AFM capabilities in investigating plasma polymerized films applied onto metal substrates

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With metals and alloys used as construction materials special measures are required for their anticorrosion protection. With this purpose protective polymeric coatings have widely been used. Among them are the polymers prepared in low-pressure glow discharge plasma, which are low permeable, insoluble and infusible – the qualities that make them highly suitable for using as protective coatings. Since plasma polymerized protective films are usually rather thin (nanometer scale), it is often difficult to study their characteristics. The thickness range covered by AFM makes it possible to determine physicochemical characteristics of thin polymer films on metal substrates. Therefore, it allows studying mechanisms of film formation and growth, which offers great opportunities in producing films with targeted characteristics.

The paper suggests methods and examples of measuring thicknesses and strengths of plasma polymerized films applied onto metal substrates. Films with different degrees of polymerization, cross-linking and branching were taken, and phase inhomogeneities and changes in surface polarity were measured.

Polymer films deposited onto iron (steel) substrates in low temperature plasma of saturated hydrocarbons were taken as samples. The methods, regimes and the description of the device were given in [1].

The investigations were performed by means of the AFM-technique using apparatuses P4-Solver and P47-Solver from the NT-MTD Company, which were adjusted to contact and semi-contact modes according to the methods described in [2]. Silicon probes of the same Company were used, with the tip curvature radius of ~10 nm. Chemical composition of films was studied using XPS. Contact wetting angle measurements were performed to study the integral surface polarity of films.

Polarity changes of films were estimated based on variations of interaction force between the sample and the probe ($\mathbf{F_z}$) by taking force-distance curves using a local force spectroscopy mode [2].

The film thickness was determined by measuring the depth of a scratch after indentation of the film with a copper needle. The needle material was taken patently softer than steel to avoid the substrate damage. The imaging was performed after adjusting to the scratch edge (Fig. 1).

Film strength was measured by estimating the least pressing force of a probe tip to a sample, at which a typical rectangular pit remained. The sizes of the film were 2x2 μm with scanning area being 0.5x0.5 μm (Fig. 2). If the film remained undamaged, a new scanning area was taken with larger loading applied. The pressing force was calculated using a formula:

$F = \Delta Sp \cdot (\Delta x/\Delta y) \cdot K$, where

-ΔSp is the difference between the set value “Set point” and the initial level of a signal “DFL”;

-$\Delta x/\Delta y$ is a conversion factor, which connects linear cantilever movements with current signal changes;

-K is a cantilever force constant, which is determined using the instrument rating.

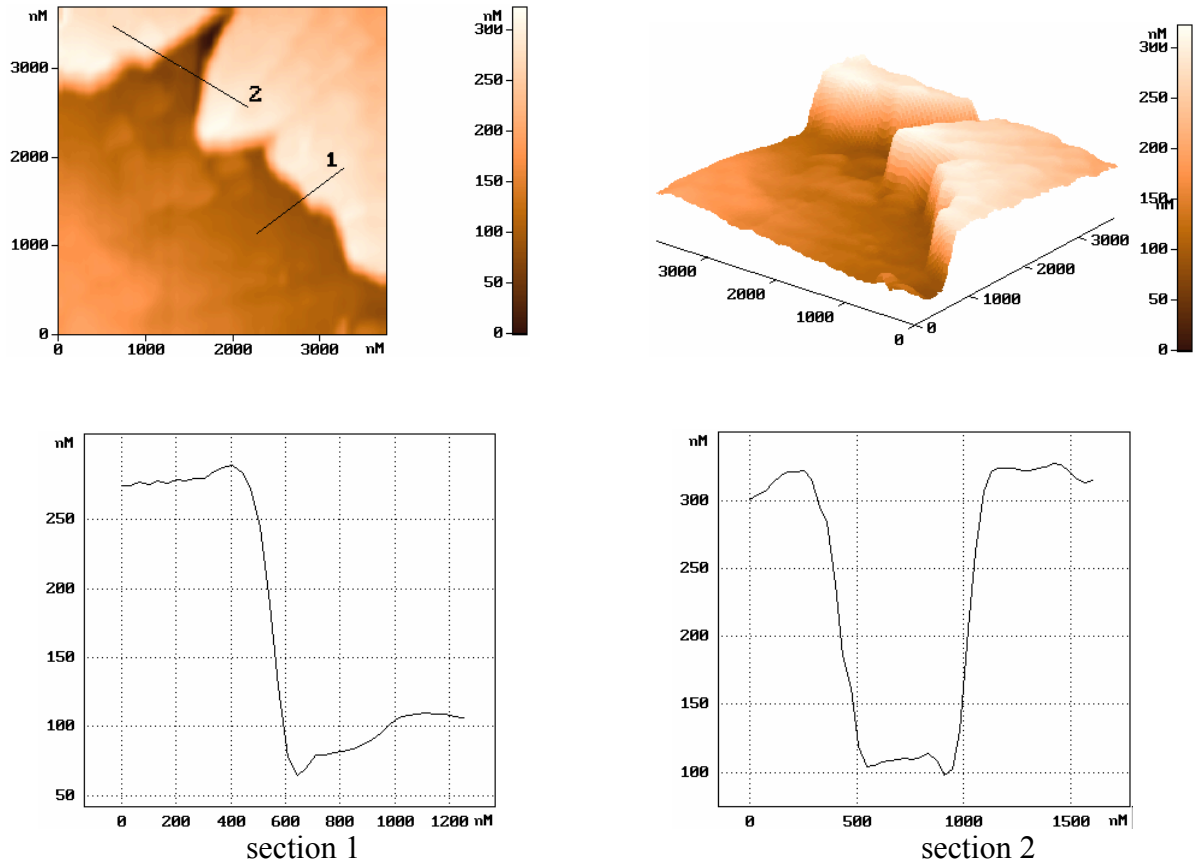

Fig.1. Thickness measurements for undecane plasmapolymerized film applied onto steel substrate.

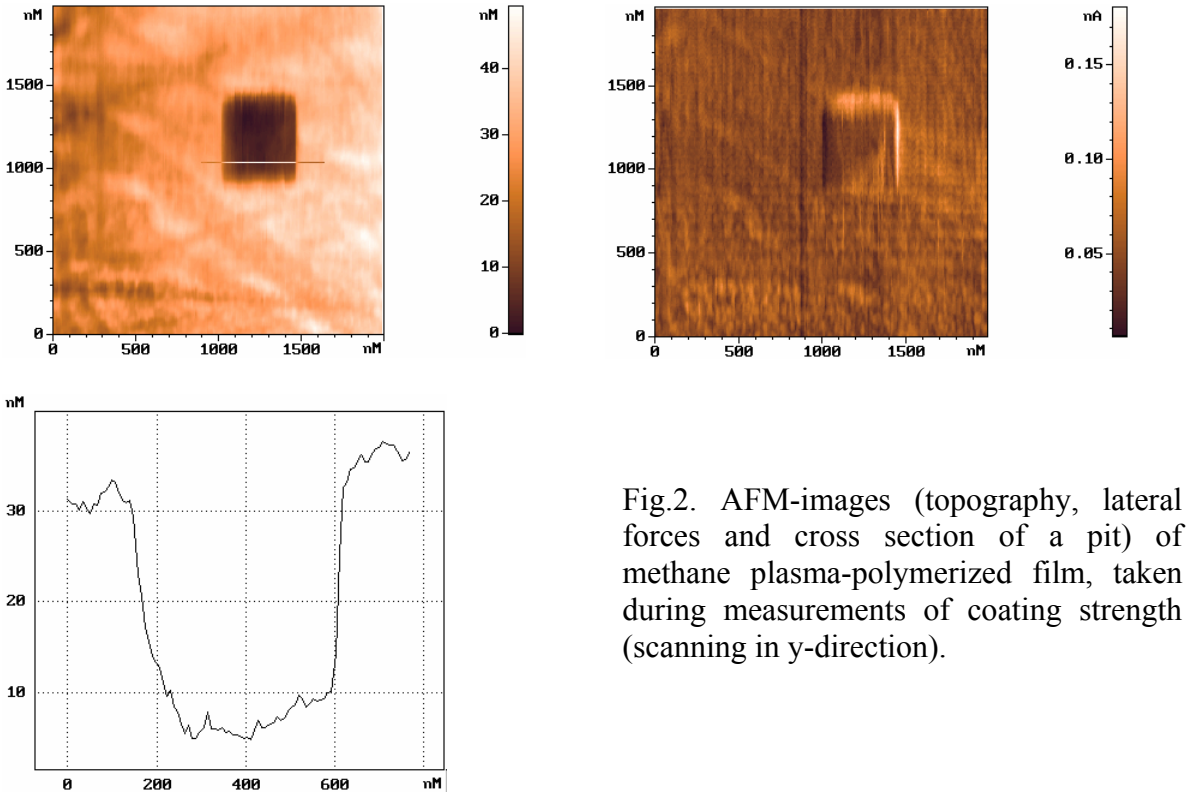

Fig.2. AFM-images (topography, lateral forces and cross section of a pit) of methane plasma-polymerized film, taken during measurements of coating strength (scanning in y-direction).

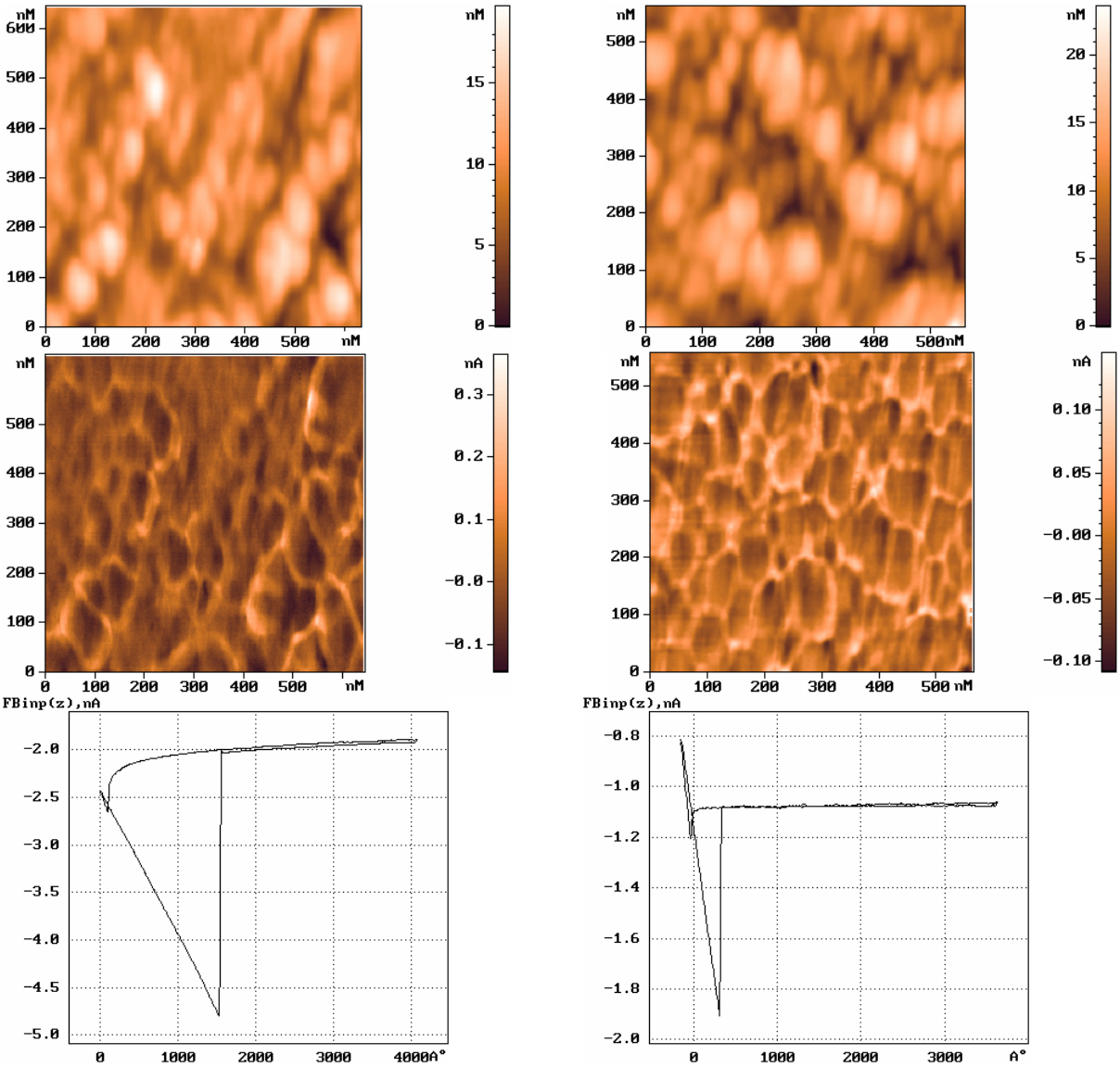

Fig.3. Topography, phase contrast (MAG*Sin) and surface spectroscopy of plasma-deposited film: a – methane, b – octane (cantilever constant K during spectroscopy is 0.02 and 0.06, respectively).

It is seen from the Fig.3. that while surface topographies of methane and octane plasma-polymerized films are almost similar, their phase contrasts are different. With a practically single-phase octane film surface, the methane film has at least two different phases. According to spectroscopy-based adhesion force calculations adhesion force values between the probe and the film are 2,9 nN and 1,7 nN for methane and octane films, respectively. These results are confirmed by X-ray photoelectron spectroscopy data and contact wetting angle measurements. Thus, contact wetting angle values on the surfaces of methane and octane films make up 72^{o} and 80^{o}, respectively. Besides, the content of oxygen-containing groups in the surface layer is 16 % and 5 %, respectively. All this indicates different degrees of structurization, that is different degrees of polymerization, cross-linking and chain branching in films under consideration.

[1] A.M.Lyakhovitch, A.M.Dorfman, S.G.Bystrov, and V.I.Povstugar. Phys. Low-Dim. Struct.,3/4 (2001) 277.
[2] S.N. Magonov, M.-H.Whangbo. Surface Analysis with STM and AFM, Weinheim, New York, Basel, Cambridge, Tokyo. VCH, Weinheim, 1996.