

Competitive Nanotechnologies for Fabrication of Thin Films and Powderlike Nanomaterials

T. N. Khoperia^{1,2,*}, T.I. Zedginidze^{2,†}

¹ Georgian Technical University, 77 Kostava Str., 0175 Tbilisi, Georgia

² E. Andronikashvili Institute of Physics at Iv. Javakhishvili Tbilisi State University,
6 Tamarashvili Srt., 0177 Tbilisi, Georgia

(Received 18 May 2012; revised manuscript received 14 June; published online 17 August 2012)

The present paper contains new data on the nanotechnologies for fabrication of fine-grained powderlike particles, films, bulk materials, nanocomposites, nanochips and devices for microelectronics, nanoelectronics, photonics and photocatalysis. The technology providing the replacement of precious metals by nonprecious ones and the exclusion of the use of toxic substances is presented. The developed methods of metallization of various materials have been widely used at the enterprises of the NIS for production of quartz resonators and filters, monolithic piezoquartz filters, photomasks, piezoceramic devices for hydroacoustics and delay lines of colour TV sets (several hundreds million devices were produced), casings of integrated circuits and semiconducting devices, ceramic microplates, precise microwire and film resistors, capacitors, catalysts, etc.

Keywords: Quartz resonators, Nanotechnology, Photomask, Electroless deposition.

PACS numbers: 81.07. – b, 81.15.Pq

1. RESULTS AND DISCUSSION

As a result of usage of the developed technology, Au, Ag and Pd were adequately replaced with nonprecious metal alloys, the time for production of piezoquartz and piezoceramic devices was reduced by a factor of 4 (in the case of fabrication of piezoquartz devices) and by a factor of 20 in the case of fabrication of piezoceramic devices.

A method of electroless nickel deposition on polished quartz, glass and other nonmetallic polished materials was developed [1-6] The optimal conditions of metallization were established. This technology for the first time provided high adhesion of Ni deposited by the electroless method to polished nonmetallic substrates and high ductility, deposition of thick films on polished piezoquartz being the most important for obtaining the monolithic quartz filters, in which the effect of energy capturing is necessary.

The 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 [1-20]: 1. The frequency stability of piezoquartz devices increased 1.8 times (the change in the piezoelectric resonator frequency decreased from $15 \cdot 10^{-6}$ for the silvered piezoquartz element to $8 \cdot 10^{-6}$ for the nickel-coated one for the first year of operation). 2. The absolute value of dynamic resistance of piezoquartz resonators decreased by 30%, and the resistance scattering decreased by about 40-50 % as compared to the resonators with silver-plated piezoelements. 3. Good quality and long-term stability of piezoquartz devices increased. 4. Reduction of dynamic capacity of piezoquartz devices provides better conditions for the formation of radio circuits. Owing to the abovementioned improvements, the process of radio circuit optimization was simplified, and narrower-band quartz resonators

were obtained. 5. Amplitude-frequency characteristics (spectral characteristics) were improved. 6. Labor intensity and energy consumption decreased sharply, hazardous chemicals and expensive materials being excluded. 7. The output of final products increased. 8. High adhesion reliability (2 times higher than that of silver films deposited by vacuum sputtering). 9. High mechanical reliability of resonators with piezoelements manufactured by the proposed methods. 10. The time of the metallization process of piezoquartz reduced by a factor of 4. 11. The production volume per square meter of the production increased 8 times as compared to metallization by fusing the silver paste. 12. The articles metallized by this method are blanching by means of acid-free fluxes with lead-free solders by the group method and can be subjected to thermocompression and microwelding.

The proposed patentable nanomethod is 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 [4, 7, 13, 15-17, 20]. The proposed method allows us to eliminate surface treatment by e-beam. It can save about \$4 000 000 (the price of e-beam exposure equipment). It also eliminates the application of X-ray masks with gold masking elements [7, 20].

At adding HCl (1 milliliter of concentrated acid per gram of $\text{PdCl}_2 \cdot 2\text{H}_2\text{O}$), chloropalladic acid is formed according to the reaction:



which affects favorably the activation process.

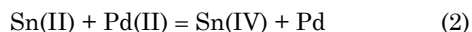
The mechanism of sensitization and activation was established, involving the concept of an equilibrium shift towards formation of complex palladium anions and predominance of the number of palladium ions

* teimurazkhopera@yahoo.com

† tinikozedginidze@yahoo.com

over tin ions on the surface.

It was established that part of palladium ions were not reduced by sensitization-activation:



can be partially reduced at subsequent interaction with hypophosphite in the solution of electroless deposition according to the reaction (3)



The investigation results showed for the first time that, when the aqueous-alcoholic solution was used as a solvent for tin chloride at the sensitization, at subsequent activation the amount of adsorbed palladium ions increased as compared with the application of the aqueous solvent for tin chloride. This could be referred to the fact that the addition of the organic compound to water changes the solvent configuration and the solvation degree of dissolved substances. Under these conditions, dissolution 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 possibility of obtaining the nanometer-scale pore-free films can be explained by the 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 after using a water-spirit solvent for sensitization could be explained on the basis of the Debye-Hückel theory. The relation between the ionic-activity coefficient (γ) and the ionic strength (I) is expressed by the Debye-Hückel equation:

$$\lg \gamma_i = -Az_i^2 \sqrt{I} \quad (4)$$

The use of the water-spirit solvent for the sensitization solution reduces the total number of ion charges (Z_i^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 a decrease in the force of attraction between the ions and the solvent, a decrease in the interaction between the ion and the dipole and an increase in the ionic-activity coefficient.

A method of production and a new design of defect-free two-layer (Si-Ni) photomasks with selectively semitransparent (semitransparent 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 based on single conventional optical UV photolithography is proposed [1,2,20].

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 semitransparency 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.

The competitive electroless method of fabrication of thermo-absorbing micro- and nano-sized magnetic particles was developed [1-3, 8-11, 15-18, 20]. Applications of high-dispersive magnetic particles could include information storage systems, biomedical fields, targeted delivery of drugs for cancer treatment, sensors, etc. In the magnetic field with specific frequency, the magnetic nanoparticles can absorb energy. As a result, an increase in the local temperature around the high-dispersive powder-like particles takes place. This effect could be applied to selective destruction of cancer tumors at 42°C by means of irradiation (their selective heating) with infrared light or with an alternating magnetic field, while leaving nearby tissues unharmed.

The possibility of electroless deposition of metals on nonmetallic, high-dispersive dielectric and semiconductor particles without their preliminarily activation by palladium chloride was developed.

By means of selective local electroless deposition of nanocrystals having specified properties on high-dispersive powder-like semiconductor photocatalysts, many problems of solar energy applications and photocatalytic splitting of water can be overcome or mitigated: I. Recombination of the photoexcited electrons and holes. II. Simultaneous proceeding of oxidation and reduction reactions at the same sites of photoelectrodes. III. The possibility of using the low-energetic visible-light irradiation. IV. Low quantum efficiency of energy conversion. V. Difficulty in deposition of nanosized clusters on nano-sized particles [18,20].

The following methods are used for overcoming the problems in this field [8, 20]:

- 1) Electroless deposition of nanoclusters with specified properties on semiconductor photocatalysts.
- 2) Reduction in the recombination of photoexcited electrons and holes by means of nanotraps.
- 3) Separation of the active centers of reduction and oxidation reactions.
- 4) Changes in the solvent structure and the increase in the ionic-activity coefficient.

The developed a local electroless method of deposition of amorphous and crystalline quantum dots, nanocrystals on powder like nanoparticles [20]. The method provides both low and high degree of covering of nanoparticle surfaces. The high-dispersive particles with low surface covering with nanocrystals are characterized by high catalytic activity.

It was established for the first time that the irradiation with γ -rays increased sharply the light absorption ability of semiconductor powders [9, 10, 20].

It was demonstrated that the selection of optimal sizes of powder particles could also enhance the optical absorption over the specified wavelength range.

By using purposefully the abovementioned factors, it is possible to shift the optical absorption spectra of high-dispersion $\text{Ni}_2\text{B/Ti}_2\text{O}_2$ (anatase) powders to the visible light region, i.e. to the wavelength range of 400-800 nm. This allows bringing the optical properties of Ni-

B/TiO₂ powders closer to the requirements of photocatalytic reaction, which will promote the production of hydrogen and oxygen from water by using the light energy, the conversion of light energy into electric power, the destruction of undesirable bacteria, cancer treatment etc.

The photocatalysts having the peak of optical absorption spectra 3 times higher than that of ordinary TiO₂ photocatalysts (St-01 and P-25) were obtained [18, 20].

Monograph *Electroless Deposition of Metals and Alloys for New Challenges in Nanotechnology, Electronics and Photocatalysis* has been prepared for publishing (in English). The research and development results presented in this monograph will facilitate the implementation of new methods of metallization. This monograph will promote reaching a new level of nanotechnology.

The above-mentioned monograph will be very much in demand of enterprises and research institutes. One of the aims of this monograph is to make the readers aware of wide possibilities of electroless deposition of metals and alloys for fabrication of competitive devices for micro- and nanoelectronics, piezoengineering, photocatalysis, composites and instrument-making.

This book may be used both as a textbook for engineering students and as a reference book for specialists in the field of electronics, instrument-making and photocatalysis.

The monograph is intended for the scientists and specialists in various fields of research and industry, for example in microelectronics, nanoelectronics, piezoengineering, photocatalysis, and composites fabrication. It could also be used as a handbook for students of chemical and electronics faculties.

REFERENCES

1. T. N. Kopperia, *Electroless Nickel Plating of Non-metallic Materials* (Moscow: Metallurgia: 1982).
2. T. Kopperia, In: *Proceedings of the 10th World Congress of Metal Finishing* (Kyoto: Interfinish' 80, 147, 1980).
3. T. Kopperia, T. Tabatadze, T. Zedginidze, *Electrochim. Acta* **42**, 3049 (1997).
4. T. Kopperia, *Microelec. Eng.* **69**, 384 (2003).
5. T. Kopperia, T. Tabatadze, T. Zedginidze, In: *Proceedings of the International Conference of Micro Materials*. (Berlin, 818, 1997).
6. T. Kopperia, *Microelec. Eng.* **69**, 391 (2003).
7. T. Kopperia, N. Kopperia, *A photomask and devices with nano-sized elements*, International Publication number WO 106903, European Patent Application No. 09713937.2; Georgian Patent P 4788 (2009).
8. T. Kopperia, T. Zedginidze, G. Mamniashvili, A. Akhalkatsi, *Bulletin Georg. Nat. Acad. Sci.* **2**, 92 (2008).
9. M. Nadareishvili, K. Kvavadze, G. Mamniashvili, T. Kopperia, T. Zedginidze, 2009, E-print arXiv: Cond-mat 0903.5104.
10. T. Kopperia, T. Zedginidze, T. Gegechkori, *ECS Trans.* **25**, 97 (2010).
11. T. Kopperia, In: *Proceedings of the International Conference Micro Materials* (Berlin, 771, 2000).
12. T.N. Kopperia, R.G. Kharati, *J. Plating* **59**, 232 (1972).
13. T.N. Kopperia, In: *The Electrochemical Society Proceedings Series* (Pennington, USA: 2000, PV 2000-31, 182).
14. T.N. Kopperia, In: *The Electrochemical Society Proceedings Series* (Pennington, USA: 2000, PV 99-33, 147).
15. T.N. Kopperia, T.I. Zedginidze, *Nano Studies* **2**, 127 (2010).
16. T. N. Kopperia, T. I. Zedginidze, T. G. Petriashvili, In: *Proceedings of the First International Conference on Nanochemistry and Nanotechnologies* (Tbilisi: Universal: 2011, 121).
17. T. Kopperia, N. Kopperia, *ESC Trans.* **35**, 1 (2011).
18. T. Kopperia, T. Zedginidze, N. Kopperia, *ESC Trans.* **35**, 17 (2011).
19. T. Kopperia, *ESC Trans.* **35**, 95 (2011).
20. G.I. Mamniashvili, T.O. Gegechkori, T.N. Kopperia, T.I. Zedgenidze, F.K. Akopov, A.M. Akhalkatsi, T.A. Gavasheli, *Spectra of the magnetic video-pulse influence on the nuclear spin echo in multidomain magnets in New Developments in Materials Science* (New York: Nova Science Publishers Inc.: 2011, 35).

2. CONCLUSION

1. A new method of production of precise piezoelectric quartz resonators and monolithic piezoquartz filters with electrodes made of electroless Ni-P and Ni-B alloys for spacecraft, hydroacoustics and communication devices was developed. Unique metallized piezosensors for gas analysis were developed.

2. As a result of usage of the developed technology, Au and Ag were adequately replaced with non-precious metal alloys. Electrical characteristics of quartz resonators with the deposited Ni-P coating are better than when gold and silver were used as electrode layers.

3. The devices manufactured using the developed methods were installed on artificial satellites, aircraft, used in the equipment for Navy fleet and special communication, installed on space systems "Luna", "Mars" and "Venus" etc.

4. The competitive method of fabrication of thermo-absorbing micro- and nano-sized magnetic particles was developed. Applications of high-dispersive magnetic particles could include information storage systems, biomedical fields, targeted delivery of drugs for cancer treatment, sensors, etc.

5. The proposed invention simplifies and makes cheaper the technology of fabrication of photomasks with nano-sized elements, nanodevices, nanowires and nanochips.

ACKNOWLEDGEMENTS

The author is grateful to the ISTC for their support.