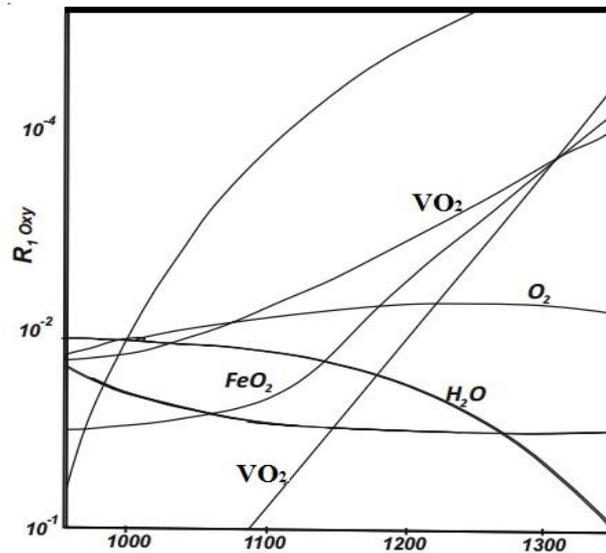


Fig 2. Temperature dependences of the partial pressures of gaseous components in the FeV₂O₄-H-Cl system; a) $\alpha = 10^{-3}$ atm. b) $\alpha = 10^{-2}$ atm.

$$V_i = D(T)\Delta P_i/SRT \quad (28)$$

where T is the temperature of the diffusion area;

ΔP_i - the pressure difference between the components in the source and deposition zones;

S -is the length of the diffusion section;

D-is the diffusion coefficient depending on temperature according to the law

$$D(T) = D_0 \left(\frac{\sum P_o}{\sum P_i} \right) \cdot \left(\frac{T}{T_0} \right)^{1.8} \quad (29)$$

where $\sum P_o = 1$ atm.; $T_0 = 273$ K; $D_0 = 0.1$ cm²sec⁻¹.

Estimates show that for a given temperature region at $\alpha = 10^{-3}$ - 10^{-2} atm. transfer rate is 10^{-4} - 10^{-5} a / sec.

To obtain single-crystal Fe_xV_{3-x}O₄ films, the method of chemical transport reactions in a small gap was used.

5. Conclusion

The Fe₂V₂O₄ source was prepared by sintering in air powdered oxides FeO₃ and V₂O₅ of classification O Midrange on a plate heater at a temperature of 1200 - 1300 K for 2-3 hours. The distance between the source and the substrate was 0.5 ± 1 mm, the temperature gradient between the source and the substrate was 50-100 K. Before deposition, the synthesis chamber was evacuated at a pressure of $15.79 \cdot 10^{-3}$ atm. both the source and the substrate were heated at a temperature of 1000-1200 K. Transport was carried out in an atmosphere of essential hydrogen chloride produced in the Kipp apparatus by the reaction of ammonium chloride with sulfuric acid. The optimal pressure of the transport agent was $(9.87+22.7) \cdot 10^{-3}$ atm, the oxygen pressure in the synthesis chamber was $(9.87 + 25.66) \cdot 10^{-3}$ atm.

As a result of the work done, the possibility of obtaining single-phase single-crystal films Fe_xV_{3-x}O₄ where X = 0.1-2.8, with a thickness of 300-5000 Å is shown. In general, the growth conditions correspond to the results of the above calculation. It was found that the stoichiometry of the transferred spinel at a constant oxygen pressure depends on the pressure of hydrogen chloride and the deposition temperature.

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