About chemical Methods for Depositing thin and ultra-thin Layers

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Abstract: The report examines the specific and less frequently used chemical methods for depositing thin and ultra-thin layers. Galvanic deposition, chemical reduction, anodic oxidation, electrophoretic and chemical vapor deposition and combined methods, known in practice as CVD methods (Chemical Vapor Deposition), are considered. Chemical methods can be assisted and by laser irradiation, have reactive sputtering variants and coating application by plasma spraying. The principles of operation are also explained and the basic designs of the systems and tools for their implementation are shown. The characteristic parameters, materials, advantages and disadvantages, as well as examples of their application are indicated. Overall, the publication offers a wealth of experience gained over the past decades in the field of obtaining thin and ultra-thin layers in mechanical engineering and microtechnology.

Keywords: Chemical Vapor Deposition galvanic deposition, chemical reduction, anodic oxidation, electrophoretic and chemical vapor deposition, CVD-combined methods

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1. Introduction

The methods for modifying and structuring layers are mainly physical in nature and therefore known in practice as PVD methods (Physical Vapor Deposition). In addition to them, there are a number of chemical methods: electrolytic or galvanic deposition, chemical reduction, anodic oxidation, electrophoretic and chemical vapor deposition, known in practice as CVD methods (Chemical Vapor Deposition) and combined methods [1, 2]. The most commonly used deposition method is carried out as a heterogeneous thermodynamic reaction of gaseous components on the upper surface of the substrate, subsequently catalyzed by inert carriers or by an oxidation or reduction reaction of metal halides (atomic layer deposition ALD). The subdivision of chemical methods can also be made depending on the pressure and vacuum - at atmospheric pressure or in open systems and at vacuum from 10 to 100 Pa or in closed systems (Low pressure LPCVD, atmospheric pressure APCVD). These methods are generally suitable for almost all refractory metals and non-metals, with high layer purity, very uniform coating thickness (from 1 to 100µm) and high adhesion to the substrate surface.

2. Problem Formulation

Thin layers are up to 1 µm thick. This size is comparable to the wavelength of light 0.4 – 0.8 µm. Other authors extend the range from a few Å to 10 µm. Thin layers are obtained using vacuum technologies, which differ significantly from the technologies for obtaining thick layers. The thickness of the layers is most often from 15 to 25 µm. In integrated circuits, the layers are obtained using the methods of vacuum-thermal evaporation, cathodic sputtering and its varieties, after which they are additionally processed chemically or galvanically. These layers have different physical properties compared to bulk solids. For example, depending on the thickness of the layer, they can partially transmit light, their specific resistance is significantly higher and the coefficient of thermal expansion is smaller than that of solids (60 - 80%).

The technological process for the production of parts and electronic elements based on thin films proceeds in the following sequence:

- Preparation of the substrate;
- Application of the layer;
- Configuration of the layer (only for electronic elements);
- Setting the nominal value (only for electronic elements);
- Coating.

Thin layers are obtained by:

- Vacuum evaporation (PVD process or physical evaporation at negative pressure $P<1.33.10^{-1}$ Pa);
- Thermal evaporation in high vacuum ($P = 1.33.10^{-2} \div 1.33.10^{-4}$ Pa);
- Ultrahigh vacuum evaporation ($P>1.33.10^{-4}$ Pa, most often 1.10^{-5} Pa to 1.10^{-8} Pa);
- Cathodic sputtering in vacuum and its varieties (ion-plasma and high-frequency sputtering, magnetron sputtering);
- Electrolytic deposition, which serves to strengthen the layer;
- Anodic oxidation, which is used to obtain insulating layers thinner than 10 µm on suitable metal surfaces (mostly tantalum).

It is also known as an accelerated, combined technological process [1].

The disadvantages of the vacuum evaporation method include the non-uniform chemical composition of the layers (especially when evaporating alloys) and the insufficient stability of the layers. The advantages are the deposition of pure, impurity-free and independent materials in precisely defined concentrations and the production of layers with defined properties in one facility.

The advantages of the combined technological process are:

- higher temperatures in the places where the evaporation must take place and the use of refractory metals such as tungsten, tantalum, molybdenum, platinum and rhodium; the irradiation power is coordinated and regulated with the evaporation temperature.
- the crucible is cooled with water and the coating material does not enter into a chemical reaction with it.

The structure of the layer depends on the combination of the material of the workpiece or the substrate - the evaporated material, the temperature and the evaporation rate. Substrates with a high degree of roughness also lead to coatings with a mirror shine if the layer thickness does not exceed 1 µm and no alloys are used, but they have poor adhesion. Thicker layers or layers with intermetallic inclusions are matte. The substrates can be made of plastic, metal, glass, paper, textile, ceramics... In principle, all materials that do not release or release very little gas in a vacuum are suitable. Table 1. shows the possible combinations between the materials of the substrate and the coating layer. As the area increases, the speed increases linearly, and the efficiency decreases due to losses from thermal radiation and thermal conductivity. It increases with increasing temperature, but at the same time the durability of the crucible is reduced.

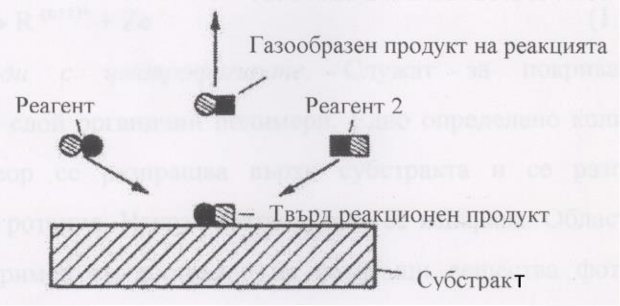
Table 1.

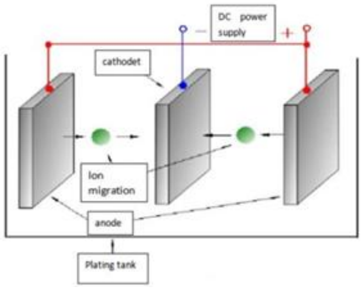
Backing/covering material combinations

	Al_2O_3	Cr	Mo	W	WC	TiC	TiN	Si	SiC	Si_3N_4	Silizid	B	Borides	B_4C	BN	Teflon
Kera-mic	2		2	2		3			2	2		3				
Gra-phit		2	2	2	2	2	2	2	2	1		3		3	3	3
AlO	2	2	2	2		3	2		2	2		3				
Hard metal	2	2	2	2	2	1	1	2				3	2			
Glas	3		2	2		3										2
Si	2															
Ta, Nb	3	2				3	3		2		2	2	3	2	3	
Mo		2	2	2		3	3		2		2	2	3	2	3	
W		2		2	2	3	2	2	2			2	3	2	3	
Ni-alloys		2	2	2		3	2				2		1			
Co-alloys		3	2	2		3					2		2			
Cu-alloys			2	2		3							3			3
tool steel		1	2	2		1	1			2	2		3			2
carbon steel		2		2		3	2				2		3			2
corrosion steel		2		2		3	2			1	2	3	3	3	3	

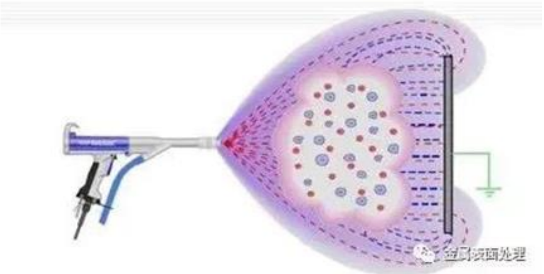
Legend: 1-industrial method, 2-developed method, 3-partially developed method.

The deposited materials are: the metals beryllium, aluminum, titanium, niobium, tantalum, chromium, molybdenum and tungsten, graphites and carbides, nitrides, borides, silicon and silicides, oxides of aluminum and silicon, organic materials such as Teflon, which has been used a lot recently in everyday life. Fig. 1: Principle of chemical vapor deposition and galvanic deposition with/without an electrical source. The degree of deposition depends on the gas flow rate, the position and inclination of the substrate, the presence of reagents, and the increase in gas temperature. The subdivision of chemical methods can be made depending on pressure and vacuum - at atmospheric pressure or in open systems and at vacuum from 10 to 100 Pa or in closed systems. Fig. 2a,b,c,d: Scheme of a device for combined layer deposition. Device for applying a coating layer in a gas environment (on the right) and principle designs of diversionary (separate) reactors. The temperature gradient is built up by heating in three zones (Fig.2.c).





Legende: gaseous reaction product, reactant, solid reaction product, substrate [3]



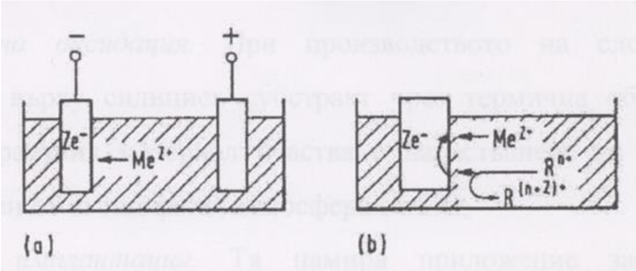
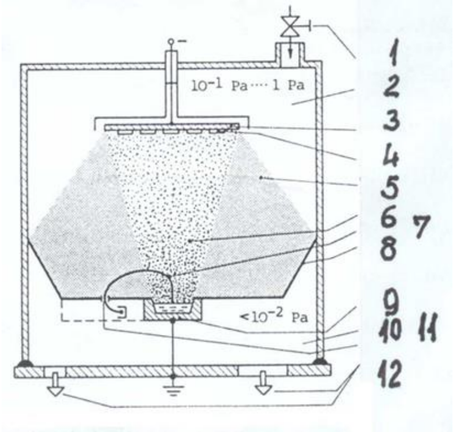


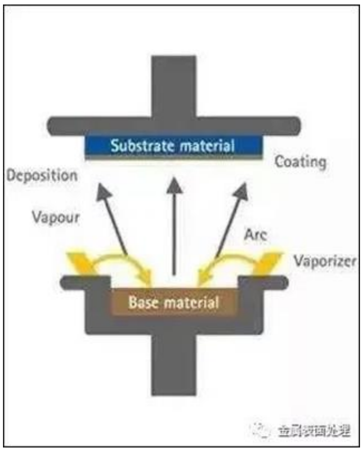
Fig. 1. Principle of chemical vapor deposition and galvanic deposition with/without an electrical source

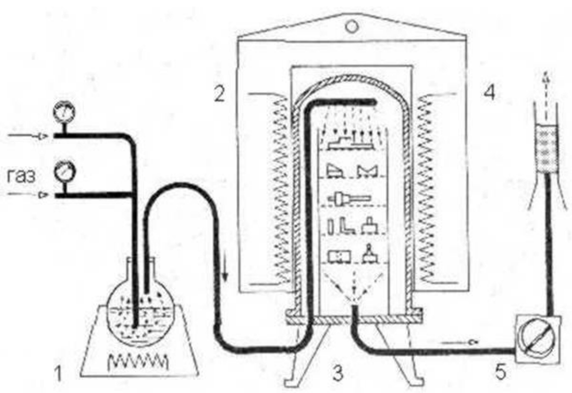
The main chemical methods are:

2.1. Chemical vapor deposition

The deposition of a solid material in a gaseous state to cover the surface layer with characteristic, thicker or very clean coatings can also be achieved by targeted introduction of chemical elements or chemical treatment (Fig. 2). For example, when depositing non-metallic inclusions, hard and brittle layers are obtained, which have very good adhesion up to a thickness of 10 µm. The thickness of the layer can be from 0.1 µm to several tens of micrometers. Various materials are used such as the metals beryllium, aluminum, titanium, niobium, tantalum, chromium, molybdenum, tungsten, rhodium; graphite, diamond and carbides - carbon, tetraboron carbide (B_4C), silicon, titanium, tantalum and tungsten carbide, trichromium dicarbide (Cr_3C_2); nitrides - boron, titanium and tantalum, trisilicon tetranitride (Si_3N_4); boron and its borides - tantalum and titanium diboride, tungsten, iron and nickel







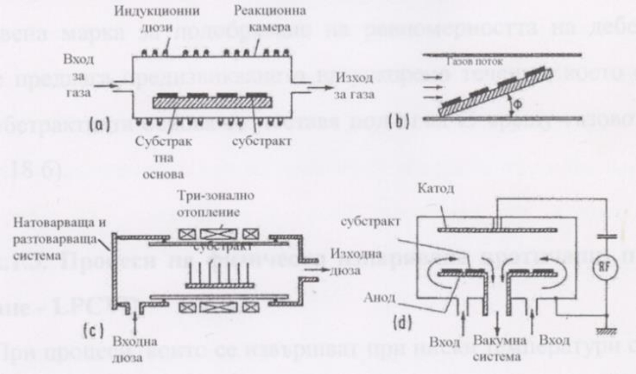


Fig. 2. Scheme of a device for combined layer deposition. Device for applying a coating layer in a gas environment (on the right) and principle designs of diversionary (separate) reactors

Legende: 1-gas release valve, 2-reactor chamber for coating application, 3-crucible (tigel), 4- substrate, 5-gas discharge plasma, 6-evaporated beam, 7-electron beam, 8-screen, 9-evaporator, 10-high vacuum chamber, 11-lock chamber, 12-outputs for the diffusion pump and the pre-vacuum pump.

Legende: 1-evaporator, 2-fireplace, 3-reactor, 4-filter, 5-pump

boride; silicon and the various silicides of molybdenum, iron, nickel; oxides - alumina (Al_2O_3), silicon oxide and dioxide; organic compounds such as Teflon (PTFE) and its derivatives.

2.2. Anodic oxidation

Anodizing (elision) is anodic oxidation of parts or conductive rails in an aluminum IC or other metals (Ti, Ko, Mg and alloys) in details, in which their oxide layer is obtained or increased. An oxide film is formed on the surface of a metal or alloy as an anode by electrolysis. The metal oxide film changes the state and performance of the surface, such as coloring the surface, improving corrosion resistance, increasing wear resistance and hardness, protecting the metal surface, etc. Thanks to the anodic oxidation film in the natural environment, the chemical properties are very stable, the aluminum coating acquires anti-corrosion properties. The coating is porous and very suitable as a base for paints, organic and inorganic dyes, varnishes and adhesives. The thin layer of oxide film has a large number of micro-holes, can absorb various lubricants, suitable for the manufacture of engine cylinder or other wear-resistant parts; The membrane has a strong adsorption capacity and can be colored into various beautiful and wonderful colors. The parts are immersed in baths with an aqueous solution of sulfuric, oxalic or chromic acid and a constant voltage is applied. Depending on the operating mode, normal and hard anodizing are distinguished. The parameters of the two types of anodizing for parts are given in Table 2.

Table 2.

Usually and hard anodizing operating modes for details

Usually anodizing	**Hard anodizing**
AC voltage12 - 20 V	20 - 150 V
Temperature 15 – 22 - 25 ^{o} C	< 15^o C
Time 20 - 60 min	20 - 60 min
Current density 1 - 2,5 A/dm^2	6 A/dm^2
Acid concentration 15 - 28 %	15 - 28 %
Layer thickness 2 – 3 - 5 - 10 - 14 - 18 μm	до 180 μm

The most common concentrations of ordinary anodic oxidation are about 20%, while those of hard anodization are about 15% or less, and the current density of ordinary anodic oxidation is 1-1.5 A/dm^2, while those of hard anodization are 1.5-3A/dm^2. Electrolyte concentration: When sulfuric acid electrolyte is specifically and most commonly used for hard anodization, it is usually in the concentration range of 10% ~ 30%. When the concentration is low, the hardness of the oxide film is high, especially for pure aluminum, only the high-copper aluminum alloy ($CuA1_2$) is an exception. Since the aluminum alloy with a higher copper content $CuAl_2$ is easy to produce, it is for compounds that dissolve faster during oxidation. Therefore, it is generally not appropriate to use a low concentration of sulfuric acid electrolyte, it should be in a high concentration (H_2SO_4 in 300~400g/L) in the oxidation treatment or the use of AC-DC superposition method. The temperature of ordinary anodic oxidation is about 18~22^{0}C, and with additives it can reach 30^{0}C, but too high a temperature is a prerequisite for easy occurrence of dust or crack (when the oxidation rate is much higher than the dissolution rate). The temperature of the electrolyte has a great influence on the wear resistance of the oxide film. Generally speaking, if the temperature drops, the wear resistance of the anodic oxidation film of aluminum and aluminum alloy will increase, which is due to the decrease in the dissolution rate of the electrolyte for the film. In order to obtain higher hardness of the oxide film, the temperature should be in the range of $\pm 2^{0}$C in the hard anodizing treatment. It is generally at a temperature below 5^{0}C to -10^{0}C, relatively speaking, the lower the temperature, the higher the hardness. The heating between the layer and the metal is the most serious problem in the contact, and if it is not solved in time, the local surface of the workpiece will be burned due to the temperature rise. The solution is a combination of cooling equipment and stirring. Cooling equipment for forced cooling of the electrolyte, stirring should make the electrolyte temperature in the entire tank uniform, so as to obtain a high-quality hard oxide layer. The thickness of the layer after hard anodizing is greater than 15 µm, which is too low to meet the hardness requirements, while the thickness of the ordinary oxide layer is relatively thin and depends on the type of acid. Ordinary anodic oxidation has high porosity, while hard oxidation has low porosity. After all, the difference between hard anodic oxidation of aluminum alloy with sulfuric acid and ordinary anodic oxidation is that there are some side reactions if acid hard oxidation is mixed.

(1) Cathodic reaction: $4H + + 4E = 2H_2\uparrow$

(2) Anodic reaction: $4OH-- 4E = 2H_2O + O_2\uparrow$

(3) Aluminum oxidation: oxygen deposited on the anode is in the atomic state, more active than the molecular state of oxygen, easier to react with aluminum: $2Al + 3O \rightarrow Al_2O_3$.

The layer obtained by chromic acid anodizing is relatively thin, only 2-5 µm, which can maintain the original surface roughness grade of the workpiece; the porosity is low and difficult to paint and can be used without sealing; the layer is soft and has poor wear resistance, but the elasticity is good; the corrosion resistance is strong. It is suitable for castings and other structural parts such as threaded parts. This process is more used in the military because the quality of the parts can be checked.

Oxalic acid has a low solubility for the alumina layer, so the porosity of the oxide layer is low, and the layer itself has better wear resistance and electrical insulation than that treated with sulfuric acid. The disadvantage is the price of oxalic acid, which is 3~5 times higher than that of sulfuric acid. The color of the oxalic acid oxide layer is easy to change with the process conditions, resulting in color difference in the product, so the application of this method is subject to certain limitations. Oxalic acid can be used as an additive for sulfuric acid oxidation.

The oxide layer is more soluble in phosphoric acid electrolyte than in sulfuric acid, so the oxide layer is thin (only 3 µm) and the pore size is large. Typically, anodic oxidation is carried out in an electrochemical cell containing ~ 0.4 L of aqueous solutions of sulfuric acid, hydrogen peroxide, and phosphoric acid at ~ 77°F (~ 25° C). Because the phosphoric acid layer has strong water resistance, it can prevent the aging of the adhesive due to hydration and make the adhesive bond better, so it is mainly used for surface treatment of metal plates and pretreatment of aluminum parts [4].

With the economic development of society and the continuous emergence of various new technologies, as well as the continuous expansion of the application fields of titanium and its alloys, in the past ten years, research on surface treatment technologies of titanium alloys has been intensified all over the world. The use of anodizing process on the surface of titanium and its alloys to improve wear resistance, corrosion resistance and biocompatibility has become one of the hot spots of research. The anodic oxidation process is a process of forming an oxide layer on the metal surface by electrolysis, electrochemically generating oxygen on the anode, and reacting with the titanium surface of the anode to form an oxide layer. The technological process of anodic oxidation and coloring of titanium and its alloys is: Degreasing (strong alkaline degreasing agent) → washing with water → primary etching (aqueous solution of hydrofluoric acid) → washing with water → secondary etching (hydrofluoric acid + aqueous solution of hydrogen peroxide) → washing with water → anodizing (aqueous solution also of phosphoric acid with constant voltage Electrolysis) → washing with water → sealing → drying [5]. It finds application for implants in medicine.

The surface oxidation of titanium and titanium alloys can generate various colors, including gray, brown, purple, ultramarine, dark blue, sea blue, gray-blue, yellow, rose red, light yellow, green, etc. from ten color layers. The technological process for obtaining a single-color, gradient color by anodic oxidation consists of the operations: polishing/sandblasting/painting→degreasing→anodic oxidation→neutralization→painting→pore sealing→drying.

The technological process for types of parts with a two-color layer is:

① polishing/sandblasting/painting→degreasing→screening→first anodic oxidation→second anodic oxidation→pore sealing→drying;

② polishing/sandblasting/wire drawing→ degreasing→first anodic oxidation→other operations as necessary (e.g. thread etching)→second anodic oxidation→pore sealing→drying (Fig. 3).

When processing with anodic oxidation, there are requirements for manufacturability [7]. The parts should not have sharp edges, and the radius of the beveled edge should not be less than 0.5 mm due to the occurrence of an exothermic reaction. The surface quality of the parts changes after the completion of hard anodizing. The surface of ordinary anodic oxidation has a higher roughness class, while the surface of hard anodizing has a lower roughness class.

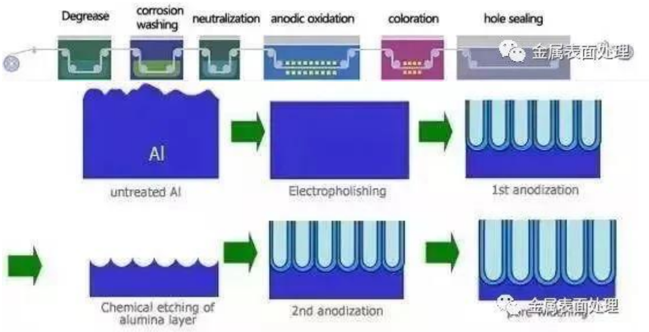


Fig. 3. Technological process for types of parts with a two-color layer [6]

When the thickness of the hard oxide layer is higher, the aluminum parts need additional processing if they are to be assembled, as well as to provide a certain allowance for the specified joints with assemblies in advance. This means that the size of the parts must change during hard anodizing.

In machining, it is necessary to predict the possible thickness and size tolerance of the oxide layer in advance, and then determine the actual size of the parts before anodizing, so that after machining, they are in accordance with the prescribed tolerances of the assemblies. Generally speaking, the size of the part is approximately half of the thickness of the oxide layer. The protection of the same parts, both in ordinary anodic oxidation and hard anodic oxidation, must be of constant precision for the entire specific process. The first pass of ordinary anodizing in the hard anodizing operation does not always need to be a hard anodized surface for insulation, but can be with a gun or brush for nitro rubber or perhydrogen vinyl glue on the surface, and the insulation layer should be evenly coated. Each coating should be dried at low temperature for 30 ~ 60 minutes for a total of 2 ~ 4 layers. Anodic oxidation is not applicable to white color.

Applications: ordinary anodizing is mainly used for decoration in wire drawing, polishing, grinding. The more diverse the colors of oxidation for different metals, the better the decorative effect. Hard anodic coating is given priority to the function of black or dark brown color, the thicker the layer thickness, the more saturated the color. This method is used for wear-resistant, electric shock-proof products up to 2000V, widely in machine parts and extruded profiles, aircraft and automobile parts (decorative glass frames), precision instruments and radio equipment, daily necessities and architectural decoration. In microtechnology, anodic oxidation is applied to obtain insulating layers thinner than 10µm on suitable metal surfaces (mostly tantalum).

Fig. 4. Examples of parts with different colors through anodic oxidation [7, 8, 9]

2.3. Chemical reduction

Chemical oxidation belongs to the pure chemical reaction. It does not require power supply, but most often the aluminum profile is soaked in chemical solutions, so that the aluminum on the surface of the aluminum profile reacts to oxidation to produce an oxide layer. The anodized layer in ordinary treatment, as mentioned above, can reach 10-15µm, and the chemical oxidation layer is thinner, only 0.01-0.15-0.3 to 0.5µm. This thin layer does not affect the conductivity of the aluminum profiles, so chemical oxidation is also called conductive oxidation. Aluminum profile products with conductivity requirements are usually produced by the chemical oxidation method, which improves the hardness and wear resistance and pollution resistance, and is easy to clean. The conductive electrical aluminum oxide is not resistant to pollution and is easy to leave a fingerprint, but it is resistant to atmospheric corrosion [10].

Oxidation (also known as armor plating) is used to protect the surface layer of steel parts from corrosion.

When immersing them in a salt solution, intentional oxidation (Fe_3O_4) of a layer up to 1 μm thick is caused. The processing time is 15 - 30 min, and the temperature is 150° C. The coating has a gray-black color, is suitable for decorations and is a good base for applying various lubricants. Its application is mainly in the production of firearms.

In **planar technology** in semiconductor production of silicon ICs and preparation of silicon substrates for micromechanics, the following main methods are used to obtain SiO_2:

- o thermal oxidation;
- o silane pyrolysis;
- o anodic oxidation;
- o glow discharge oxidation;
- o reactive sputtering of silicon and other CVD methods.

Each of the mentioned methods has certain advantages and disadvantages when used in the production of semiconductor structures. For example, silane pyrolysis and reactive sputtering allow the production of oxide layers not only on silicon, but also on other materials.

Thermal oxidation is the most common method in planar silicon technology, as the oxide layers are obtained by deposition on a substrate in an oxidizing environment. The requirements are to obtain high-quality oxidation of the substrates on both sides and the thickness to comply not only with the usual, but also with specific requirements in specific cases. There are two main varieties of the thermal oxidation method:

- high-temperature oxidation in an atmosphere of dry or humid oxygen, as well as in water vapor at atmospheric pressure;
- oxidation of silicon in water vapor at high pressure and temperature 500^0 - 800^0 C.

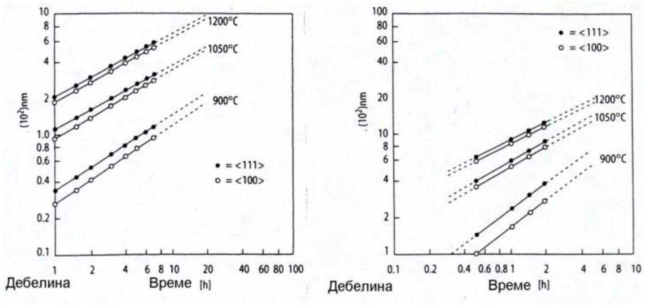
The thermal oxidation process includes adsorption of oxidizing substances on the oxide surface, diffusion of the oxidant from the gas phase to the silicon surface and a chemical reaction of silicon oxidation at the SiO_2-Si interface. During thermal oxidation in dry oxygen, the following reaction occurs at the interface: $Si + 2O = SiO_2$, and in water vapor: $Si + 2H_2O = SiO_2 + 2H_2\uparrow$ (4). Oxidation in dry oxygen produces the densest and most homogeneous oxide layers, but the oxidation rate is the lowest. In a water vapor atmosphere, the oxidation rate is the highest, but the oxide layer is not sufficiently dense and homogeneous. A compromise option is oxidation in humid oxygen or the use of the combination dry oxygen - water vapor - dry oxygen. The quality of the oxide layer can be further improved by including a few percent of hydrochloric acid or chlorine-containing gases. Performing dry oxidation improves the electrical and protective properties of the layer.

Oxidation occurs at the Si/SiO_2 layer boundary, so the oxidizing gas must diffuse through the already formed oxide layer to the boundary layer. The latter moves into the silicon during the process. The volume increases, the silicon atom (r_{si} = 0.042 nm) is bonded to two oxygen atoms (r_o = 0.132 nm) in SiO_2. The outer SiO_2 layer is bonded coplanar to the silicon surface layer or a silicon layer of thickness $0.44d_{ox}$ is used to build a layer of thickness d_{ox}. The mathematical model is given by the formula (5):

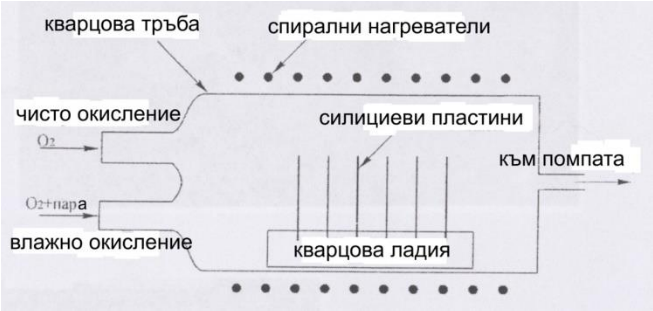
(5) $d_{окс} = A/2[1 + (t + \tau).4B/A^2]^{1/2}.A/2$, μm

where t is the oxidation time, s; τ – the initially obtained oxide layer, μm; A and B are constants that depend on the oxidation conditions (temperature, amount of hydrochloric acid, orientation of the disks). B is a constant that characterizes the process in the limiting case, varying according to a parabolic law (longer oxidation time, thicker oxidation layer), B/A is a constant that describes the process in the limiting case of small thickness and short oxidation time in humid oxygen according to a linear law of layer growth.

Thermal oxidation is carried out in single-zone high-temperature quartz glass furnaces at a temperature of $900\text{-}1200^0$ C (for example, SFO 125 [11]), which is maintained with an accuracy of no worse than ± 1^0 C. The boat with the semiconductor substrates is placed in the high-temperature zone of the furnace-quartz tube with a diameter of 120-130 mm, and the corresponding oxidizing gas (dry or wet oxygen or water vapor) passes over the substrates. The thickness of the SiO_2 layer depends on the oxidation time (about 6 h), the oxidation method and the temperature. Figure 5a. shows the dependence of the layer thickness (most often 0.1 μm) on the duration of the oxidation process at a constant temperature during oxidation in dry oxygen, in Figure 5b. – the same dependence during oxidation in water vapor [12], and in Fig. 5c –scheme of the thermal oxidation furnace [11]. Oxidation in a humid oxygen atmosphere proceeds faster and therefore it is used to obtain thicker protective layers (up to 1 - 3μm). A significant improvement of the process and its profiling towards nanotechnology in order to increase the breakdown voltage of dielectrics has led to the recently practiced addition of chlorine-containing components to the oxidizing environment.



a). Thickness Time b) Thickness Time



c)

Fig. 5. Graphs of the dependence of layer thickness on oxidation time at a given temperature and crystallographic direction. c). Thermal oxidation furnace

Legende: quartz tube, clean oxidation, wet oxidation, spiral heaters, silicon pads, to the pump, quartz crucible

Examples of application of thermal oxidation according to the thickness of the oxide layer:

- 15-50 nm - thin oxide layer on the gate, dielectrics in capacitors;
- 200-500 nm - masks in diffusion, implantation, etching, surface passivation layers [1];
- 300-1000 nm - insulating fields in microcomponents;
- > 1000 nm - thermosensitive layers in inkjet heads (3 μm) and others.

2.4. Galvanic - Electroplating

Electroplating is an electrochemical reduction process. The basic process is to immerse the workpiece in a metal salt solution as the cathode and the metal plate as the anode, after supplying direct current, the coating is deposited on the workpiece as needed. Thus, the coated metal is on the anode, and the material to be coated is on the cathode. The anode and the cathode are connected by an electrolyte solution composed of metal positive ions. After the direct current is turned on, the metal on the anode is oxidized (loses electrons), and the positive ions in the solution are reduced (gains electrons) on the cathode to form atoms and accumulate on the surface of the cathode. The reverse process of material removal is electroplating.

Electroplating is the use of electrochemistry to make the metal surface attached to the metal layer, so as to prevent corrosion, improve wear resistance, electrical conductivity, reflect to shine and enhance the beautiful design. The technological process is from the operations: pretreatment→alkaline copper without cyanide→white copper tin without cyanide→chromium plating.

In some cases, when the required properties of the layers cannot be achieved by PVD and CVD methods, electroplating is used. In this case, a positively charged metal ion is reduced by accepting Z e-. To reduce the required electrons, a reducing agent is added to the electrolyte:

$$Me^{Z+} + Ze^{-} = Me^{-};\ R^{n+} \qquad R^{(n+z)+} \underline{+ Ze^{-}} \longrightarrow \qquad (6)$$

Galvanic deposition (Fig. 6) can be performed with or without an external power source. The possibilities for sourceless deposition are: Ni-P (7-10%) and $NiSO_4$ with Na-hypophosphite as a reducer, Ni-B (5%) and $NiCl_2$ with demethylamine borate, Cu and $CuSO_4$ with formaldehyde and Au with $K[Au(CN)_2]$ and Na-hypophosphite. The advantage is the uniform thickness of the coating layer, the gloss of the coating is high, high-quality metallic appearance; materials SuS, Al, Zn, Mg, etc.; the cost is lower than PVD methods, the appearance of the coated object after electroplating is related to the magnitude of the current.The disadvantage is the limited deposition rate and the greater risk of environmental pollution.

The working principle of electroplating is explained in Figure 6. The pre-made model is immersed in a bath, connected to a constant voltage source as a cathode and placed between one or more anodes, which are made of the metal to be coated. The chemical solution in the bath consists of positive ions of the specific metal and negative molecules of the remaining component (for example, in a bath with copper sulfate electrolyte, dissociation occurs, and in a bath with nickel sulfate electrolyte $NiSO_4 \rightarrow Ni^{++} + SO_4^{--}$). Examples from many years of practice are given here. In nickel-coated molds, no wear is observed up to about 50 polystyrene parts, in polyamide B3 parts - slight wear after the production of another 40 parts, and in polyamide parts with a phase-bonded composite - severe wear [13, 14, 15]. Copper-coated molds show slight wear during the production of about 50 polystyrene parts and are applied to parts with relatively less pronounced relief (e.g. coins) [16, 17]. The parameters that influence the electroplating process are: temperature, current density, type and movement of the electrolyte [18].

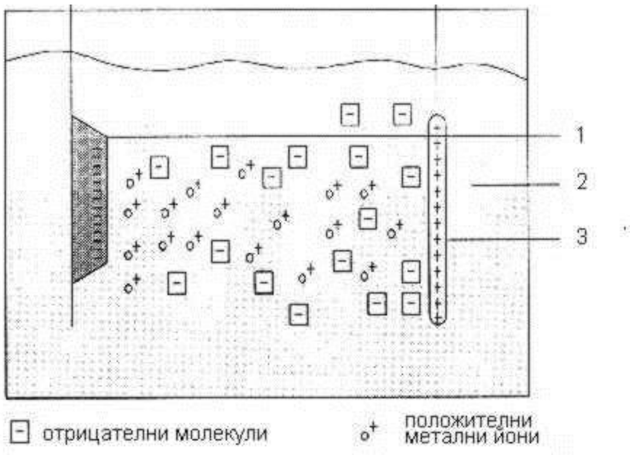


Fig. 6. Principle of operation in electroplating
Legende: 1-cathode, 2-electrolyte, 3-anode

The sequence of the technological process for electroplating parts is:

- making the model for the bath (for example, by turning, milling or using a ready-made sample);
- applying a layer of silicone;
- applying a metal coating;
- covering the model with metal, plastic material, plaster (depending on the retention requirement in the specific case) and placing the model in the mold;
- removing the model from the mold;
- covering the casting or injection mold;
- injection molding and removing the part.

Figure 7. shows a diagram of the operations used for electroplating.

The advantages of electroplating over galvanizing are:

- application of thinner layers with high separation strength from the base;
- high copying accuracy with a surface layer roughness class of up to 50 μm. Direct transfer of tolerances from the model in the bath to parts manufactured by electroplating; possibility of manufacturing parts with complex configuration (including internal surfaces), since in the model manufactured in the bath these surfaces are external;
- relatively high speed of manufacturing, economic efficiency and possibility of fitting to the parts;
- when reusing the model in the bath, identical parts in shape, dimensions and roughness class (counterfeiting) can be manufactured;
- simple manufacturing of injection molds and molds for pressure casting in small-scale production.

A disadvantage of the method is the short life of the manufactured models.

In addition to the above-mentioned details, electroplating is applied to the production of press matrices for gramophone records, screens and screen printing cylinders, razor blades and for copying works of art and unique details [19, 20]. The method is suitable for the production of tools as samples and in small batches of up to 5000 pieces, of details with a high degree of accuracy and high requirements in terms of shape such as combustion chambers and conductive details with certain contact points in electronics and a major part of the LIGA-method in microsystems technology [21, 22].

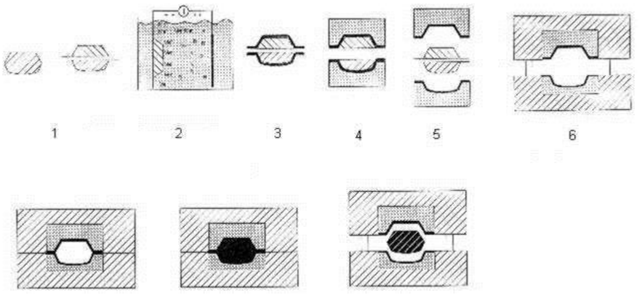


Fig. 7 . Operations in different variants of electroplating
Legende: 1-model with the parting plane, 2-galvanizing, 3-model with metal coating, 4-filling, 5-separation from the mold, 6-installation in the injection molding tool

Metal microforms and elements for hot stamping and injection molding operations, as well as for direct X-ray or UV lithography, can also be produced by electroplating of fusible patterns of synthetic material. A prerequisite for the electroplating process is the presence of an electrically conductive layer at the base of the structure, previously obtained by vacuum sputtering or chemical deposition of NiFe or NiP alloys. The features of this process are: the possibility of depositing metals in small capillaries (of the order of μm) on large areas (up to 150 cm^2) and electroplating with gold in structures for X-ray masks with dimensions of the order of nm. The microsensor illustrated in Figure 8 is a typical example of a product manufactured by the electroplating method. For the production of microsystems with movable elements, a combination of the LIGA method with surface layer deposition technologies can be used. In this case, on an insulating substrate, for example ceramic, a metal layer is first formed as a base for the established details, and then a metal layer is applied to form the moving details. This is followed by a LIGA process with structuring of the resist and galvanic deposition of metal (Figures 8c, 8d). After the resist is removed by etching the removed layer, the moving structures are formed. This method is also applied with X-ray or special ultraviolet depth lithography [23]. Figure 8 shows a capacitive acceleration sensor.

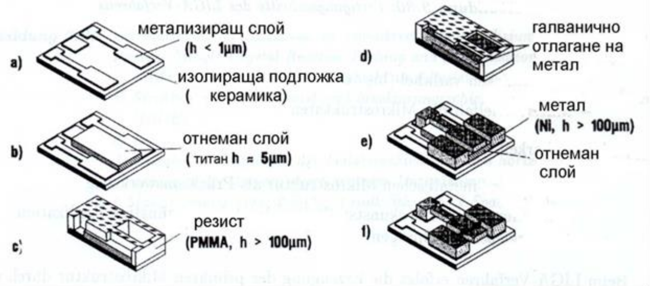


Figure 8. Capacitive acceleration sensor
Legende: metallization layer, substrate, stripped layer, resist, electroplating of metal, metal and stripped layer

The high repeatability of the structures during copying is maintained if the absorbing structure (most often made of gold) is applied to a material that transmits X-rays well. As such, beryllium is primarily used, which has high thermal conductivity and very good X-ray transparency at a large layer thickness (typically 0.5 mm). In addition, diamond membranes with optical transparency upon repeated exposure, as well as polyamide foils with low repeatability requirements, are used as carrier materials.

Examples of applications are structurally accurate reproduction of polymer masks and GSM-telephones; selective and rapid coating of the substrate by laser-assisted metal deposition without a mask; dispersed, blocking layers to increase hardness; deposition of metal layers on hard-to-reach areas or artificial materials. Due to the off-topic nature of the topic, only the coating operations copper plating, nickel plating, gold plating, nickel with palladium plating, tin plating, silver plating and other noble materials will be mentioned here. Metal coatings obtained by electrochemical methods are discussed in detail in [1].

2.5. Deposition (Electrophoresis)

Electrophoretic coating or E-coating is similar to electroplating. The substrate is immersed in a bath that may consist of paint, epoxy, or other water-based solution. An electric current is then used to attract particles that are suspended in the liquid solution and deposit them on the surface of the substrate. Electrophoresis continues until the desired thickness of the coating is achieved, which can be adjusted by increasing or decreasing the voltage. The coated substrate is then cured in an oven. There are two types of electrodeposition: anodic and cathodic [7]. The anodic process was invented earlier, but the cathodic process is more popular today. In the anodic process, a negatively charged material is deposited on a positively charged component; while in the cathodic process, a positively charged material is deposited on a negatively charged component.

Electrophoresis is used for stainless steel, aluminum alloy, etc. parts. It can produce a variety of colors with metallic luster and improve the surface characteristics, and has good anti-corrosion properties. The technological process includes: pretreatment→electrophoresis→drying. The advantages are rich in color parts; the method can be combined with sandblasting, polishing, wire drawing, etc. It is usually the better option when coating parts that contain hard-to-reach places. This is because immersing an object in a liquid promotes a more uniform and complete distribution of the coating than can usually be achieved by a spray gun or other means. Therefore, processing in a liquid medium can realize the surface treatment of complex structures; electrophoresis is a technology suitable for mass production. The disadvantages of electrophoresis are: the ability to cover defects, it is not suitable for injection molding parts. The ultra-thin layer has drawbacks when it comes to durability and corrosion resistance. In addition, most e-coatings are not UV-resistant, which means that after baking, another layer of protection must be applied. Often, this additional layer is applied via powder coating.

A variety is micro-arc oxidation (MAO). It is a process in which a high voltage is applied to an electrolyte solution (usually a weak alkaline solution) to obtain a ceramic surface film. This process is the result of a synergistic effect between physical discharge and electrochemical oxidation. The Technological process is: pretreatment→hot water washing→MAO→drying. The advantages are: Ceramic texture with dark appearance, fine feel and anti-fingerprint. Wide range of substrates: Al, Ti, Zn, Zr, Mg, Nb and its alloy. Simple pretreatment, product corrosion resistance, excellent weather resistance, good heat dissipation efficiency. Disadvantages: the achievable color is limited, currently it is difficult to achieve only black, gray or other bright colors. The price is mainly affected by high energy consumption, which is one of the highest costs of surface treatment (Fig. 9) [6].

Fig. 9. Examples of details by electrophoresis and microarc oxidation [6, 7]

2.6. Combined methods

A metal surface can be coated first with a hard, highly wear-resistant ceramic decorative coating obtained by PVD (Physical Vapor Deposition). Chemical methods can be assisted and by laser irradiation and have reactive sputtering variants, as well as by plasma spraying coating - Plasma enhanced PECVD (Fig. 10). In the first case, gas molecules are selectively stimulated by inducing a chemical reaction or heating the surface layer of the substrate to obtain thermal deposition. In the second case, a sputtering reaction or transformation of gaseous substances is required by mixing nitrides, sulfides and carbides with nitrogen, aqueous sulfuric acid for oxide layers, acetylene, etc. [1, 6]. Therefore, reactive sputtering is based on the introduction of an additional gas that interacts with the substrate, causing a chemical reaction and contributing to the production of layers with different properties.

2.7. Coating application by plasma spraying

In this operation, a high-frequency arc is ignited between a toroidal tungsten cathode and a copper nozzle (anode). The gases-nitrogen, hydrogen, argon, helium, and their mixtures-entering the nozzle are intensely heated. Monatomic gases become partially ionized, while diatomic gases undergo dissociation and partial ionization.

The sprayed material is introduced into the gas mixture in powder form via a carrier gas. The powder particles melt at temperatures exceeding 20,000°C and are propelled at high speed onto the workpiece to form a coating. The most commonly used equipment for this process are direct current plasma torches, which operate with nitrogen or a nitrogen-hydrogen mixture. These torches feature a continuous arc and operate at power levels ranging from 1 to 100 kW.

The powders used in this process are typically metal, ceramic, or metal-ceramic materials, particularly those that are difficult or impossible to process using conventional flame or arc spraying methods. The selection of additional materials is critical to achieving the desired coating quality. The powders are usually spherical, with diameters ranging from 15 μm to 75μm.

The distance between the plasma torch and the workpiece should be maintained within 80–150 mm. The influence of individual process parameters on coating quality is discussed in detail in [24].

To prepare the surface layer of a part for optimal coating adhesion, sandblasting is commonly employed, providing the desired degree of roughness. After the coating is applied, mechanical compaction methods such as rolling, pressing, or hammer pressing can be used to enhance the coating's integrity. During heat treatment, the applied coating alloys with elements present in the base material, creating a stronger bond. In contrast, chemical treatments fill the pores in the coating by modifying the surface layer.

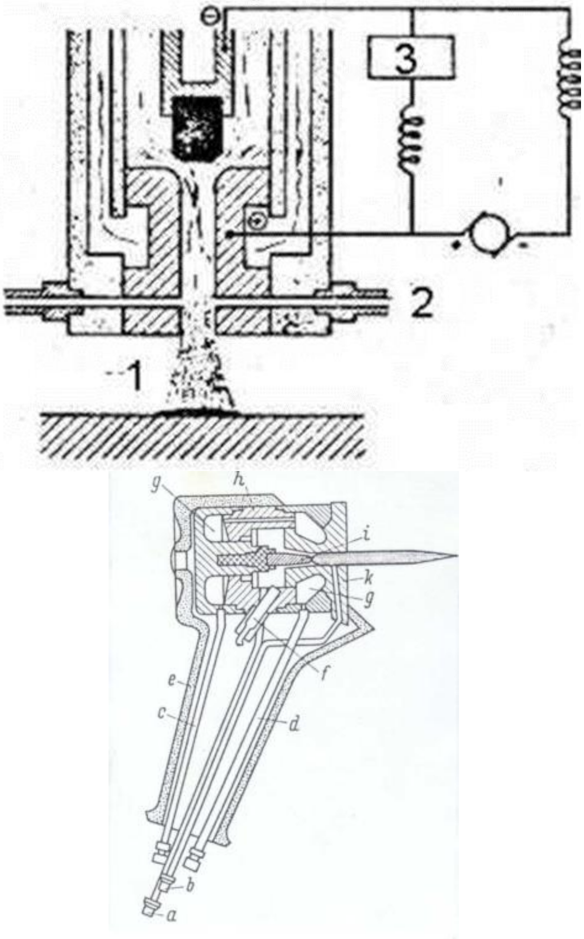


Fig. 10. Application of coatings with a plasma jet and a spray gun [1]

Legende: 1-plasma, 2-powder, 3-HF-generator, a-gas supply, b-powder supply, c-cathode power supply and water outlet, d-anode power supply and water inlet, e-plastic housing, f-ignition electrode, g-water cooling, h-plastic housing, I-tungsten cathode, k-copper anode

The principle of applying coatings using a plasma jet is illustrated in Fig. 10. The design of a plasma spraying gun is shown in Fig. 10 (right) [25]. The production of reinforced canvases with phase-bonded composites is conducted in conjunction with the plasma spraying process. A semi-finished phase-bonded material is first covered with a foil, onto which a layer of powder with a specific structure is applied using a plasma jet. Fig. 11. illustrates the principle of operation in the production of canvases reinforced with phase-bonded material. On the right, a photo of plasma spraying on silicon carbide is shown [26]. The chemical reduction method is characteristic of specific materials with specific properties and is rarely applied.

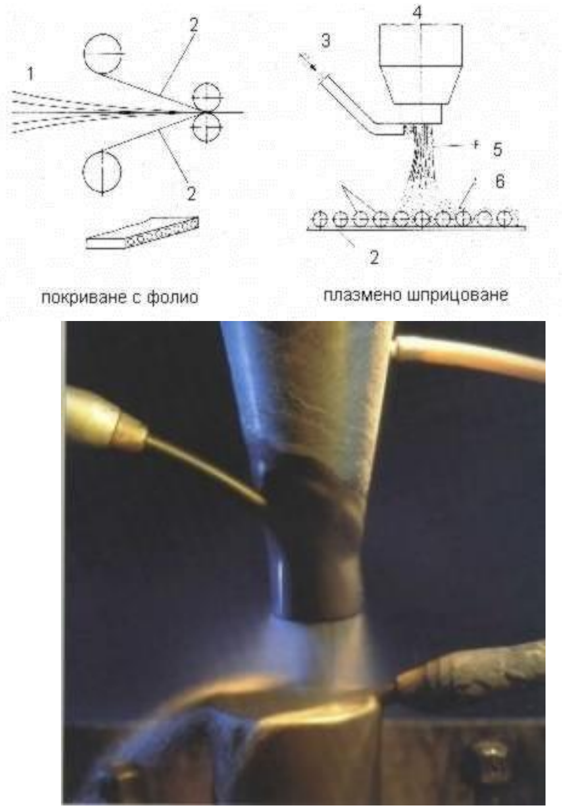


Fig.11. Application of coatings with a plasma jet and a spray gun [1]

Legend: 1-fiber, 2-foil, 3-powder, 4-plasma torch, 5-plasma beam, 6-sprayed layer

The advantages of chemical treatment (CVD methods) are:

- increasing wear resistance and corrosion resistance;
- the crystal structure of the layers is determined by the structure of the substrate, the growth rate, the impurity content, the temperature and the vacuum of the process;
- the possibility of applying layers with high electrical, magnetic and optical properties from homogeneous, mono- and polycrystalline and amorphous materials.

The disadvantages of this method are:

A major disadvantage of chemical methods is that they are only suitable for substrate materials whose melting point is sufficiently above the temperature required for the reaction.

- limited possibilities for combinations between the layer and the substrate;
- additional operations are often required to strengthen the coating.

3. Problem Solution

Chemical methods are applied in the production of layers in integrated circuits by evaporation [27, 28, 29]. Combined evaporation with chemical treatment is used in the production of camshafts, pulleys, gears, mirror foils, car accessories such as headlights and decorative glass. This method contributed to the rapid development of bearings coated with titanium carbide, which operate without lubrication. The use of Teflon dishes in the household and for industrial purposes is also known.

The possible combinations in CVD systems from the point of view of their application have not yet been sufficiently fully investigated, which may be the subject of future research, for example in combination with laser processing [30]. Nevertheless, the demand for such equipment is growing successfully, forming a suitable niche in the market. There are also factors that hinder its spread: rapid wear of the element base, which reduces the longevity of the tools, high requirements for ensuring quality, economic reasons, etc. Thanks for the assistance of WSEAS Press.

4. CONCLUSION

1. With the specific and less frequently used chemical methods than the physical ones for depositing thin and ultra-thin layers, we have limited possibilities for combinations between the materials of the layer and the substrate, as well as the details. this also determines the most frequent application of the evaporation deposition method with subsequent treatment.

2. Whether the surface of aluminum and aluminum alloy can generate a high-quality hard oxide layer depends mainly on the composition of the electrolyte concentration, temperature, current density and the composition of the raw materials. the process of anodising of titanium and its alloys is comparatively simple, and the colors formed on the surface are rich. the productivity of anodising is related to the price of the final product. the price is relatively low, so the method can be popularized in the industry and this is a promising prospect for development. the key to improving productivity is the appropriate combination between the industrial parameters, which requires part

manufacturers to continuously research the production process and seek optimization.

3. The appearance of the coated object after galvanic coating is related to the amount of the current. the smaller the current, the more beautiful the object that will be coated; otherwise, an uneven shape appears.

4. Chemical methods can be assisted by laser irradiation, have reactive spraying variants, as well as by coating application through plasma spraying with a specific purpose, taking into account the possible combinations between the layer and the substrate, what the author considers to be original and innovative aspects of the publication.

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