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Investigation of opal nanostructures using scanning probe microscopy

A B Syritskii\textsuperscript{1} and E V Panfilova\textsuperscript{2}

\textsuperscript{1}Department of Metrology and Interchangeability, Moscow State Technical University Bauman, Moscow, 105005, Russia
\textsuperscript{2}Department of Electronic Technologies in Mechanical Engineering, Moscow State Technical University Bauman, Moscow, 105005, Russia

syritsky@bmstu.ru, panfilova.e.v@bmstu.ru

Abstract. The paper presents the research results on the creation of multilayer structures based on opal films using the methods of atomic force microscopy, tunnelling microscopy, and current spectroscopy. It is found that tunnelling microscopy methods are applicable for studying chromium-opal-gold-carbon layered structures. Surface images and current-voltage characteristics of each layer are shown. It is shown that the formation of film structures on the surface of opal matrix starts with "islands" on tops of silica spheres. It is found that the deposition of carbon films on the surface of the chrome-opal-gold structure leads to increase in tunnel currents in the probe-sample gap. The presented results may be used for the formation of a variety of layered structures and particle arrays on the surface of opal matrix, e.g., photonic devices, sensitive elements, and emission devices.

1. Introduction

Possible application areas of opal films are not only photonics, but also plasmonics, sensor technology, emission, laser and microwave technology, medicine, and a number of other ones. Development of technologies for the formation of appropriate structures requires a significant number of different studies. Therefore, it is necessary to elaborate the equipment, methods, and techniques for comprehensive studies of the formed structures [1,2].

One method of research is scanning probe microscopy (SPM), using techniques of atomic force (AFM) and scanning tunnelling microscopy (STM). SPM can be easily used because of the ability to place the sample in the atmosphere. The advantage of AFM is the ability to study almost any materials, and this method is widely used in the study of opal structures [3]. The advantage of the STM method is ultra-high resolution: up to $10^{-3}$ nm normally to the surface (vertical) and up to $10^{-2}$ nm along the axes of parallel surfaces (lateral). Modern equipment allows studying the topography and morphology of the surfaces, moving individual atoms, carrying out local chemical reactions, manipulating individual molecules, investigating the direction of the atom spins [4], displaying the density of states and the work function, obtaining the dependences $I(U)$, $I(Z)$, $dI/dU$ and $dI/dZ$, where $I$ – tunnel current, $U$ – voltage in the gap, $Z$ – the gap, and determining the chemical type of bond between the atoms of the object surface and the chemical composition of the surface layer of the object (current spectroscopy). The tunneling current recorded during scanning is sufficiently small (0.5 pA...50 nA), which makes it possible to study samples with low conductivity [5].
This paper presents the results of a layer-by-layer study by AFM and STM methods of a metal-dielectric film composition created on the basis of an opal film (opal sublayer). Such structures can be used to create giant Raman scattering substrates, emission and sensor devices.

2. Samples description
The choice of the films compositions was due to the prospect of creating emission structures based on the opal matrix. A schematic representation of the sample structure under study is shown in Figure 1. The opal film with the sizes of silica spheres 220 ... 250 nm and thickness of about 700 nm was formed by vertical pulling from colloidal liquid on the chromium sublayer deposited on the glass substrate by magnetron sputtering. The gold film with the thickness from 20 to 200 nm was applied to the opal film by magnetron sputtering. A carbon layer α-CH with the thickness from 10 to 100 nm was deposited on the gold surface by chemical deposition from the gas phase. The gold and carbon films thicknesses were controlled on a witness sample – a glass substrate. The chromium film provided the conductivity for the study on STM and acceptable adhesion of opal to the substrate. Opal layer served as a matrix for formation of the upper layers’ topology.

The gold film was a catalyst for the growth of carbon nanostructures. The choice of layer thickness was determined by the results of previous studies [3]. When analysing STM images of opal films, it was found that acceptable image quality could be obtained only for a film with small thickness, consisting of one to three globular layers (200...750 nm). The choice of the thickness of gold films was determined by the revealed dependence of the gold layer surface topology deposited on the surface of the opal matrix on the thickness of the gold film measured on a smooth witness sample. Previously, it was shown that at the initial stage of film growth the metal was deposited on the tops of the opal matrix of silica spheres, then the film grew and the relief began to smooth, but to thicknesses of about 200 nm with a diameter of spheres 200...250 nm its relief repeated the relief of the matrix.

3. Results
The samples were studied using scanning probe microscope Solver P-47 (NT-MDT, Russia) by means of AFM in semi-contact mode and STM in topographic mode by direct current method and current spectroscopy mode. Minimum step STM-scanning was 0,006 nm. Previously it was found that the image of the relief of opal films on the metal sublayer depended on the tunnel voltage generated in the gap. This effect was most likely not related to mass transfer and was explained by the presence of emission processes. During scanning the voltage was from 0.1 to 1.0 V.

The results of the study indicate the possibility of studying metal-dielectric multilayer opal structures using STM. To be able to scan, the sum of the thickness of the opal, gold, and carbon layers should not exceed 1 µm. Moreover, it is possible to obtain both direct images of the sample surface and current-voltage characteristics.

Figure 1. Chrome/opal/gold/carbon structure on the glass substrate.
Figure 2. Three-dimensional view of multilayer structure relief obtained by (a) AFM, (b) STM.

Image quality depended on the thickness of individual films. It was found that for the compositions of chromium-opal-gold STM method was available at the gold films thickness from 100 to 200 nm. This fact is confirmed by the mechanism of formation of metal films on the opal matrix presented in Ref. [3]. When the thickness reached 100 nm, interspherical voids began to be filled with the deposited material, reaching at a small thickness of the opal film of the chromium sublayer; the metal "islands" formed at the tops of the spheres grew and merged, starting to form a continuous film. Tunnel currents increased, and the sample became available for study by STM. The structure and, hence, conductivity of the carbon layer also depended on the thickness. Thus, for the samples under consideration, the quality of the images of the surface of the composition chromium-opal-gold-carbon with a thickness of the upper carbon film of 100 nm was better than that of the thinner films and close to the quality of the image obtained by AFM. For comparison, Figures 2 and 3 present three-dimensional views, surface images, and profiles of such a sample obtained by AFM and STM.

Figure 3. Surface images and profiles of carbon structures obtained by (a) AFM, (b) STM.
4. Discussion

The schematic representation of the studied structures and the systematized results of the layer-by-layer study of the samples are presented in Figures 4-6.

Comparison of the surface films formed of opal and the layer of gold once again confirmed previously identified mechanism of growth of metal films on the surface of opal matrix [3]. The study of images and profiles of the surface of the carbon deposited on the gold layer showed that carbon structures were formed mainly in areas located above the tops of the silica spheres on the "islands" of gold, which led to an increase in the elevation of these areas. The carbon layer has a "bumpy" surface, which is noticeable on the surface images (Figs. 2a, 3a) and on relief profiles (Figs. 3, 5c). At the same time, the relief of the peaks became more developed. Moreover, the application of carbon not from the gas phase, but by magnetron method, performed for comparison on some samples, led to the formation of a surface with a similar nature of the relief.
Figure 6. I-V curves of the gaps: (a) tip-opal film, (b) tip-gold film, (c) tip-chromium film.

When analysing current-voltage characteristics of the samples and the film compositions of the individual layers, it was established that I-V curve demonstrated hysteresis. Appearance of a small hysteresis can be attributed to the nonlinearity of piezoceramics. I-V curve analysis confirms the dependencies found in topographic studies. For opal films, the I-V curve has a nonlinear symmetric form typical for the metal-dielectric contact. The deposition of gold with a thickness of 100 nm or more on the surface of the opal film retains the nature of the dependence, but leads to an increase in the magnitude of the currents. Subsequent carbon deposition entails a change in the nature of the U(I) dependence, expressed more strongly for samples with a greater thickness of the carbon film in the studied thickness range. Quantitative assessment of the amplification of the electric field on the samples with carbon films with a thickness of 100 nm on the witness, made in the coordinates of the Fowler-Nordheim, testifies that at a voltage of 1.0 V for a number of points, the gain field in the gap between tip and substrate reached values of 400...420.

5. Conclusion
The results of the work indicate the prospects provided by scanning probe microscopy for the study of topography and electrophysical properties of structures based on opal films. The advantage of the method is the ability to conduct comprehensive studies of the formed structures. The authors see the development of the work in the creation and study of emission structures formed on the opal sublayer.

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