JOURNAL OF NANO- AND ELECTRONIC PHYSICS
Vol. **11** No 6, 06024(5pp) (2019)

ЖУРНАЛ НАНО- ТА ЕЛЕКТРОННОЇ ФІЗИКИ
Том **11** № 6, 06024(5cc) (2019)

Research of Microhardness of Thin Ceramic Coatings Formed by Combined Electron-beam Method on Dielectric Materials

V.S. Antonyuk[1], Yu.Yu. Bondarenko[2], S.O. Bilokin'[2], V.O. Andrienko[2], M.O. Bondarenko[2]

[1] *National Technical University of Ukraine "Igor Sikorsky Kyiv Polytechnic Institute", 37, Peremogy Ave, 03056 Kyiv, Ukraine*
[2] *Cherkasy State Technological University, 460, Shevchenko Blvd., 18030 Cherkasy, Ukraine*

(Received 22 June 2019; revised manuscript received 01 December 2019; published online 13 December 2019)

The peculiarities of obtaining thin ceramic coatings ($TiO_2 + Al_2O_3$, Al_2O_3, ZrO_2) on the surfaces of dielectrics (on the example of Kr1 silicon) during their formation by thermal evaporation in vacuum have been established. The mechanism of increase of microhardness of such coatings by their surface modification by a ribbon-shaped electron steam is investigated. It is shown that the combined thermal vacuum deposition of thin ceramic coatings from powder materials on the surface of Kr1 silicon, followed by their modification by low energy electron flow in one technological cycle, allows to significantly reduce the micro relief and to stabilize the homogeneity of the coating surfaces, as well as to increase the chemical and biological resistance of these coatings to the influence of the environment. The conditions of qualitative determination of microhardness of the studied material with the use of atomic force microscopy are determined. Microhardness studies, both of modified coatings and of dielectric surfaces on which they were applied, were carried out. The fact of nonlinear increase of microhardness (by 13-17 %) of thin coatings deposited on the surface of dielectric material by the combined electron beam method as the thickness of these coatings is established. The possibility of determining the microhardness of multilayer multifunctional ceramic coatings obtained by combined electron beam technology under different conditions and different modes of technological experiment is shown.

Keywords: Ceramic coatings, Dielectric, Silicon, Microhardness, Electron beam modification, Atomic force microscopy.

DOI: 10.21272/jnep.11(6).06024 PACS number: 42.79.Bh

1. INTRODUCTION

In modern industry, such promising directions as functional electronics, microelectronics, micro electro-mechanotronics and others are gaining more and more development [1]. Particular attention in the process of improving the elemental base of functional electronics is given to the technologies for creating fine functional coatings and structures based on them, which makes it possible to create multifunctional products on a single dielectric basis, for example, by applying thin ceramic coatings to silicon [2].

However, long-term operation of products based on these coatings is impossible without increasing their microhardness. Researches carried out earlier [3] show that an increase in microhardness is possible due to an increase in the uniformity of coatings in thickness. In this case, the measurement of the microhardness of thin (up to 100 nm) ceramic coatings on dielectric materials remains a complex task, and known methods allow only qualitative studies [4]. The authors of works [5-8] have shown the possibility of obtaining thin oxide (ceramic) coatings on dielectric materials in microelectronics and optics by various methods. However, in these works there is no information about the microhardness of ceramic coatings deposited on the surfaces, as well as their impact on the accuracy and reliability of the products based on them.

Earlier, studies were carried out [9], which showed the possibility of obtaining thin (up to 100 nm), including ceramic, coatings with a structure ordered in thickness formed on the dielectric surface by a combined thermal vacuum deposition technology with further electronic surface modification. Further optimization of the regimes of this technology made it possible to significantly improve the formation process and improve the degree of ordering of such structures [10]. However, the use of a combined technology for the formation of thin coatings on dielectrics is not possible without studying the mechanical properties of such coatings, namely, their microhardness. Therefore, studying the microhardness of thin ceramic coatings on dielectric materials is a topical issue.

The aim of the work is to justify the increase of microhardness of single and multi-layer thin ceramic coatings on dielectric materials after their combined electron-beam technology.

Studies conducted in [11] have shown the possibility of forming thin (up to 100 nm) functional coatings on the dielectric surface (piezoelectric ceramics PZT-5) using a combined technology of thermal deposition in vacuum. This paper is devoted to the study of the mechanism for increasing the microhardness of such coatings after their surface modification by a ribbon-shaped electron beam.

2. THE PROCEDURE OF THE EXPERIMENT

A combined thermovacuum application of thin ceramic coatings $TiO_2 + Al_2O_3$, Al_2O_3, ZrO_2 (the thickness of each layer was 40-100 nm) to the silicon surface was carried out by the team of the educational and scientific center "Micronanotechnologies and Equipment" (ESC MNTE) created on the basis of the Department of Physics of the Cherkasy State Technological University.

 © 2019 Sumy State University

The starting material for obtaining thin coatings on the samples was a powder of TiO_2 (rutile modification, dispersity 1.8-2.3 μm), Al_2O_3 (corundum modification, dispersity 1.9-2.8 μm) and ZrO_2 (dispersity 0.6-0.8 μm) calibrated according to particle size. Powder manufacturer – «Powder nanotechnology» (Cherkasy).

Previously, the powder was weighed on electronic scales VLA-200 g-m. Each of the powders with the selected material was loaded into two baths, which were placed in a special tungsten evaporator, the temperature of which was maintained at the level of 2300-2800 K. The coatings were applied to plane-parallel plates of circular shape (diameter 20 mm and thickness 0.2; 0.4; 0.6 mm) made of silicon. The silicon plate, preheated to a temperature of 840 K, was placed in a vacuum chamber above the evaporator unit by means of a rotary movement mechanism, where oxide coatings were carried out for 5-8 s under the following conditions: heating current of the evaporator $I = 185\text{-}305$ A; evaporator voltage $U = 20\text{-}26$ V; distance from evaporator to substrate surface $h = 120$ mm; application time of coating 3-8 s.

Further modification of the obtained coatings by a low-energy electron stream was carried out under the following regimes [12]:

– TiO_2 coating (coating thickness 40-60 nm): specific power of the electron stream $6.9 \cdot 10^3$ W/m^2; beam current 50 mA; exposure time $1.6 \cdot 10^{-6}$ s;
– Al_2O_3 coating (coating thickness 70-100 nm): specific power of the electron stream $11.3 \cdot 10^3$ W/m^2; beam current 75 mA; exposure time $7 \cdot 10^{-6}$ s;
– ZrO_2 coating (coating thickness 50-80 nm): specific power of the electron stream $3.5 \cdot 10^3$ W/m^2; beam current 36 mA; exposure time $1.2 \cdot 10^{-6}$ s.

This allowed to significantly reduce the average values of microroughness of coating surfaces (for example, for TiO_2, the average height of micro-irregularities is 25.8 nm, for Al_2O_3 – 30.1 nm, for ZrO_2 – 23.7 nm), to stabilize the uniformity of these coatings in thickness and to ensure a sufficiently high resistance of these coatings to the influence of the external environment.

The thickness of the coatings was measured by two methods. In the deposition process, the quartz resonator method was used. This makes it possible to select the desired speed of deposition (~ 5-12 nm/s). Further, the obtained coating was measured by Linnik optical interferometry on the MII-4 device.

Microhardness studies were performed by micro-identification using the Vickers method on a DuroScan-10/20 device (Centre of collective usage «Melitek-Ukraine», Kiev) and also on atomic force microscope NT-206 («Laboratory of nanometric research» ESC MNTE, Cherkasy). Measurements of surface microrelief and microhardness of thin ceramic coatings on dielectric samples by atomic force microscopy (AFM) were performed in a static mode on the surface areas with a maximum size of 13 × 13 μm, according to the developed methods and recommendations [13].

3. DISCUSSION OF EXPERIMENTAL RESULTS

As a result of the studies carried out using AFM methods, the following values of microroughness of thin TiO_2, Al_2O_3, ZrO_2 coatings on the silicon (Si) surface were established after their modification by a low-energy electron stream (Fig. 1-Fig. 3).

Fig. 1 shows an AFM image of the penetration zone of a probe-nanoindenter on the surface of the TiO_2 coating applied on Si (1a), and also the approach curve – retreat of the probe to the surface (1b).

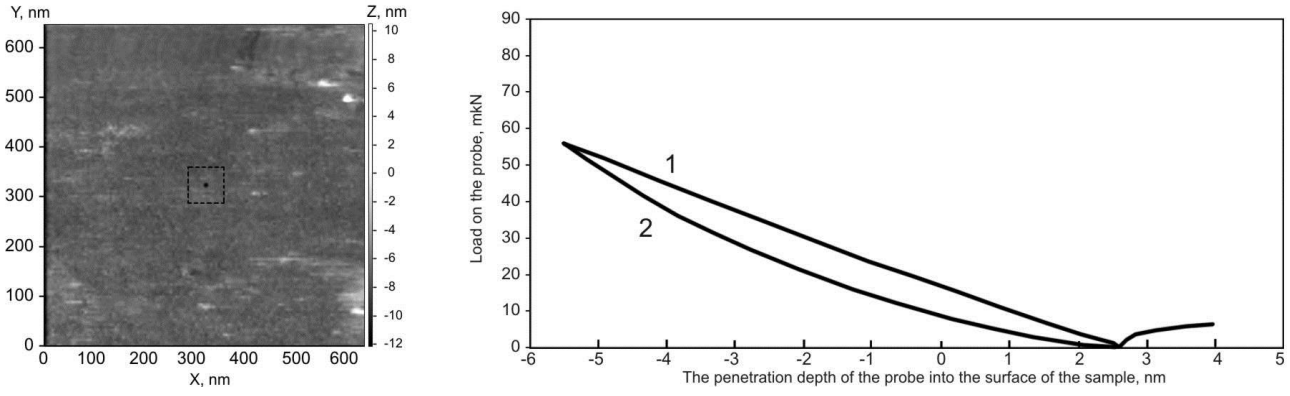


Fig. 1 – Appearance of the surface of the TiO_2 coating applied on Si (platform 13 × 13 μm) with the nanoindenter imprint obtained by the AFM method (a), the approach (1) and retraction (2) curves of the probe to the surface under study (b)

The load on the probe was $0.5 \cdot 10^{-4}$ N, the probe penetrated into the sample to a depth of about 5.5 nm, and the contact area was $45 \cdot 10^{-16}$ m^2.

Calculations of microhardness using data obtained with the help of AFM are carried out according to the following algorithm.

1. The atomic force microscope is switched on and the detection module is set up.
2. A sample is scanned to select the location of the nano-indentation. After that, the point of penetration of the probe into the surface is chosen, which must be homogeneous, without insertions and sharp changes in the relief.
3. We assign an increasing load of not more than 47 mN (the critical load at which the probe collapses) and a gradual load time of 5-7 s. The choice of such a large value of the penetration time is due to a qualitative transition from elastic to plastic deformation.
4. The depth of penetration of the probe into the sample is determined from the approach and retraction curves

of the probe to the surface under investigation (see Fig. 1b, Fig. 3b).

5. By the retraction curve of the indenter of Si conical probe it is possible to determine the projection area of the print under the maximum load by the following formulas:

– when the probe is inserted into the surface at a depth $h \le 10$ nm: $A_c = \pi \cdot r \cdot h_c$;

– when the probe is inserted into the surface at a depth $h > 10$ nm:

$$A_c = \frac{\pi \cdot (r_1 + r) \cdot (h_c - r)}{\cos\varphi} + \pi \cdot r^2,$$

where r is the radius of the probe tip; h_c is the depth of print at maximum load; r_1 is the radius of the probe base; $r_1 = h_c \cdot tg\varphi$; φ is the angle of inclination of the vertex of the conical probe (for probes CSC38: $\varphi = 25°$). Making the substitution of r_1 in the previous formula, we get:

$$A_c = \frac{\pi \cdot (h_c \cdot tg\,\varphi + r) \cdot (h_c - r)}{\cos\varphi} + \pi \cdot r^2$$

or, after simplification ($\cos\varphi = 0.906$; $tg\,\varphi = 0.466$),

$$A_c \approx 1{,}1 \cdot \pi \cdot (0{,}466 \cdot h_c + r) \cdot (h_c - r) + \pi \cdot r^2.$$

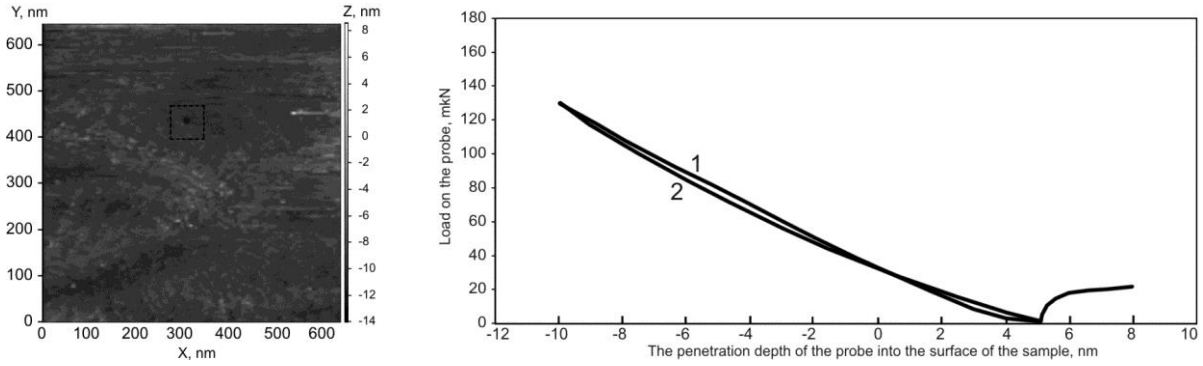
Calculation of the microhardness of the coating under investigation is carried out by the formula:

$$H = F_{max}/A_c,$$

where F_{max} is the maximum load on the probe at indentation; A_c is the projection area of the contact between the probe and the surface of the test material; k is the coefficient taking into account the form of the indenter.

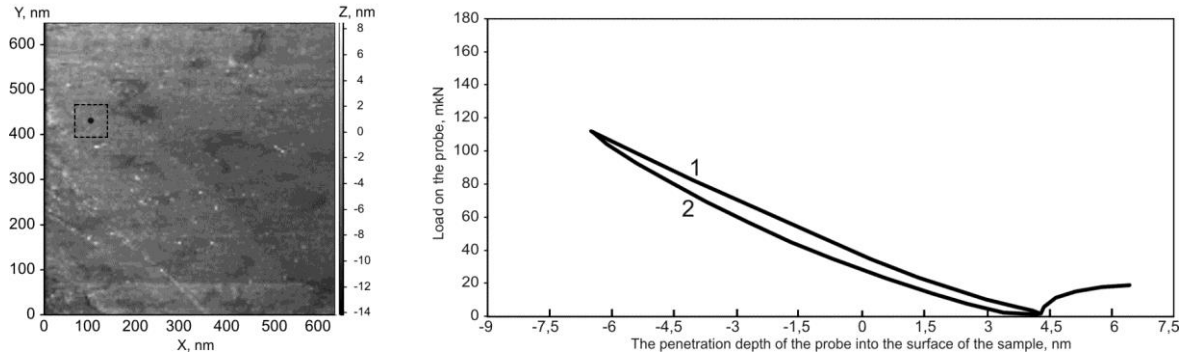
To qualitatively determine the microhardness of the test material, one should adhere to the following conditions: smooth insertion of the probe into the sample with a duration of 2-8 s; smooth removal of the main force 1-5 s after applying maximum force; the distance between the centers of two adjacent indentation prints must be at least 4 diameters of the indenter; the distance from the center to the edge of the sample must be at least 2.5 diameters of the indenter; after the indenter replacement, the first three measurements are carried out without taking into account their results. After calculating the above algorithm, we have found that the microhardness of the test sample is 4.2 GPa.

Fig. 2 shows an AFM image of the penetration zone of a probe-nanoindenter on the surface of an Al_2O_3 coating deposited on Si (Fig. 2a), and also the approach-retraction curve of the probe to the surface (Fig. 2b). The load on the probe was $1.3 \cdot 10^{-4}$ N, the probe penetrated into the sample to a depth of 10 nm, and the contact area was $82 \cdot 10^{-16}$ m^2.



a b

Fig. 2 – Appearance of the surface of the Al_2O_3 coating deposited on Si (13 × 13 μm area) with the nanoindenter imprint obtained by the AFM method (a), the approach (1) and retraction (2) curves of the probe to the surface researching (b)



a b

Fig. 3 – Appearance of the surface of the ZrO_2 coating deposited on Si (13 × 13 μm area) with the nanoindenter imprint obtained by the AFM method (a), the approach (1) and retraction (2) curves of the probe to the surface researching (b)

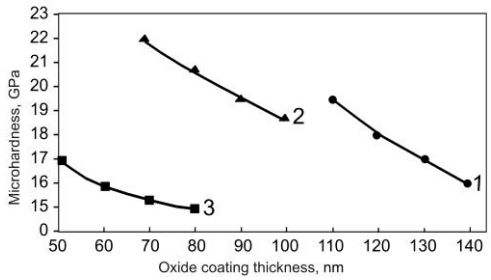


Fig. 4 – Dependence of microhardness of coatings $TiO_2 + Al_2O_3$ (1), Al_2O_3 (2), ZrO_2 (3) on Si after electron-beam modification from their thickness

According to calculations, the microhardness of the test sample is 21.9 GPa. Fig. 2 shows an AFM image of the penetration zone of a probe-nanoindenter on the surface of a ZrO_2 coating deposited on Si (Fig. 2a), and also the approach-retraction curve of the probe to the surface (Fig. 2b).

The load on the probe was $1.1 \cdot 10^{-4}$ N, the probe penetrated into the sample to a depth of 7 nm, and the contact area was $58 \cdot 10^{-16}$ m^2. Wherein, the micro-hardness of the test sample, according to calculations, was 17 GPa.

Thus, the studies of the microhardness of thin ceramic coatings on Si modified by an electron stream showed a significant increase in comparison with coatings obtained under the same regimes, but without electron-beam modification (from the value of 16.4 GPa to 19.2 GPa for $TiO_2 + Al_2O_3$ coating; from the value of 18.9 GPa to 21.9 GPa for Al_2O_3 coating; from the value of 15 GPa to 17 GPa for ZrO_2 coating).

In the authors' opinion [14], this increase in microhardness is associated with the compaction of the coating material under thermal and mechanical action of the electron beam on it, a decrease in the porosity of this material, and diffusion of the lower layers of the coating into the Si surface.

This hypothesis is also confirmed by a decrease in the microhardness of the applied coating with an increase in its thickness. In studies carried out by us, there is a clear relationship between microhardness of ceramic coating ($TiO_2 + Al_2O_3$, Al_2O_3, ZrO_2) on Si after electron beam modification of their thickness, Fig. 4.

As can be seen from these dependences (Fig. 4), the microhardness of the coatings in question increases nonlinearly by 18-24 % (for TiO_2 coating), 7-8% (for Al_2O_3 coating), 8-10 % (for ZrO_2 coating) as the thickness of coatings decreases.

At the same time, by micro-identification using the Vickers method on the DuroScan-10/20 device, the control values of the microhardness of such coatings were established at the Centre of collective usage «Melitek-Ukraine» (Kyiv): $TiO_2 + Al_2O_3$ (17.92 ± 0.28 GPa), Al_2O_3 (20.4 ± 1.5 GPa), ZrO_2 (16 ± 0.65 GPa) and Si (4.56 ± ± 0.18 GPa), which correlate with the data obtained earlier using the AFM method.

It should be noted that when measuring the microhardness of ceramic coatings by microindentation on DuraScan-10/20, the thickness of these coatings was about 6500-7300 nm.

4. CONCLUSIONS

It has been established that modification by low-energy electron beam ($E \leq 6$ keV) of Si surfaces with thin ceramic coatings deposited on them allows to increase the microhardness of such coatings: for $TiO_2 + Al_2O_3$ coating by 1.17 times; for Al_2O_3 coating – by 1.16 times; for ZrO_2 coating – by 1.13 times. These data are comparable to the microhardness values obtained by microidentity on a DuraScan-10/20 device (17.92; 20.4; 16.0 GPa respectively).

The dependence of the microhardness of the coatings ($TiO_2 + Al_2O_3$, Al_2O_3, ZrO_2) on Si on their thickness after the electron beam modification is constructed, according to which the microhardness of the coatings in question increases nonlinearly by 13-17 % as the coating thickness decreases.

It is also shown that it is possible to study the microhardness of multifunctional ceramic coatings formed on Si under various conditions and different regimes.

REFERENCES

1. M. Bondarenko, I. Bondarenko, *6th International Symposium – Energy Challenges & Mechanics*, 245 (14-18 August 2016: Inverness: Scotland: UK: 2016).
2. M.A. Bondarenko, S.A. Bilokon, V.S. Antonyuk, Iu.Iu. Bondarenko, *J. Nano- Electron. Phys.* **6** No 2, 02018 (2014).
3. V.S. Antonyuk, M.O. Bondarenko, Yu.Yu. Bondarenko, *J. Superhard Mater.* **34** No 4, 248 (2012).
4. V.S. Antonyuk, S.O. Bilokin, M.O. Bondarenko, Yu.Yu. Bondarenko, *J. Superhard Mater.* **37** No 2, 112 (2015).
5. H. Qin, P. Sutter, G. Zhou, *J. Am. Ceram. Soc.* **97** No 9, 2762 (2014).
6. V.S. Antonyuk, *J. Superhard Mater.* **20** No 4, 72 (1998).
7. C. Polzin, D. Günther, H. Seitz, *J. Ceram. Sci. Technol.* **6** No 2, 141 (2015).
8. B. Kupfer, *Adv. Energ. Mater.* **5** No 1, 1401007 (2015).
9. M. Bondarenko, I. Bondarenko, V. Antonyuk, *Materials Science. Non-Equilibrium Phase Transformations* **3** No 2, 53 (2017).
10. I. Yatsenko, V. Antonyuk, M. Bondarenko, V. Vashchenko, *Intern. Sci.-Tech. Conf. – Innovations in Ingeneering*, 64 (9-12 September 2015: Burgas: Bulgaria: 2015).
11. E. Skoryna, V. Medyanyk, M. Bondarenko, I. Bondarenko, *XV Intern. Sci. Congress – "Machines. Technologies. Materials 2018"*, 90 (14-17 March 2018: Borovets: Bulgaria: 2018).
12. I.I. Bondarenko, V.V. Medianyk, M.A. Bondarenko, V.S. Titarenko, *Science Conf. – Physics, Electronics, Electrical Engineering, 2018*, 86 (05-09 February 2018: Sumy: SumSU: 2018).
13. M. Bondarenko, Iu. Bondarenko, S. Bilokin, *IX Int. Sci. Conf. – Electron. Appl. Phys.*, 54 (23-26 October 2013: Kyiv: NTUU "KPI": 2013).

Дослідження мікротвердості тонких керамічних покриттів, сформованих комбінованим електронно-променевим методом на діелектричних матеріалах

В.С. Антонюк[1], Ю.Ю. Бондаренко[2], С.О. Билокінь[2], В.О. Андриенко[2], М.О. Бондаренко[2]

[1] *Національний технічний університет України «Київський політехнічний інститут імені Ігоря Сікорського», просп. Поремоги, 37, 03056 Київ, Україна*
[2] *Черкаський державний технологічний університет, бульвар Шевченка, 460, 18030 Черкаси, Україна*

Встановлені особливості отримання на поверхнях діелектриків (на прикладі кремнію Кр1) тонких керамічних покриттів ($TiO_2 + Al_2O_3$, Al_2O_3, ZrO_2) при їх формуванні термічним випаровуванням у вакуумі. Досліджено механізм підвищення мікротвердості таких покриттів шляхом їх поверхневого модифікування електронним потоком стрічкової форми. Показано, що комбіноване термовакуумне нанесення тонких керамічних покриттів із порошкових матеріалів на поверхню кремнію Кр1 з наступним їх модифікуванням електронним потоком низької енергії в одному технологічному циклі, дозволяє суттєво зменшити мікрорельєф та стабілізувати однорідність поверхонь покриттів, а також підвищити хімічну і біологічну стійкість цих покриттів до впливу оточуючого середовища. Визначено умови якісного знаходження мікротвердості досліджуваного матеріалу із залученням методу атомно-силової мікроскопії. Проведені дослідження мікротвердості як модифікованих покриттів, так і поверхонь діелектриків, на які проводилося їх нанесення. Встановлено факт нелінійного збільшення мікротвердості (на 13-17 %) тонких покриттів, нанесених на поверхню діелектричного матеріалу комбінованим електронно-променевим методом по мірі зменшення товщини цих покриттів. Показана можливість визначення мікротвердості багатошарових мультифункціональних керамічних покриттів, отриманих комбінованою електронно-променевою технологією, за різних умов та різних режимів проведення технологічного експерименту.

Ключові слова: Керамічні покриття, Діелектрик, Кремній, Мікротвердість, Електронно-променеве модифікування, Атомно-силова мікроскопія.