PRODUCTION OF METAL AND DIELECTRIC FILMS IN A COMBINED RF AND ARC DISCHARGE

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In the presentation we investigate the possibilities to deposit metallic and dielectric films on metal and dielectric materials by means of vacuum technology with application of high frequency (RF) electric fields. As a base-model the device "Bulat-6" was used with proper arc evaporators. The leading-in of a RF power (3 kW, f=1-10 MHz) was realized by connecting the RF generator to a planyclic system of the device. Before the film deposition the samples were conditioned by plasma of RF discharge (without arc discharge) at the gas pressure $p=10^{-4}$ Torr. The multi-layer coatings of the type Cr-CrN, Cr-TiN-Cr, Ti-TiN-Ti deposited on complicated shape wares of aluminum alloys had a microhardness value up to 2000 kg/mm^2. The properties of such coatings were studied depending on the vacuum conditions in the process of deposition. Taking into account the potential well developing under RF field, the experiments were provided on depositing the drip-free coatings by placing the wares in that region of vacuum chamber, which is closed from the direct ingress of particles from the arc vaporizer. The Al_2O_3 and AlN dielectric coatings were obtained and their characteristics were studied by using the electron microscope technique.

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1. INTRODUCTION

In the review paper we consider the deposition of metal and dielectric films onto various surfaces including metal and dielectric one by means of plasma-vacuum methods in combination with HF-field. Deposition of wear-resistant coating based on Ti, Cr, and Ai on different surfaces involves some difficulties. Firs and foremost, there is a need in strong adhesion to the backing. To accomplish this, high energy's and high ion density during bombardment are required for cleaning and activating the surface for the following condensation. As a result, a rapid heating up of the surface layer occurs alongside with the initiation of discharge breakdown [1-2]. This also impacts on the depth of the anisotropy etching of the surface layer leading to the modification of morphology and cleanness of a treated surface. The combination of vacuum-arc methods with HF-discharge allows to overcome such disadvantages providing deposition of coatings on dielectrics alongside with strong adhesion properties [3].

2. EXPERIMENTAL

2.1 SELECTION OF HF-GENERATOR FREQUENCY

The method of coating was carried out using "Bulat-6" type device. This device was been detailed in [2]. For our experiment this device was additionally equipped with HF-generator and variable condenser, which allowed the selection either "Bulat" or HF-mode (Fig.1). HF-generator with condenser provide plasma creation at the working gas pressures $P=10^{-1}–10^{-5}$ Torr (argon, oxygen, nitrogen). Such HF-generator can be directly connected to the backing or via the condenser. The frequency of HF-generator was selected in such a way that the minority carrier of the electrons in the E field comprised several centimeters but ions were almost static:

$$Z=eE/M\omega^2 \quad [1],$$

where: e – particle discharge, M – electrons or ions mass, $\omega = 2\pi f$ - frequency.

When creating HF-plasma with closed HF-input the resulting signal consist of three components: sinusoidal voltage, positive voltage and negative shift. The value of the negative shift is almost equal to the HF-amplitude.

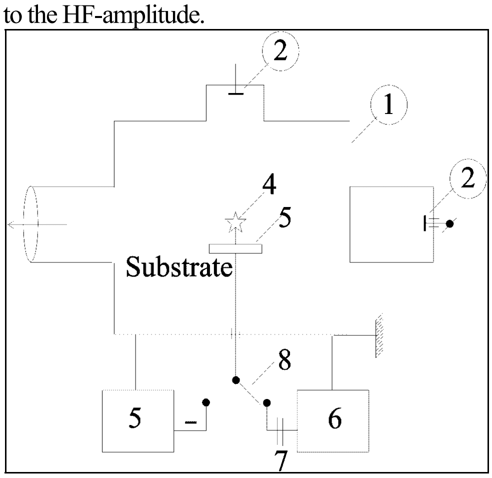

Fig.1. Experimental device

The choice of the HF-generator frequency according to the electron movement near the surface is problematic, because we consider a single-particle model instead of plasma (Fig.2.).

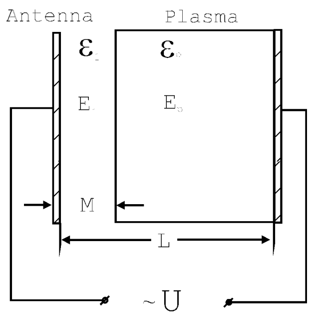

Fig.2. The schematic model

Let us assume that:

1. Plasma is described by dielectric coefficient for cold plasma.
2. HF-field wavelength in free space is grater as compared to the dimensions of antennae.

ε_l – dielectric constant in layer; E_l – electric field in layer; $\varepsilon_p = \varepsilon_0\ \kappa = \varepsilon_0\ (1 - \omega_p^2\ /\ \omega^2)$, where: ε_0 – vacuum dielectric constant; E_p – electric field in plasma; ω_p – electron plasma frequency; ω - frequency of HF-generator;

$\varepsilon_l\ E_l = \varepsilon_0\ \kappa\ E_p$.

From Kirchhoff's law: $U = ME_l + (L - M)\ E_p$,

then: $E_l = U/L\ \ (1 - (\omega_p / \omega)^2) / (1 - M/L\ (\omega_p / \omega)^2)$,

$E_p = U/L\ (1./ (1 - M/L\ (\omega_p / \omega)^2)$.

Concerning these equations one model the dependence of E_l and E_p electric fields on the frequency (Fig.3).

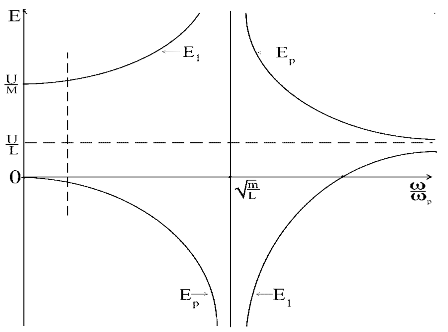

Fig.3. The distribution of the electric fields as a function of frequency

The resonance area √ m/L for our plasma parameters is in the high-frequency range ($\omega > 2\pi\times10^6$). We are interested in a low frequency range. It can be noticed that the field in E_l layer is higher then in plasma E_p. So, HF-field operates in E_l layer.

2.2. HF-CLEANING

To provide strong adhesion one should perform the cleaning of treated surface. It is common knowledge, that adsorbing gases form 2.5×10^{14}atom/ sм^2 on a surface layer with adsorbing energy of 2-4 eV/at. Thus, the high-temperature heating up to 500 C or ion bombardment is required in order to eliminate various gases formed on surface (oils, hydrogen). In "Bulat" type device for these purposes the negative potential of 1 kV is applied to the backing. The plasma discharge is created by sputtering metallic cathodes made of Ti, Cu, Al etc. The accelerated ions of the metallic plasma bombard the target and provide sputtering and surface cleaning. But there exit some disadvantages: metallic plasma ions, breakdown discharges, surface heating. It is also impossible to apply coatings on dielectrics. In this connection special attention has been paid to the possibility of surface cleaning with the use of plasma, generated by HF-method without cathode discharge. Below, we consider the method of physical sputtering. In plasma with closed HF-input it is possible to realize optimal cleaning conditions. High plasma density prevents adsorbing and provides sputtering under high ion energy of the working gas. The sputtering (cleaning) decreases at energies of up to 2-3 keV due to increasing of ion incorporation inside the material. Low average electron energy (less then 17 eV) is required in order that dissociation of oxygen or hydrogen molecules would dominate over ionization processes. Then, atomic oxygen reacts with nitrogen forming volatile compositions, which were drown away with a vacuum pump. Similar processes occur with water drawn from the surface. Atomic hydrogen enters into reaction with oxygen decreases the amount of oxides. The dissociation starts at U=11.4-11.5 eV that is 4 eV lower to start ionization processes.

With a closed HF-input a Langmuir thermal insulation conditions are obeyed. Such conditions are possible to from during the cleaning and deposition modes when operating with arc cathode. The main idea of these conditions is as follows: If a positive or negatively charged particles form the two layers on a target surface then the electrons incorporated into the layers from plasma are exposed to reflecting electric field reverting the electrons back in plasma. Such isolation became possible when T_e»T_i on a plasma filament boundary, and T_i » T_e in plasma layer. Such conditions are involved when choosing the definite frequency and intensity of HF-field, wherein the electron flows with great rates on a plasma boundary, and cold plasma ions gain the energy in a positive potential well in a layer depleted in electrons.

The following experimental has been carried out. Two aluminum samples have been used. (20mm in diameter, h=5mm). The first sample was placed on a substrate, the second one was attached to the chamber. The HF-input was closed. After HF-cleaning at the pressure $P=10^{-4}$ Torr during 5 minutes took place, a coating was applied using Al cathode at oxygen pressure of $5*10^{-5}$ Torr for 15 minutes. The coating thickness was 2μm. The temperature of the first sample placed on a substrate was below 100°C. The second sample was overheated (above 100°C). A similar experiment has been carried out with open HF-input. As a result, the sample on the substrate was melted whereas the sample attached to the camera was covered with Al film.

3. TI, CR, TIN$_X$ AND CRN$_X$ BASED MULTI-LAYER COMPOSITE COATINGS

The main parameters of the condensation process as well as the characteristics of the obtained coating are presented in the Table.

The structure and characteristics of multilayer coating Ti, solid solution

I

Structure	τ, min	h, mkm	P_N, torr	H_V, kg·mm^{-2}
Ti+Ti(N)	20	1,5	$4\cdot10^{-5}$	1600 ±100
Ti Nx	60	4,0	$6\cdot10^{-4}$	
Ti	10	0,7	$1\cdot10^{-5}$	

II

Structure	τ, min	h, mkm	P_N, torr	H_V, kg·mm^{-2}
Ti	10	0.7	$1\cdot10^{-5}$	1700 ±100
Ti Nx	60	4,0	$6\cdot10^{-4}$	
Ti(N)	20	1.4	$4\cdot10^{-5}$	
Ti	10	0.7	$1\cdot10^{-5}$	

III

Structure		τ, min	h, mkm	P_N, torr	H_V, kg·mm^{-2}	
A	B				A	B
Cr_x N		30	2	$7\cdot10^{-4}$	1010 ± 100	860 ± 80
Cr_x N	Cr_x N	30	2	$2\cdot10^{-4}$		
Cr	Cr	10	0.7	$1\cdot10^{-5}$		
Ti Nx	Ti Nx	30	2.0	$5\cdot10^{-4}$		
Ti	Ti	10	0.7	$3\cdot10^{-5}$		

I- N_2 in Ti-Ti(N) and TiN_x;

II- Ti, Ti(N) and TiN_x;

III-Cr, Cr_xN, Ti and TiN_x;

τ – condensation time; h – layer thickness; P_N – hydrogen pressure during condensation; H_V – microhardness;

A,B – coating type.

The steel of X18H9T type and D-16 aluminum alloys were used for the experiment. The obtained multi-layer structure of the coating which consisted of alternating hard (nitride) and “soft” (metallic) layers prevented the brittle fracture of the coating under the load, as it was revealed by the cone impression during the microhardness tests. By changing the thickness of different layers, their number and relative position, the optimal structure of the composite material can be obtained. In our case, the average microhardness value was changed from 500 kg/mm^2 to 1700 kg/mm^2. No exfoliation was observed during metal hardness test with the load of 20 N. This indicated to a strong adhesion.

We have succeeded in application of multi-layer coating on some specimens made of Al alloys that were used for medicine purposes. Such coatings had the required wear-resistant properties and were ideally suited to the decoration and esthetical requirements.

4. OXIDE COATINGS

The use of the assisting HF-field and cathodes made of Al or Al alloys in oxygen atmosphere allowed to apply coatings on metal, glass polystyrene materials. When changing the oxygen pressure the conducting and dielectric coatings can be obtained. The application of coatings at the oxygen pressure $P=10^{-5}$ to 10^{-2} Torr allows to obtain different coloring from steel blue to black one. A specially designed technology permitted to apply dielectric coatings on electrical connectors made of Al alloys (AMG-7 and TSAM-4.1). Dielectric coatings based on Al_2O_3 were deposited on high-cutting steels and had electrical durability of 50 kV/mm^2. Mirror coatings were prepared on glass substrates by using Al cathode at the pressure 10^{-4}Torr. Next, a protection Al_2O_3 layer was deposited at $P=10^{-3}$Torr during 2-5 minutes.

SUMMARY

1. The method of HF-cleaning used before the coatings deposition has been developed. Such method of surface cleaning has proved completely reliable in service and rather simple as compared to “Bulat” one.
2. HF cleaning allows to operate with metallic and dielectric surfaces without their being heated to the high temperatures. Various working gases (N_2, O_2, Ar) can be used during condensation.
3. The combination of arc and HF-plasma sources provided low temperature coatings application (below 200°C) with the optimal adhesion properties.

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ОДЕРЖАННЯ МЕТАЛЕВИХ І ДІЕЛЕКТРИЧНИХ ПЛІВОК В КОМБІНОВАНИХ ВИСОКОЧАСТОТНОМУ І ДУГОВОМУ РОЗРЯДАХ

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Вивчались можливості нанесення металевих і діелектричних плівок на метали й діелектрики в вакуумі з застосуванням високочастотних (ВЧ) електричних полів. Експерименти проводились на установці “Булат-6” . Підвід ВЧ енергії (3кВТ, f =1-10мГц) було здійснено шляхом підключення ВЧ-генератора до поворотного пристрою установки. Перед нанесенням плівок поверхня зразків оброблялась плазмою газового ВЧ-розряду (без дугового розряду) під тиском $p=10^{-4}$ Тор. Багатошарові покриття складу Cr-CrN, Cr-TiN-Cr, Ti- TiN-Ti, осаджувані на вироби різних форм із сплавів алюмінію, мали мікротвердість до 2000кГ/мм². Вивчалась залежність властивостей таких покриттів від вакуумних умов під час осадження. Хороше проникнення ВЧ-електричного поля в плазму давало можливість одержувати покриття без макрочастинок за рахунок розміщення зразків в місцях вакуумної камери, куди макрочастинки з дугового випаровувача не попадали. Одержано також діелектричні покриття Al_2O_3 й AlN. Їх характеристики досліджувались за допомогою методів електронної мікроскопії.

ПОЛУЧЕНИЕ МЕТАЛЛИЧЕСКИХ И ДИЭЛЕКТРИЧЕСКИХ ПЛЕНОК В КОМБИНИРОВАННЫХ ВЫСОКОЧАСТОТНОМ И ДУГОВОМ РАЗРЯДАХ

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Исследованы возможности осаждения металлических и диэлектрических пленок на металлы и диэлектрики при помощи вакуумной технологии с применением высокочастотных (ВЧ) электрических полей. Эксперименты проводились на установке “Булат-6”. Подвод ВЧ энергии (3кВт, f = 1-10мГц) обеспечивался подключением ВЧ-генератора к поворотному устройству установки. Перед нанесением покрытий образцы подвергались воздействию плазмы высокочастотного газового разряда (в отсутствие дугового разряда) при давлении $p=10^{-4}$ Тор. Многослойные покрытия Cr-CrN, Cr-TiN-Cr, Ti-TiN-Ti, осажденные на изделия различной формы из алюминиевых сплавов имели микротвердость до 2000 кГ/мм. Исследованы свойства этих покрытий в зависимости от вакуумных условий процесса осаждения. Учитывая хорошее проникновение высокочастотного электрического поля в плазму, были выполнены эксперименты по нанесению покрытий, не содержащих макрочастиц, путем помещения изделий в те части вакуумной камеры, куда макрочастицы из вакуумно-дугового испарителя не попадают. Получены, также, диэлектрические покрытия Al_2O_3 и AlN. Их свойства исследованы с помощью методов электронной микроскопии.