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Deposition of Nanofilms by the Electroless Method

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In the result of application of the developed technology, Au, Ag and Pd were adequately replaced with non-precious metal alloys. The nanotechnologies using the electroless deposition are much more advantageous and simpler than other expensive methods of nanotechnology and allow the fabrication of photocatalysts and catalysts by means of deposition of nanocrystals having the specified properties on high-dispersive powder like semiconductors.

Keywords: Nanofilms, Nanotechnology, Piezoengineering, Ductility tester.

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1. RESULTS AND DISCUSSION

The advantages of electroless deposition of metals are the following: a possibility of obtaining the coating of uniform thickness on arbitrary shaped-surfaces, providing of good mutual attraction of the elements, good solderability, sufficient chemical resistance, high hardness and wear-resistance, a possibility of varying of mechanical properties and electrical conductivity of the films in a wide range [1-29]. Thus, this opens up new avenues for wide application of electrolessly deposited films.

The economic efficiency of electroless metallization of glass is based on the following: the possibility of mechanization and automation of the processes of formation of films and their selective etching, which is due to, particularly, the fact that the metallic film deposited by this method does not contain impregnations of oil and oxides in contrast to the films deposited by vacuum sputtering and the significant reduction in the amount of metal used for deposition. This is due to a higher utilization factor of the method of electroless metallization than of thermal vacuum sputtering. At the latter method, a significant amount of metal deposits on the parts of vacuum chamber and is difficult to remove. This the vacuum metallization rather laborconsuming. In spite of the small amount of materials needed for the formation of thin films, with consideration of high purity of metals used in nanoelectronics and microelectronics (and wide application of rare and precious metals), the high utilization factor of electroless metallization reduces significantly the production cost.

For development of the optimum technology, we improved the entire cycle of the electroless metallization process: the preliminary treatment of various substrates (sensitization and activation), the composition of solutions and the parameters of electroless deposition, the parameters of heat treatment after deposition, the conditions of photolithography and the selective etching processes [1-8].

A new method of production of precise piezoelectric

- quartz resonators and filters, and monolithic piezoquartz filters with electrodes, made of electroless nickel-phosphorous alloy, for spacecraft, hydroacoustics and communication devices was developed [1-8, 18, 20, 22-29]. Electrical characteristics of quartz resonators with the deposited Ni-P coating are better than when gold and silver were used as electrode layers. It is owing to the fact that:
- 1) 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;
- 2) The improvement in the frequency characteristics of piezoquartz resonators is owing 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.
- 3) Adhesion between Ni-P electrode and piezosubstrate is higher than that between Ag or Au and the piezosubstrate. This decreases the electrical resistance between the electrode and the piezosubstrate and consequently the quality of the resonator increases.

The proposed patentable nanomethods [7] for the first time allow one to produce nano-sized adjacent elements of different thickness made of various materials (particularly of Si) by single optical UV photolithography. These advantages significantly extend the functional capabilities of the devices and simplify the removal of undesirable gases and heat dissipation.

The proposed nanomethods are much more advantageous and simpler than other expensive and complicated methods such as e-beam and X-ray lithography or fabrication of nano-sized elements by a light phase shift photomasks [7].

A method of production and a new design of defect-free two-layer (Si-Ni) photomasks with selectively semitransparent (transpatent in the visible region and non-transparent in the UV region of spectrum) edges of the Si masking elements in the lower layer of the pattern

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based on single conventional optical UV photolithography is proposed. (Fig. 1)

It should be noted that the well-known methods of fabrication of metalized photomasks cannot guarantee completely a faultless structure of the pattern because of at least the defects of photolithography. In this connection, there was stated the problem of the possibility of fabrication of practically faultless and, at the same time, wear-resistant photomasks meeting the up-to-date requirements due to selective semitransparence in the visible region and opacity in the UV region of spectrum of the masking elements.

The proposed method eliminates significant draw-backs of chrome photomasks - parasitic intensive chrome film reflection (about 70 % of light), resulting in the multiple exposing radiation reflection, the decrease in the photoresist resolution, and the decrease in the circuit image sharpness. The reflection coefficient of the masking films (about 8 %) used in the present invention is less by several times than that of chromic ones, which increases the photoresist resolution and sharpness of the circuit image. The abovementioned goal was achieved by using the double-layer coating from silicon and nickel [3].

This photomask has a number of advantages over the existing ones: 1) much less porosity; higher optical density; less thickness and higher wear resistance of the masking elements and 2) selective semitransparence of the masking elements, which simplifies and enhances the alignment precision. These photomasks were widely introduced in the microelectronic industry with a large economic effect.

A method of coating of nano-particles of different sizes from different materials (for example, Ni-B) was developed. These nanostructures were fabricated using the method of electroless deposition.

With the aim of elaborating the methods which would give the possibility of changing the optical properties of Ni-B/TiO₂ powders in the desirable direction, the optical absorption spectra of the photocatalyst powder and the effect of heat treatment on the optical absorption spectra of the TiO₂ nano-powders coated with Ni-B nano-clusters were investigated [19].

The competitive method of fabrication of thermoabsorbing micro- and nano-sized magnetic particles (coated with biologically compatible material) was developed. Applications of high-dispersive magnetic particles could include information storage systems, biomedical fields, targeted delivery of drugs for cancer treatment, sensors, etc.

The conversion of glucose into fructose with the aim of production of high-fructose corn syrup is rather topical. Currently this conversion is considered as an intermediate step in a possible route from biomass to fuel and chemicals [30]. Here it is shown that a new catalyst that contains tin (Sn-Beta) is able to transform glucose into fructose in aqueous media with high activity and selectivity. The new catalyst can be used for multiple cycles.

The developed a local electroless method of deposition of amorphous and crystalline quantum dots, nanocrystals on high-dispersive powder like nanoparticles. The method provides both low and high degree of covering of nanoparticle surfaces. The high-dispersive parti-

cles with low surface covering with nanocrystals are characterized by high catalytic activity.

We present some investigation results on the ductility of Ni-P coatings. The ductility was studied with the help of the tester designed by the author [1, 6, 23].

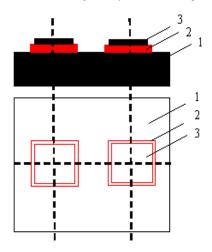


Fig. 1 – Two-layer photomask with metallized by the electroless method masking elements: 1 – glass substrate; 2 – selective semitransparent Si layer; 3 - opaque masking layer of Ni-P alloy

As compared to the scale of NILK (a ductility tester), the proposed tester has some advantages:

- 1. High accuracy, that allows to reveal the difference in the ductility, which cannot be detected using the NILK scale.
- 2. Convenient operation due to the use of lens and mechanical bending of the sample. Small dimensions, a simple design and easy maintenance allow to operate the tester both in lab and industry. (Fig. 2).

For expanding the sphere of application of the method of electroless nickel deposition, the investigation of physical-chemical properties of Ni-P alloy coatings deposited on various materials is of primary importance [2, 25-33].

Physical and chemical properties represent an important index of quality of metallic, varnished and painted coatings. Elastic and ductile properties of metallic coatings are some of basic physical-chemical characteristics determining the quality of coatings. For the items subjected to deformation, the value of coating ductility is especially important.

The principle of operation of the tester is based on the detection of cracks formed in the coating because of sample bending.

The sample with the deposited coating is placed between Λ -shaped base 1(Fig. 2) and two pressing rollers 2, which are of an eccentric shape in the cross-section. Before bending, pointers 3 are in a horizontal line with the sample and point to zero on scale 4. This position of the pointers is maintained because the spring presses the pointers to stop arresters. The scale is graduated from both sides from 0 to 65° and shows the maximum bending angle of 130°. When flywheel 5 rotates counterclockwise, the link with pressing rollers goes down. As a result, the pressing rollers bend the sample symmetrically in relation to the base center, and the pointers move along the scale.

The pressing rollers should be lowered until there appear cracks on the bended sample with the coating under investigation. The cracks are observed through lens 6. The bending angle of sample at the moment of initiation of cracks on the coating is taken as a measure of ductility. The bending angle is determined by indications of two pointers.

Besides the Λ -shape base, the ductility tester has readily replaceable bases (D) with curvatures of different radii, which allows us to vary testing conditions. For this purpose, the pressing rollers are fitted on eccentrically. By swinging the rollers, we can change the distance between them and to bend the samples on the bases with curvatures of different radii. So the pressing rollers can approach the vertical axis or move away from it. This allows us to establish the equality between L and sum of values D plus doubled thickness of the sample, where L is the distance between the pressing rollers; D is the diameter of the base used (Fig. 2). When cylindrical bases are used, the diameter of the base curvature, at bending around which there appear cracks on the sample, is taken as the measure of ductility.

Due to the design of the tester, we can watch the development of cracks in the process of sample deformation. The tester allows determining a relative value of the ductility. The values of the bending angle the sample until occurrence of cracks on the coating can be

different when the substrates are made of different materials and the samples are of different thickness. Though, when there are tested the coatings deposited on the substrate of the same origin and thickness, the tester gives rather correlated results.

The developed ductility tester by bending automatically makes possible:

- 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 (to photograph) 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 (merging of cracks).
- 3) To observe in-situ the cracks initiation, their growth and propagation rate at different rates of specimen deformation (bending).
- 4) The suggested ductility tester enables us to determine in-situ the ductility at different temperatures, i.e. in-situ investigation of temperature dependence of ductility. The working drawings of the tester can be presented. The above-mentioned peculiarities of the suggested device for determination of ductility by bending automatically can help to overcome several cracking problems and particularly some problems of micromechanics as well as flip-chip technology.

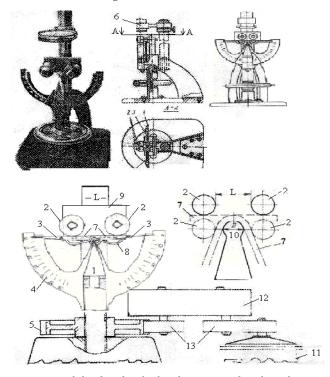


Fig. 2. – The new device for determination of the ductility by bending: 1 – wedge-shaped support; 2 – pressure shafts; 3 – arrows showing the bending of the specimen; 4 – scale calibrated in degrees; 5 – flywheel by rotating of which the lowering of the pressure shafts and bending of the specimen are provided from the opposite sides of the wedge-shaped support; 6 – microscope; 7 – the specimen under testing; 8 – spring; 9 – rod for pressure shafts; 10 – support of spherical shape; 11 – electromotor; 12 – gear box; 13 – gears

2. CONCLUSION

1. A method of production and a new design of defectfree two-layer (Si-Ni) photomasks with selectively semitransparent edges of the Si masking elements in the lower layer of the pattern based on single conventional optical UV photolithography is proposed. This photomask has a number of advantages over the existing ones: a) much less porosity; higher optical density; less thickness and higher wear resistance of the masking elements and b) selective semitransparence of the masking elements, which simplifies and enhances the alignment precision. These photomasks were widely introduced in the microelectronic industry with a large economic effect.

2. The proposed patentable nanomethods for the first time allow one to produce nano-sized adjacent elements of different thickness made of various materials (particularly of Si) by single optical UV photolithography.

REFERENCES

- 1. T.N. Khoperia, Electroless Nickel Plating of Non-metallic Materials (Moscow: Metallurgia: 1982).
- T. Khoperia, Proceedings of the 10th World Congress of Metal Finishing (Kyoto: Interfinish' 80, 147, 1980).
- T. Khoperia, T. Tabatadze, T. Zedginidze, Electrochim. Acta 42, 3049 (1997).
- 4. T. Khoperia, Microelec. Eng. 69, 384 (2003).
- T. Khoperia, T. Tabatadze, T. Zedginidze Proceedings of the International Conference of Micro Materials. (Berlin, 818, 1997).
- T. Khoperia, Microelec. Eng. 69, 391 (2003).
- T. Khoperia, N. Khoperia, International Publication number WO 106903, European Patent Application No. 09713937.2; Georgian Patent P 4788 (2009).
- 8. T. Khoperia, Electroless Deposition of Metals and Alloys for New Challenges in Nanotechnologies, Electronics and Photocatalysis (Monograph has been prepared for publication in English)
- K. Gorbunova, A. Nikiforova, G. Sadakov, V. Moiseev, M. Ivanov, *Physical-Chemical Bases of the Process of Electroless Cobalt Plating* (Moscow: Nauka: 1974).
- G. Gavrilov, Chemical (Electroless) Nickel Plating (Portcullis Press Limited: UK: 1979).
- K. Petrov, Galvanizirune na Plastmasi (Sofia, Bulgaria: 1982).
- M. Shalkauskas, A. Vashkyalis, Electroless Metallization of Plastics (Chimia: Leningrad: 1977).
- G.O. Mallory, J.B. Hajdu, Electroless Plating: Fundamentals and Applications (AESFS: Orlando: 1990).
- W. Riedel, Electroless Nickel Plating (ASM International: Ohio: 1991).
- 15. A.S. Petrov, J.B. Talbot, J. Electrochem. Soc. 3, D92

3. A new device of small size for precision determination of ductility at different temperature by bending automatically was designed and introduced in industry.

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- (2009).
- 16. R.N. Duncan, J. Appl. Surface Finish. 1 No2, 133 (2006).
- 17. Sh. Yagi, T. Koyanagi, H. Nakanishi, T. Ichitsubo, E. Matsubara, *J. Electrochem. Soc.* **9**, D583 (2008).
- T. Khoperia, T. Zedginidze, G. Mamniashvili,
 A. Akhalkatsi, Bulletin Georg. Nat. Acad. Sci. 2 No4, 92 (2008)
- M. Nadareishvili, K. Kvavadze, G. Mamniashvili, T, Khoperia, T. Zedginidze, Cond-mat E-print arXiv: 0903.5104, (2009).
- T.N. Khoperia, T.I. Zedginidze, Nano Studies 2, 127 (2010).
- M. Yoshino, H. Aramaki, It. Matsuda, Y. Okinaka T. Electrochem. Solid-State Lett. 4, D19 (2009).
- T. Khoperia, T. Zedgenidze, T. Gegechkori, ECS Trans. 25 Is 24, 97 (2010).
- T. Khoperia, Proceedings of the International Conference Micro Materials (Berlin, 771, 2000).
- T.N. Khoperia, R.G. Kharati, J. Plating 59 No3, 232 (1972).
- T.N. Khoperia, The Electrochemical Society Proceedings Series (Pennington, USA: 2000, PV 2000-31, 182).
- T.N. Khoperia, The Electrochemical Society Proceedings Series (Pennington, USA: 2000, PV 99-33, 147).
- 27. T. Khoperia, N. Khoperia, ESC Trans. 35 No10, 1 (2011).
- T. Khoperia, T. Zedginidze, N. Khoperia, ESC Trans. 35 No.10, 17 (2011).
- 29. T. Khoperia, *ESC Trans.* **35** No28, 95 (2011).
- 30. K. Kupatadze, R. Gakhokidze, J. Kereselidze, M. Gvertsiteli, J. Biolog. Phys. Chem. 11 No2, 60 (2011).