The silicon breakdown-proof coatings deposition in RF discharge plasma

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Abstract. The technology of silicon coatings deposition on various materials complex formed wares in RF discharge plasma is described briefly. The precursor’s choice and its polymerization mechanism on ware’s surfaces are explained. Perspective constructions of inner-chamber equipment and characteristic deposition regimes of breakdown-proof and corrosion-proof coatings deposition are presented. The advantages and shortcomings of the polymerization with auxiliary covered ware’s constant potential are noted.

1. Introduction
The organic precursors plasma polymerization processes are known long ago and described rather thoroughly in [1] whereas in later fundamental monographs deduced to plasma-chemical technology the polymerization is not mentioned at all [2]. One should mention multilayered coatings for high voltage isolation, various types of antifriction coatings, at last three-layered coatings “polymer-metal-polymer” as natural applications of this technology. It’s marked [3] that such coatings exhibit low electroconductivity ($10^{-16}$-$10^{-14}$ (Om*cm)$^{-1}$), low dielectric loses ($\varepsilon \sim 2$–4, $\tan \delta \sim 10^{-3}$-$10^{-2}$) and high breakdown voltages ($10^{6}$-$10^{7}$ V/cm).

To acquire polymer films they generally use two discharge types: DC and AC (frequency below 100 kHz) as well as RF discharge (up to 100 MHz). At this the RF discharge polymerization is executed with either interior or exterior electrodes; they use the electrode less discharge too. Chemical reactions providing polymer films due to glow discharge are very complex and multivariate and take place either on the ware’s surfaces or right in the chamber volume. Polymer compounds formed due to the volume polymerization deposited on wares are mostly powder substances having large porosity and low adhesion to surfaces. The surface polymerization takes place at such pressures in the gas phase that the molecules free-length is comparable with the distance between electrodes, one of which may be the treated ware itself. It means that from the coatings quality viewpoint the process must be carried out at minimal pressures.

2. The main experimental data
The main investigated and proved dependencies of the polymerization processes are:

– the electric field strength into films (across the film) is nearly proportional to the current density and inversely proportional to the field frequency [4] – table 1.
Table 1. The dependence of the electric field strength across the film on the discharge frequency and current density.

| Discharge frequency (MHz) | Current density (mA/cm²) | Electric field (across the film) (V/µm) |
|---------------------------|--------------------------|----------------------------------------|
| 0.01                      | 5.0                      | 30.0                                   |
| 0.1                       | 5.0                      | 3.0                                    |
| 1.0                       | 5.0                      | 0.3                                    |
| 1.0                       | 50.0                     | 3.0                                    |

– the film deposition rate on the isolated substrate is sufficiently lower than on an electrode but at the pressure decrease the former’s rate constantly increases whereas the later one constantly decreases, so they become equal at some pressure [5];

– it's shown in [6] that the greater the input power the stronger the influence of the interelectrode’s distance alteration on the deposition rate but if this distance is greater than 50–60 mm this rate becomes constant;

– the film deposition rate on an auxiliary electrode located near two main RF electrodes dependence on its negative potential is maximal in the vicinity of around – (120–150)V. At lower potentials this rate decreases due to monomer molecules desorption from the treated surface under the action of “too hot” ions, at higher – the film is sputtered [7];

– with the frequency increase the cathode (electrode) polymerization ratio decreases but this polymerization provides the best protective coatings on metals [8].

3. The choice of precursors

To acquire coatings by plasma polymerization in a gas phase the precursors cardinal characteristics must be: availability, volatility, decomposition in low-temperature plasma. Many silicon-organic compounds having at least one bond Si-O, Si-N, Si-H, besides Si-C, satisfy this condition. The analysis of a large group silicon compounds has permitted to choose some mostly perspective compounds. Further investigations have permitted to stop the choice on the octamethyltetrasiloxane (Me2SiO)₄ (D₄) [9].

At its thermal decomposition (it’s precisely what occurs inside plasma) these main initiation reactions are possible: 1) redistribution of bonds Si-O-Si and Si-O-C; 2) Si-C bonds rupture; 3) bonds with a substrate occurrence (Al-O-Si, Fe-Si(C)). At thermal reactions the destruction of siloxane chains methyl surroundings is not typical. For these siloxanes the main thermal transformation direction is the redistribution of Si-O-Si bonds. The destruction of dimethyl-cyclosiloxanes D₄, D₅ and D₆ terminates in the cycle opening stage with the biradicals formation and their different recombination either between each other or at the interaction with other dimethyl-cyclosiloxanes molecules.

Besides the thermal radical process the ionic one is possible inside plasma. The reaction of a positively charged particle X⁺ or a negatively charged particle A⁻ leads to the cyclodimethylsiloxane’s cycle opening with the anionic or cationic polymerization centers. In this case there occurs no low-molecular products formation but the polymer formation, for example:

\[ \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \]

\[ X^+ + D_4 \rightarrow X - O - Si - O - Si - CH_3 \]

\[ \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \]
These processes are analogous to the industrial chemical synthesis of PMS liquids. However, a great deal depends upon the residual atmosphere composition – air, inert gas or, for instance, oxygen. The last two are used to previous ion-plasma cleaning of treated surfaces. One cannot give any universal recommendations that’s why the concrete parameters of a technological process one has to choose accounting treated wares peculiarities – form, conductivity, physic-chemical surface properties.

To carry out the surface $D_4$ polymerization process successfully it is desirable that the $D_4$ destruction in gas phase terminates at the cycle opening stage. It constrains the power introduced in plasma as well as the pressure. Further power increase leads to molecules fragmentation that is to surface polymerization rate decrease and consequently to the pressure increase. On the other hand, at too low pressures only a small part of $D_4$ molecules collide with active particles opening the cycle. Thus, there exists the optimal power and pressure interval which may be found only experimentally.

4. The inner-chamber equipment
The inner-chamber equipment construction is not less important, particularly precursors input gear. The author consequently has designed some of these gears applied in industry at “Autosvet” and “OSVAR” factories at the end of the last century 90th. One of the latest has permitted the triple decrease of the protective coatings deposition time (from 15 to 5 minutes), to refuse the $D_4$ container heating and the use of auxiliary constant potential shift source.

Later in 2000th the US patent of the similar gear has been taken out [10]. Its priority date is 16.07.1997, so that our gear has been made and tested earlier – in 1996. Almost at one time also in US the gas injector for plasma enhanced chemical vapor deposition has been patented [11]. It contains the squeezed dielectric detail with a hole through which a gas is input. At the dielectric use in the gas injector the plasma torch is not formed and the working gas mix is not decomposed prematurely.

We have solved this problem otherwise though with the gear uniting different schemes advantages and free from their shortcomings at the same time. This construction may be tentatively named electrodeless lengthy RF ion source – figure 2.
Figure 2. The lengthy RF ion source: 1 – the combined gas, $D_4$, RF power and constant potential shift input, 2 – the plane RF electrodes, 3 – isolators, 4 – the protective metal cover.

Its ion sources alliance consists in the fact that the discharge is sustained only in the small gas discharge chamber (GDC) volume, not in the whole deposition chamber. At that RF electrodes are made in the form of parallel planes isolated from plasma by dielectric planes and from the side exterior relative to discharge chamber by the metal cover too, so that the RF wave doesn’t come out the GDC limits. The glow discharge may be sustained at rather small RF power levels – 60–100 Wt whereas the auto-shift is compensated by surface charges and isolators polarization. The gas distributing tube lying along the discharge camera and connected with a metal plate located between RF electrodes normal to them is under a small positive potential relative to earth (~100–200 V) providing the extracting field enough to create the oriented active particles flow from the GDC volume to the treated wares surfaces. At the same time this potential is too small to excite micro-arcing and the active particles energy isn’t enough to somehow remarkable sputtering of the growing protective film.

5. Conclusion
The analysis of thermal properties and ability to ionic transformations of individual silicon-organic compounds together with known physic-chemical data of different oligoorganosiloxanes permits one to make the conclusion about the some of these compounds applicability to produce multilayered coatings by plasma polymerization. Depending on the metal’s nature one should recommend the concrete compounds. In particular for aluminum the most effective compound is octamethyltetrasiloxyane – $D_4$. The rather wide set of technological parameters and concrete gears allows one to use this technology for breakdown and corrosion-proof coatings deposition on different wares that favorably differs it from alternative PVD and CVD methods dominating nowadays in various branches.

References
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