High-rate deposition of silicon films in a magnetron discharge with liquid target

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Abstract. Silicon coatings have been deposited on substrates made of low-carbon and high-carbon steels and tungsten in a magnetron discharge with liquid target at substrate bias voltages ranging from +100 V to -600 V. The structure of obtained coatings was examined by a scanning electron microscopy. The strong influence of substrate bias voltage on the coating structure was observed. The corrosion resistance of coated steel samples was examined in concentrated sulphuric, hydrochloric and nitric acids and their solutions. The resistance of coated tungsten samples against high-temperature oxidation was examined by their exposure to O2 gas at a pressure of 0.2 Pa and a temperature of 1073 K. The coatings deposited under bias voltages of +100 V and -600 V had dense structures and showed the best protective properties among all deposited coatings.

1. Introduction
Silicon-based coatings have been widely used for many years in microelectronics, photonic devices, as adhesive layers for diamond-like carbon coatings, etc. In particular, siliconizing is a common method for protection of articles made of various metals (steels, titanium alloys, molybdenum, etc.) against corrosion in aggressive media and high-temperature oxidation [1-3]. However, in the latter case the coatings obtained by common methods (laser surface alloying, vapour-phase siliconizing, and powder siliconizing) usually have quite high porosity, thus they cannot provide excellent corrosion resistance. Coatings obtained by magnetron sputtering usually have a very dense structure and good adhesion to a substrate [4]. Nevertheless, the deposition rates in classical magnetron sputtering systems (MSS) are much lower than in chemical vapour deposition (CVD) and evaporation systems. A magnetron discharge with liquid target (MDLT) is a promising tool for high-rate deposition of high-quality coatings [5]. The remarkable feature of this discharge is that due to ion bombardment of the cathode, at a certain value of the discharge power the cathode material starts to melt and intensively evaporate. Thus, the flux of atoms on a sample surface is a combination of fluxes of sputtered end evaporated atoms from a cathode. This allows to reach much higher deposition rates (in comparison with that in conventional magnetron sputtering systems), to heat a substrate to high temperatures due to radiation from a cathode and energy of arriving particles, and to have an ion assistance during the deposition (i.e. to influence on the film structure by biasing the substrate).

This work is devoted to investigation of structure and protective properties of silicon films deposited in a MDLT on different substrates at various conditions.
2. Experimental
The coatings were deposited on mirror-polished plates made of low-carbon steel (transformer steel type 3) and high-carbon steel (C1035), and on 50 μm tungsten foils in a DC magnetron discharge with liquid cathode in the PINCH installation [5]. Silicon target (with a purity of 99.9%) was located in a carbon crucible, which was thermally insulated from a water-cooled magnetic system. The samples were placed on an object table located at a distance of 18 cm above the crucible. The residual pressure of about 1×10^{-3} Pa in the chamber was obtained by a turbomolecular pump in series with a rotary vane pump. Prior to deposition, the substrates were ultrasonically cleaned in an acetone and then sputter-cleaned in a DC glow discharge in Ar initiated between the object table and walls of the vacuum chamber. At the beginning, a DC magnetron discharge in Ar at a pressure of 1 Pa with a power of 2.5 kW was ignited. Due to poor heat removal from the crucible, silicon in it started to melt and then intensively evaporate. This discharge regime is referred as MDLT. The coatings were deposited under various DC bias voltages at a sample holder (-600V, -450V, -300V, -150V, 0V, +100V).

The structure of deposited films was investigated in a scanning electron microscope (SEM) TESCAN VEGA3. Both the surface and the fracture cross-sections of the deposited films were studied. From these observations the film thickness was measured. The deposition rates were estimated by dividing the coating thickness by the deposition time.

In order to check the protective properties of deposited films on steel substrates, the samples (both coated and uncoated) were exposed to concentrated sulphuric, hydrochloric and nitric acids for 30 min. The samples that were not destroyed during these tests were then exposed to 10% aqueous solutions of sulphuric, hydrochloric and nitric acids for 24 hours. After the exposure, the samples were washed in distilled water and then their surface was investigated in an optical microscope. For testing of the protective properties of obtained coatings on tungsten samples against high-temperature oxidation, the samples were exposed to O₂ gas at a pressure of 0.2 Pa and a temperature of 1073 K for 30 min. The erosion rate of the samples was estimated by their weight loss after the exposure.

3. Results
SEM investigations demonstrated that the structures of coatings deposited in the identical conditions were almost similar for all used types of substrates. Examination of the fracture cross-sections of the samples indicated that with increasing the bias voltage the structure of the coatings became denser (Figure 1. a–c). Besides, the coatings deposited at +100 V bias also had a dense structure (Figure 1. d).

The deposition rate at the bias voltages of +100 V and 0 V was about 1.2 μm/min, and decreased with increasing the negative bias voltage (to 0.2 μm/min at -600 V) due to increase in sputtering rate of the film by arriving ions.

The corrosion tests of the bare steel samples indicated their intense erosion in all used acids. The samples coated with Si films deposited at the bias voltages of 0 V, -150 V, and -300 V corroded much slower than the bare samples, albeit the coatings slowly destructed with time and the corrosion rate of the samples gradually increased. Neither substrate corrosion nor film destruction was observed for the samples with coatings deposited at -450 V, -600 V, and +100 V after their short-term exposure in concentrated acids. After the long-term exposure of these samples in solutions of these acids, the coatings deposited at -450 V partially destructed (some parts of the coatings exfoliated), whereas on the coatings deposited at -600 V and +100 V only small pinholes with a diameter of less than 50 μm were observed.

Similarly, the tests on behavior of tungsten coated with the Si films at high temperatures in oxygen environment revealed that only the coatings deposited at -600 V and +100 V bias allowed to reduce the erosion rate of tungsten by more than one order of magnitude and the coatings almost did not destruct during the tests. The coatings deposited at other bias voltages showed much smaller reduction of the erosion rate of the tungsten substrate due to exfoliations of large parts of coatings during the tests.
4. Discussion

The destruction of the coatings during the tests may be caused by the presence of large number of through channels (for acid transport to the substrate) in the coatings and also may be due to poor adhesion of the coatings to the substrate.

The results clearly demonstrated the strong influence of substrate bias on the microstructure and, possibly, the adhesion of silicon coatings deposited in a MDLT, despite the fact that the number of ions arriving on the substrate is much less than the number of neutral particles (sputtered and evaporated). The fact that the coatings deposited at the bias voltage of -600 V had the densest structure and the best adhesion to the substrate among all coatings deposited at negative bias voltages (taking into account that the thicknesses of all of them were similar) may be due to high energy of ions arriving on the substrate resulting in enhancement of surface mobility of coating atoms, and, consequently, to structural rearrangements in the growing film [6]. Besides, ion bombardment results in
increase of the coating temperature. Superior properties of the films deposited at +100 V may be explained by the fact that electron bombardment of the film leads to increase of its temperature, which was confirmed by visual observations – the sample glowed red during the deposition. One should mention that such effect was not observed during the deposition of films under negative bias voltages due to the fact that the electron current in the former case was much higher than the ion current in the latter case. It is known that elevated substrate temperature during the deposition leads to structural changes in a growing film \cite{6}. However, other effects of inelastic interactions of electrons with the film, such as activation of adsorption centres on its surface, may also contribute.

Increase in substrate temperature may also lead to enhancement of diffusion of silicon atoms into the substrate that may result in better adhesion of the coatings to the substrate due to formation of the transition layer. In the case of ion irradiation, ion-induced mixing of coating atoms and substrate atoms may also lead to formation of such layer.

4. Conclusions
Silicon coatings were deposited on steel and tungsten substrates in a magnetron discharge with liquid target at substrate bias voltages ranging from +100 V to -600 V. It was shown that the bias voltage (both negative and positive) strongly affects the structure of deposited coatings. The coatings deposited at the bias voltages of -600 V and +100 V had a dense structure and demonstrated the best protective properties against both the corrosion in acids and high-temperature oxidation. The maximum achieved deposition rate of 1.2 \(\mu\)m/min (at +100 V bias) was much higher than that obtained in a conventional magnetron discharge with solid target\cite{7}.

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