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Physical Chemistry

Competitive Methods of Nano and Micro Coatings and Clusters Deposition for Electronics and Conversion of Solar Energy

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ABSTRACT. New data are presented on the competitive nanotechnologies for fabrication of fine-grained powder-like particles, films, bulk materials, nanocomposites, devices for microelectronics, nanoelectronics, photonics and photocatalysis. The proposed nanotechnologies for electronics are much more advantageous and simpler than other expensive and complicated methods such as e-beam lithography, X-ray lithography or production of devices using light phase shift photomasks. The mechanism of sensitization and activation was established. The proposed methods of metallization are widely used in electronics and instrument-making. As a result, Au, Ag and Pd were adequately replaced with alloys of non-precious metals, the use of toxic substances was eliminated and the technology was significantly simplified. The first results are presented on the application of a new improved resolution NMR method using an additional dc pulse magnetic field to study cobalt-based materials synthesized by the proposed methods. *© 2008 Bull. Georg. Natl. Acad. Sci.*

Key words: *nanotechnology, nanoelectronics, piezoengineering, photocatalysis.*

1. Results and Discussion

1.1. The Mechanism of Reactions of Electroless Nickel Deposition

It is shown that electroless deposition of Ni-P and Ni-B alloys can be successfully used in piezoengineering, microelectronics, and so on [1-20]. For development of the optimum technology, we improved the entire cycle of the metallization process: preliminary treatment of various substrates (sensitization and activation), composition of solutions and the parameters of electroless deposition, parameters of heat treatment after deposition, conditions of photolithography, selective etching processes, etc. [1-4, 18-20].

At adding HCl (1 milliliter of concentrated acid per gram of $PdCl_2.2H_2O$), chloropalladic acid is formed according to the reaction:

$$2\ HCl + PdCl_2 = H_2PdCl_4, \qquad (1)$$

which affects favorably the activation process.

It was established that a part of the palladium ions, not reduced by sensitization-activation:

$$Sn\ (II) + Pd\ (II) = Sn\ (IV) + Pd, \qquad (2)$$

can be partially reduced at subsequent interaction with hypophosphite in the solution of electroless deposition according to the reaction:

$$PdCl_4^{2-} + H_2PO_2^- + H_2O = Pd + H_2PO_3^- + 2H^+ + 4Cl^-. \qquad (3)$$

The results of investigation showed for the first time that, when the aqueous-alcoholic solution was used as a solvent for tin chloride at sensitization, the amount of adsorbed palladium ions increased at subsequent activation in comparison with application of the aqueous solvent for tin chloride. Reference can be made to the fact that the addition of an organic compound to water changed the solvent configuration and the solvation degree of the dissolved substances. Under these conditions, dissolvation of Sn ions is simplified, because the ion-solvent (dipole) interaction is stronger in a water solvent than in a water-spirit solvent. Besides, it is more difficult for ethyl alcohol molecules than for water molecules to displace the tin ions at the interface. The small size of water molecules makes their presence at the interface energetically favorable. A new mechanism of sensitization and activation in the mixed solvent, the effect of the solvent and the feasibility of obtaining nanometer-scale pore-free films can be explained by interpretation with consideration of the reduction in the ionic strength in the mixed solvent and the increase in the ionic-activity coefficient.

As is known, the composition of the solution and the origin of the solvent affect the ionic strength (I) of electrolyte and, the ionic-activity coefficient. Taking into consideration this circumstance, the increase in the adsorption of palladium ions and the deposition of a denser film of palladium clusters by using a water–spirit solvent for sensitization could be explained on the basis of the Debye-Huckel theory.

The relation between the ionic-activity coefficient (γ_i) and the ionic strength (I) is expressed by the Debye-Huckel equation:

$$\lg\gamma_i = -A_{Zi}^{\ 2} \cdot I^{1/2}. \qquad (4)$$

The use of a water-spirit solvent for the solution of the sensitization reduces the total number of ion charges Zi^2 in the solution and the ionic strength as compared to the water solvent. The decrease in the total number of electric charges in the solution is likely to promote the decrease in the force of attraction between the ions and solvent, a decrease in the interaction between the ion and the dipole and an increase in the ionic-activity coefficient.

It was established that adding of NaCl to palladium chloride solution is favorable for the activation process [1]. To investigate the influence of chlorine ions concentration on the sign of the charge of complex palladium ions, experiments were performed on the transfer of ions in the electric field. $PdCl_2 \cdot 2H_2O$ was dissolved in water with the minimum amount of HCl. The obtained solution was poured into the electrolyzer divided into several compartments by porous glass diaphragms. In other series of experiments, electrolysis was carried out in a 1 g/l solution of Pd(II) with some amount of NaCl added. In both cases, after electrolysis, the portions of the solution taken from the cathodic, anodic and middle compartments of the electrolyzer were subjected to polarographic analysis for palladium content. The results of the investigation showed that palladium is present in the form of complex anion in the solution with a minimum amount of hydrochloric acid with or without NaCl. But in the solution containing sodium chloride, Pd (II) is completely transformed into complex anions. As a result of the electrolysis, the concentration of palladium ions in the cathodic compartment was found to be much lower than that in the anodic compartment of the electrolyzer.

The effect of addition of sodium chloride to the palladium chloride solution on the enhancement of adsorption of palladium ions and the increase in the activation effectiveness can be explained as follows. At adding NaCl to the $PdCl_2$ solution, small palladium cations (Pd^{2+}) transform into the large palladium complex anion $PdCl_4^{--}$. In this case, the energy of interaction between the palladium anions and the solvent molecules, and the number of solvation molecules decrease. The reduction in the attraction forces between the palladium ion and the surrounding solvent molecules promotes an increase in the ion activity coefficient. As a result, the palladium ions easily get rid of their solvation shield. Under these conditions, the adsorption of palladium ions and the efficiency of activation increase. The application of the abovementioned methods allowed to establish the mechanisms of sensitization and activation.

1.2. The Effect of Organic Additives Adsorption on the Process of Electroless Nickel Deposition

Below are given the results of investigation on sorption properties of organic acids in the process of electroless nickel deposition. The mechanism of action of the organic additives was studied on the basis of sorption of malonic and succinic acids added to the solution. A method of isotopic tracers was used. Fig.1 shows the relation between the adsorption value and the concentration of malonic and malic acids in the solution. When the concentration of the abovementioned organic acids increased, their sorption with the Ni-P coating increased continuously. The results of the investigation suggest the assumption that, when the concentration of the organic acid increases above a certain limit, the rate of the process decreases because of blocking of the nickel-deposited surface [1].

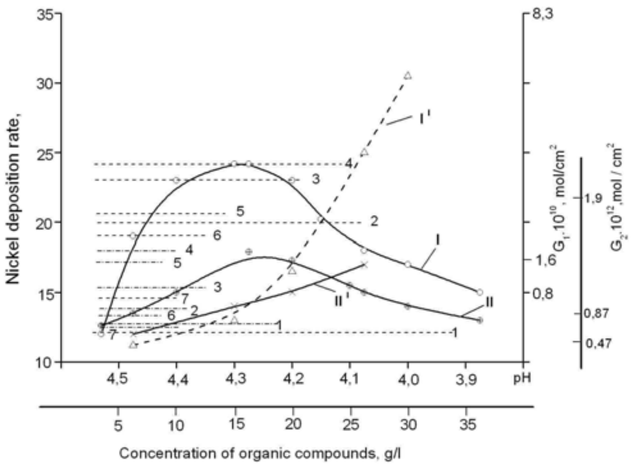

Fig.1.The effect of the concentration of malonic (I, I^1) and succinic acids (II, II^1) on the nickel deposition rate (I, II), the stability of pH (1-7) and the adsorption (G) of organic additives (I^1, II^1). Concentration of basic components, g/l: $NiSO_4 \cdot 7H_2O$ -25 (0.088M); $NaH_2PO_2 \cdot H_2O$ -16 (0.15M). Concentration of acids: from 5 to 35 g/l.

1.3. Replacement of Au and Ag with the Ni-P Alloy in Electronics

A new method of production of precise piezoelectric quartz resonators and filters, and monolithic piezoquartz filters with electrodes made of electroless nickel-phosphorous alloys for spacecraft, hydroacoustics and communication devices was developed [1-3,17-20]. The optimal conditions of metallization were established and the technological process of electroless nickel plating of piezoelectrical quartz elements with a smooth surface, including a polished surface, was developed [1,17-20]. The study of the influence of a nickel-phosphorous layer on the quartz resonator quality showed that the best device parameters are reached at the 0.2-0.4μm thickness of the metallic film. Electrical characteristics of quartz resonators with the deposited Ni-P coating turned out to be better than when gold and silver were used as electrode layers. It is due to the fact that, for assembling the quartz oscillator at Ni-P plating, preliminary fusing of the silver sublayer (made from paste), causing undesirable changes in piezoquartz physical properties, is not necessary. The technology of metallization of piezoelectrical quartz elements was entirely simplified. The improvement in the frequency characteristics of piezoquartz resonators and filters is, in particular, due to the fact that the specific weight of the Ni-P alloy (7.8) is less than that of Ag (10.5) and Au (19.3). Therefore, the Ni-P electrode film does not deteriorate the oscillation properties of the piezoelement. The method of electroless plating on polished quartz, glass and other materials was developed. This technology for the first time provided high adhesion and ductility, formation of pore-free films with given thickness, deposition of thick films being the most important for obtaining monolithic quartz filters, in which the effect of energy capturing is necessary. Bulk and miniature resonators and filters of piezoquartz and lithium niobate, manufactured on the basis of the developed technology of electroless deposition of nickel-phosphorus alloy instead of gold and silver plating, can be successfully used in communication equipment, microprocessing devices, TV and video devices, quartz balances, ultrahigh frequency (UHF) equipment, UHF transducers of surface acoustic waves watch industry, furnaces for baking rolls and buns etc [1-3,17-20]. Basic advantages and innovations of the developed technologies in the field of electroless nickel deposition on piezoquartz, lithium niobate and glass, as compared to silver and gold plating, are the following: 1. Frequency stability of piezoquartz devices increases 1.8 times. 2. The absolute value of dynamic resistance of piezoquartz resonators decreases by 30 %, and the resistance scattering decreases by 40-50 %, as compared to the resonators with silver-plated piezoelements. 3. The quality and long-term stability of piezoquartz devices improve.

A technology was developed for the production of piezoceramic devices by electroless deposition of electrode layers made of Ni-P or Cu for hydroacoustic equipment of submarines and ships, delay lines of color TV sets, capacitors, etc. As a result of using the developed technology, the time for production of the devices was reduced by a factor of 60 as compared to high-temperature fusing of silver-containing paste, and Ag was adequately substituted with non-precious metals [1,19,20].

The developed electroless methods allow producing films with specified electrical, mechanical, magnetic, optical and chemical properties. The proposed methods of metallization of various materials are widely used at the enterprises of the Commonwealth of Independent States (CIS) for production of quartz resonators and filters (several tens of millions piezoquartz devices were produced), monolithic piezoquartz filters, photomasks, piezoceramic devices for hydroacoustics and delay lines of color TV sets (several hundreds of millions piezoceramic devices were produced), casings of integrated circuits and semiconductor devices, ceramic microplates, precise microwire and film resistors and other devices. The application of the proposed technologies has given a large economic effect. As a result of the use of this method: the technology was significantly simplified; the labour intensity of the process decreased sharply; the production volume per square meter of production increased 8 times as compared to metallization by fusing the silver paste; the reliability, the quality and the operational characteristics of photomasks produced by deposition of the semitransparent masking elements improved significantly; the accuracy of fitting the precise microwire resistors increased 10 times. Many companies produce devices on the basis of ceramics and piezomaterials with gold and silver plating. To produce the same devices by the developed technologies, precious metals have already been adequately replaced with non-precious ones.

A possibility of electroless deposition of metals on nonmetallic, high-dispersive dielectric and semiconductor particles without their preliminarily activation, demonstrated in our works, could be explained theoretically in the following way. In the boundary layer, at the solid-water interface, the following factors manifest themselves: 1.The dielectric constant of water in the thin boundary water layer adjacent to the solid surface is lower by an order of magnitude than in the bulk water. 2. The configuration of solvent changes. 3. The ion-dipole interaction changes, due to which the ions attract water dipoles. 4. The activity coefficient of the ions dissolved in the solution increases. 5. On the surface of fine-grained particles, the wettability increases and the attraction and the ion adsorption are stimulated under the influence of the surface molecular field and the non-saturated surface forces. 7. The degree of hydration decreases with the decrease of the size of particles. 8. The abovementioned factors could lead to a reduction in the energy, which is necessary for adsorption and introduction of metallic ions into the surface monolayer of oriented molecules of the solvent at the solid surface-solution interface. 9. There exists the quantum size effect of high-dispersive semiconductor particles and nanosized clusters on the reaction. 10.Under the effect of the large surface area of high-dispersive particles, the presence of a large number of unsaturated surface forces and defects on the surface, the adsorption and the breaking of bonds among the reductant atoms happen more readily, which is essential for the course of heterogenic catalysis reaction of electroless metal deposition.

1.4. Industrial Application of Electroless Ni for Fabrication of Two-Layer Photomasks with Semitransparent Edges of Masking Elements

The nickel-plated photomasks fabricated by the proposed method are used in industry [1-3,18-20]. Studies of the optical characteristics of the Ni-P film (with the thickness of 100-150nm) deposited on glass by electroless method have been carried out in relation to the wavelength of exposing UV radiation, λ=200-750 nm [1].

A possibility of fabrication of faultless wear-resistant semitransparent photomasks due to semitransparency in the visible region and opacity in the UV region of the spectrum of their elements was determined. The abovementioned goal was achieved by using a double-layer coating from silicon and nickel. Silicon films were deposited by heat sputtering. Sensitization of the samples was performed. The silicon layer was activated with palladium chloride. Then electroless nickel was deposited. The samples were annealed at 300-450ºC. As a result, a two-layer film was obtained, the lower semitransparent layer (transparent in the visible light and non-transparent for UV exposing radiation of spectrum, which simplifies and enhances the alignment precision) of which is inert in respect to the etchant etching the layout of the circuit in the upper nickel layer. After the process of photolithography, the upper nickel layer was etched. The final stage consisted in the selective etching of the lower silicon film. This etchant slightly etches the edges of the upper nickel layer along the circuit layout. Around the elements located in the upper layer, a semitransparent edging in the base silicon layer was formed, which improved the precision of matching of metallized photomasks. As a result of overlapping of nickel and silicon layers healing the defects, defectless photomasks were obtained [3]. In Fig. 2, the two-layer photomask is shown.

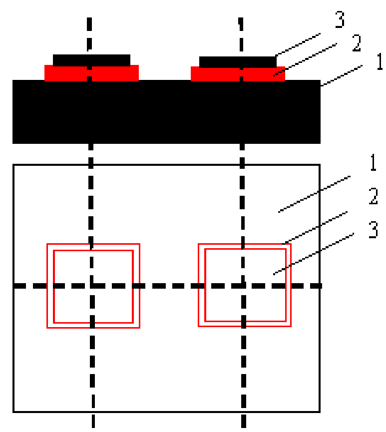

Fig. 2. Two-layer photomask metallized by the electroless method: 1 – glass substrate; 2 – semitransparent Si layer; 3 - opaque masking layer of Ni-P alloy.

1.5. Development of Competitive Photocatalysts

A new method of size selection of pure TiO_2 particles and micro-, meso- and nanocrystal-coated powder-like semiconductor photocatalysts with the aim of obtaining a uniform, relatively narrow size distribution was developed. On the basis of spectrophotometric investigation and selection of semiconductor particles with uniform size, we established that local electroless deposition of metallic nanocrystals could extend the capabilities of production of competitive fine-grained semiconductor photocatalysts. The results of the work will be promising for overcoming or mitigation of some challenging problems of conversion of light energy into electrical power, photocatalytic splitting of water, nanotechnology, and materials research (high fabrication costs, difficulty in deposition of nano-sized clusters on nano-sized and fine-grained particles, the necessity of using expensive equipment, etc.). Methods of fabrication of metallic nanostructures (using electroless deposition) with specified properties on bulk, film and semiconductor powder-like materials have been developed. We have obtained photocatalysts having the peak of the absorption spectra 3 times higher than that of ordinary TiO_2 photocatalysts (St-01 and P-25). The results of the work can be used for overcoming or mitigation of the following problems of solar energy applications: I. Recombination of photo-excited electrons and holes. II. Simultaneous proceeding of oxidation and reduction reactions at the same sites of photoelectrodes. III. The possibility of using low-energetic visible light irradiation. IV. Low quantum efficiency of energy conversion. V. Difficulty in deposition of nano-sized clusters on nano- and meso-sized particles, etc.

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1.6. A New Device for Determination of Ductility by Bending

We have designed a new device for precise determination of ductility [1,18, 20]. The ductility of electrolessly deposited Ni-P coatings was studied by bending, using a new device. The operation principle of the device is based on detection of cracks appearing due to the bending effect. The developed ductility tester allows 1) to observe the appearance of cracks and their development during bending, from start to finish, with the help of the microscope; 2) to observe the shape of cracks, their density and geometry, to measure the crack length and width, and to detect the moment of formation of a continuous crack grid; 3) to observe in-situ the initiation, growth and propagation rate of cracks at different rates of specimen deformation; 4) The suggested tester enables us to determine in-situ the ductility at different temperatures, i.e. in-situ investigation of temperature dependence of ductility. The abovementioned peculiarities of the suggested device can help overcome several cracking problems, some problems of micromechanics as well as flip chip technology. The maximum ductility and microhardness of the Ni-P coating were achieved after annealing at 600^0C and 400^0C, respectively [1,18,20].

1.7. Enhanced Resolution Nuclear Spin Echo Method for Studying Cobalt Nanopowders and Half Metals for Spintronics Applications

NMR is a unique microscopic tool for studying different local properties of magnetic nanostructures. It provides magnetism information by hyperfine fields, domain walls parameters and dynamics measurements. In this section we present the results of comparative NMR study of cobalt-copper granular powders and films, and polycrystalline CoB-Cu-CoB alloys. On quartz plates, three-layer coatings of CoB-Cu-CoB were deposited by the electroless method in a sequence. The thickness of the coating was ~ 2.24 mm. The measurements were carried out by the improved resolution nuclear spin echo method using an additional exciting dc magnetic field pulse, and the data were compared with the ones for some other magnets (half metals, ferrites, etc.). We used frequency spectra and timing diagrams for recording the magnetic pulse influence in the case of its symmetric and asymmetric application in respect to the second RF pulse. This method provides direct and visual information on the anisotropic component of hyperfine field and the domain walls parameters, which is not readily obtainable from the usual NMR spectra, thereby improving the resolution of the nuclear spin echo method in magnets.

We restrict ourselves to frequency spectra diagrams for the investigated samples. The results obtained show the NMR spectra for Co and Co-Cu alloys and, simultaneously, the frequency spectra diagrams for dc magnetic pulse influence at its symmetric and asymmetric application in respect to the second RF pulse.

In Fig.3 and Fig.4, similar data are presented for the Co-Cu granular powder and the Co film. It should be noted that the dc magnetic pulse amplitude for the first two types of samples was the same (H_d=250 Oe). For the Co film sample it was equal to H_d=10 Oe.

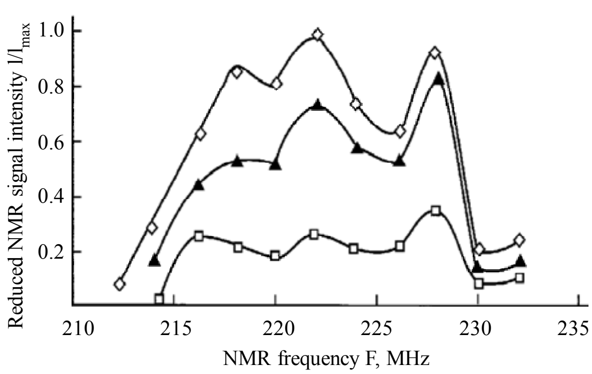

Fig. 3. NMR spectrum of CoB-Cu-CoB granular powder (o) and frequency spectra diagrams for dc magnetic pulse influence in the case of symmetric (▲) and asymmetric (□) dc magnetic pulse application (H_d=350 Oe).

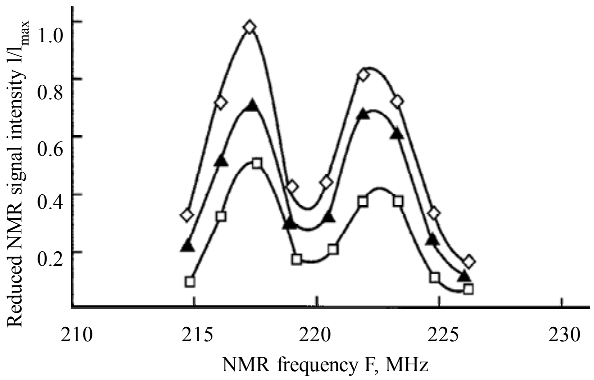

Fig. 4. NMR spectrum of Co film (o) and frequency spectra diagrams of dc magnetic pulse influence (H_d=100 Oe) for symmetric (▲) and asymmetric (□) dc magnetic pulse application.

Similar diagrams for cobalt nanopowders reflect finely their fabrication conditions. These effects are not observed in the X-ray spectra and the electron microscopy data of cobalt nanopowders, which makes such diagrams an interesting tool for fine control of the characteristics of nanopowders.

2. Conclusions

1. The present work contains new data on the proposed nanotechnologies for fabrication of fine-grained powder-like particles, films, bulk materials, nanocomposites, devices for microelectronics, nanoelectronics, photocatalysis and photonics.

2. The nanotechnologies using electroless deposition are much more advantageous and simpler than other expensive methods of nanotechnology and allow the fabrication of photocatalysts, catalysts by means of deposition of nanocrystals having specified properties on high-dispersive semiconductors.

3. The developed methods of metallization of various materials have been widely used at the enterprises of the Commonwealth of Independent States for production of quartz resonators and filters, monolithic piezoquartz filters, photomasks, piezoceramic devices for hydroacoustics and delay lines of colour TV sets (several hundreds of millions of devices were produced), casings of integrated circuits and semiconductor devices, ceramic microplates, microwire and film resistors, capacitors, catalysts.

4. As a result of application of the developed technology, Au, Ag and Pd were adequately replaced with non-precious metal alloys; the time for production of piezoquartz and piezoceramic devices was reduced by a factor of 4–60; labor intensity of the technology was reduced significantly; the frequency stability of piezoquartz devices was increased 1.8 times; the absolute value of dynamic resistance of piezoquartz resonators became 30 % lower and the resistance scattering became 40-50 % lower as compared to resonators with silver-plated piezoelements.

5. A method of production and a new design of defectless two-layer (Si-Ni) photomasks with semitransparent edges of Si masking elements (which simplify and enhance the alignment precision) based on single conventional UV photolithography and selective etching of adjacent thin films were developed. These photomasks have a number of advantages over the existing ones. These photomasks have been widely introduced in the microelectronic industry with a large economic effect.

6. The developed ductility tester permits: a) to observe the appearance of cracks and their development, from start to finish; b) to observe the shape of cracks, their density, to measure the crack length and width, and to detect the moment of formation of a continuous crack grid; c) to observe in-situ the cracks initiation, growth and propagation rate at different rates of deformation.

7. Theoretical interpretation is presented of the increase in the amount of palladium ions adsorbed during the activation after preliminary sensitization in aqueous-alcoholic solution and electroless deposition of ultra-thin pore-free continuous coating with high adhesion even to polished nonmetallic materials and obtaining of coatings with given ductility, which has been a problem to date.

8. The feasibility of electroless deposition of metals on nonmetallic, high-dispersive dielectric and semiconductor particles without their preliminary activation is explained theoretically, taking into account various physico-chemical phenomena.

ფიზიკური ქიმია

ნანო და მიკროდანაფარების და კლასტერების დატანის კონკურენტუნარიანი მეთოდები ელექტრონიკისათვის და მზის ენერგიის გარდასაქმნელად

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(წარმოდგენილია აკადემიკოს კ. ჯაფარიძის მიერ)

ნაშრომში განხილულია ნანო და მიკროტექნოლოგიების საშუალებით მაღალდისპერსიული ფხვნილების, ფირების, ფოტოკატალიზატორების და ელექტრონული ხელსაწყოების ახალი მეთოდებით დამზადების საკითხები. შესწავლილია ქიმიური მონიკელების მექანიზმი, რეაქციის კინეტიკა და დატანილი ფირების თვისებები. მოყვანილია ახალი მონაცემები ნანო და მიკროტექნოლოგიების დამუშავების შესახებ. დადგენილია, რომ პიეზოტექნიკაში ოქრო, ვერცხლი და პალადიუმი ადეკვატურად შეიძლება შეიცვალოს ქიმიურად დატანილი ნიკელ-ფოსფორის შენადნობით და რამდენიმეჯერ შემცირდეს ტექნოლოგიური პროცესის ხანგრძლივობა. ნაჩვენებია, რომ დამუშავებული ტექნოლოგიები დიდი ტექნიკურ-ეკონომიკური ეფექტით ფართოდაა დანერგილი მიკროელექტრონიკაში, პიეზოტექნიკაში, ხელსაწყოთმშენებლობაში და სხვა დარგებში.

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