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ELECTROCHEMICAL CODEPOSITION OF NANOSTRUCTURED MATERIALS FOR HIGHLY RELIABLE SYSTEMS

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Abstract. Problem of wear and friction of mechanically moving and load carrying elements of micro and nano dimensions is considered. The electrochemical plating technology of metals and alloys with inert hard nanoparticles in micromolds patterned in SU-8 negative photoresist is one of the approaches to solve the problem. The influence of process parameters on the mechanical properties of particle-reinforced coatings is described. The application of nanocomposite materials to improve the mechanical properties of micro and nano components in modern integrated systems is investigated. Codeposition model of nanocomcposite plating is developed. The outlook of these materials and technologies for advanced micro- and nanoelectromechanical systems of high reliability and their application is considered. A method for manufacturing of holographic films with high runability for roll-to-roll technology is described.

1. Introduction

Micro and nanosystems have become the integral part of human being. Such modern complex advanced systems and their production technologies require new types of material to be developed. These materials should be structured by shape and properties in nano and micro scale for fulfillment of requirements and further embedment into the systems.

One of the approaches to solve the problem of wear and friction of mechanically moving and load carrying elements of micro and nano dimensions is the use of nanocomposite materials; in particular, codeposited metal and alloy with inert hard nanoparticles by electrochemical or electroless deposition. The most exciting applications of plated nanostructured materials are microelectromechanical systems (MEMS), roll-to-roll and nanoimprint technologies.

2. Ultra-thick micromolds based on SU-8 photoresist

Currently one of the most prospective technologies for MEMS components are LIGA-like technologies. They consist of three main processing steps: lithography, electroplating and molding. We have used the SU-8 photoresists to obtain ultra-thick micromolds with parallel side walls. SU-8 is a high contrast, epoxy based negative photoresist developed and patented by IBM. It has been used extensively in LIGA-like technologies for MEMS applications due to its excellent thermal and chemical properties. Feature height is varied from tens of micrometers to several millimeters; high aspect ratios are on the order of 100:1.

We have used UV LIGA process, which utilizes an inexpensive ultraviolet light source to expose a SU-8 photoresist. As heating and transmittance are not an issue in optical masks, a simple chromium mask can be substituted for the technically sophisticated X-ray mask.

These reductions in complexity make UV LIGA much cheaper and more affordable than its X-ray counterpart [1]. Micromolds with thickness from 50 to 230 μm with the minimum feature size of 5 μm were obtained (Figs. 1, 2) on the different substrates (glass, ITO, pyroceramics, copper, etc.).

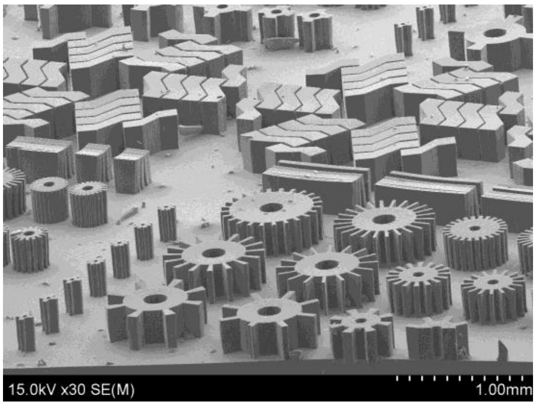


Fig. 1. SEM photo of 230 μm thick microstructures based on a SU-8 2150 photoresist.

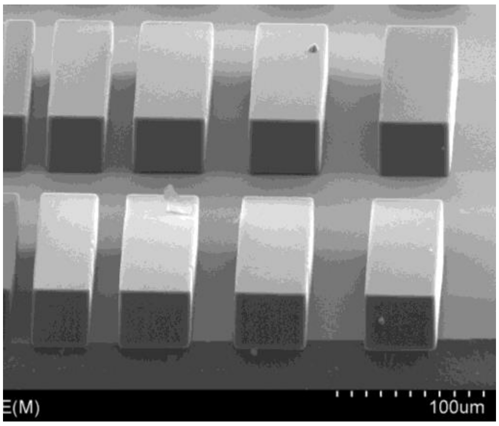
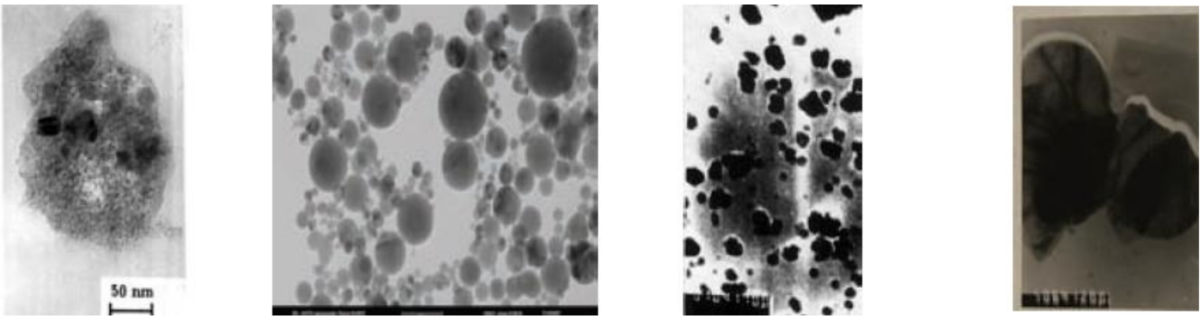


Fig. 2. SEM photo of 40 μm thick test micropattern with 5 μm minimum feature size based on a SU-8 3050 photoresist.

Photo Surface Processor PL16-110D was used to prepare the substrate surfaces by UV cleaning. The cleaning process consists of three main processing steps: generating ozone from atmospheric oxygen (with a wavelength of 184.9 nm), ozonolysis (formation of singlet oxygen at a wavelength of 253.7 nm), and decomposition of organic pollutants (strong oxidative activity of atomic oxygen allows it to react with contaminants materials to form reaction products such as water, carbon dioxide, etc., which are then simply evaporate). In the next the photoresist have been spin-coated over the substrate for uniform distribution. Then soft baking step has followed to evaporate remaining solvent in SU-8. A proper soft bake time is one of the most important control factors for a thick photoresist process. The photoresist have been exposed with UV light of i-line (365 nm) through a photomask. Lightningcure LC-L2 manufactured by Hamamatsu was used as a light source. Exposure energy was 250-300 mJ/cm^2. Further, the samples have had post exposure bake on a plate at 65-95°C. This leads local photochemical reactions to provide photoresist crosslinking. Cross-linked areas are insoluble during the next development stage, which removes the uncured resin.Subsequent electrochemical codeposition of nanocomposite materials into SU-8 micromolds allows producing free MEMS components of high thickness with a high aspect ratio [1].

3. Nanocomposite plating process

Nanocomposite coatings containing ultra-fine particles were electroplated. They included soft magnetic (NiFe, CoFeP, CoP) and hard magnetic (CoNiP, CoW, CoP) alloys as well as conductive matrixes of Cu and Ni. The thickness of the investigated deposits was up to 200 μm. Concentration of ultra-fine particles was varied from 0 to 10 $g \cdot dm^{-3}$ (dry substance). Diamond, alumina and aluminum monohydrate ultra-fine particles and boron nitride microparticles were used (Fig. 3). Average size of nanodiamond particles was 7 nm, alumina – 47 nm, aluminum monohydrate – 20 nm and boron nitride – 1 μm. Codeposition process was carried out in the electrolytic cell of flow type (Fig. 4) [2].



a) *b)* *c)* *d)*

Fig. 3. Inert particles used for codeposition: a) nanodiamond, b) alumina, c) boron nitride.

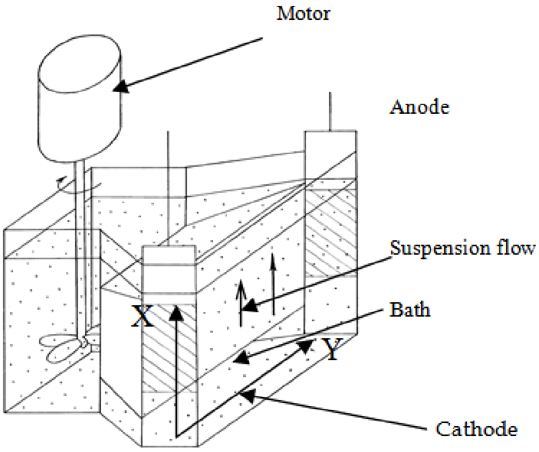


Fig. 4. Electrolytic cell for codeposition process.

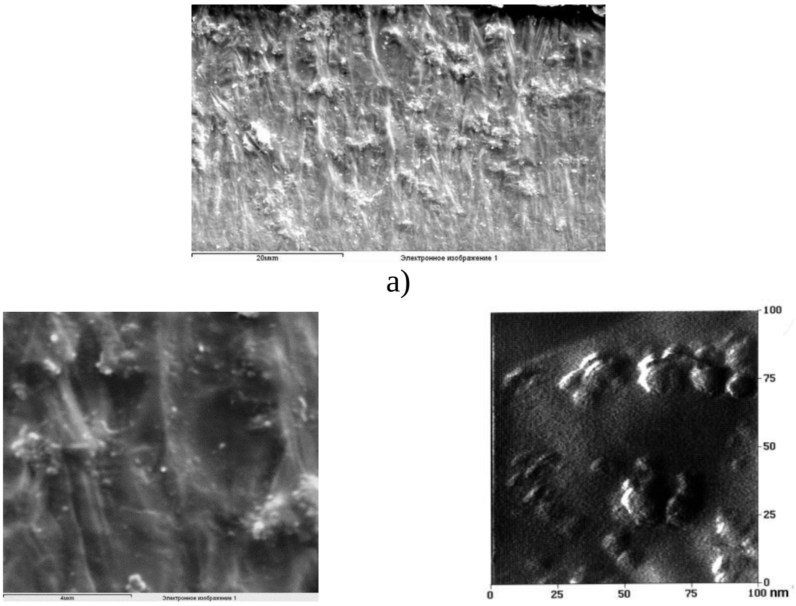
The amount of codeposited particles was determined both by integral Coulometric analysis on express analyser AH-7529 (USSR) and by local Auger spectroscopy (PHI-660 Perkin Elmer Corp., USA). The Vickers microhardness of coatings was measured at a load of 0.5 N with MICROMET-II (Buehler-Met, CH). The structure of the deposits was explored by TEM (EM-125, USSR). The coefficient of friction and the wear were evaluated by FRETTING II test machine (KU Leuven, BE). Wear volumes were estimated by RM600 laser profilometry (Rodenstok, D) after 100,000 fretting cycles.

4. Codeposition model of nanocomposite plating

During the electrolytic codeposition, the suspended inert particles interact with the surface of a growing film due to hydrodynamic, molecular and electrostatic forces [3]. This complex process results in the formation of composite coatings. Based on the experimental data [4], a qualitative codeposition model of the composite coatings with the ultra-fine particles can be suggested taking into account the peculiarities of the ultra-fine particles behavior. The model worked out is based on the assumption that the codeposition of ultra-fine particles proceeds through the following stages:

1. Coagulation of ultra-fine particles in plating solution;
2. Formation of quasi-stable aggregates and therefore change of system dispersion constitution;
3. Transport of the aggregates to the cathode surface by convection, migration and diffusion;
4. Disintegration of the aggregates in the near-cathode surface;
5. Weak adsorption of ultra-fine particles and aggregate fragments onto the cathode surface;
6. Strong adsorption of dispersion fraction (embedment).

Behavior of dispersed systems is described by DLVO theory. Stability or coagulation rate of suspensions depends on sign and magnitude of overall potential energy of interaction between the particles. Structural investigations confirm proposed model of heterogeneous nanocomposite coating formation. Cross-sections show that ultra-fine particles are effectively incorporated into the meal matrix (Fig. 5). These nanoparticles are distributed in the matrix volume uniformly. Small fragments of aggregates and separate nanoparticles form heterogeneous structure of a nanocomposite.



a)

b) c)

Fig. 5. SEM cross sectional images of Ni-Al_2O_3 nanocomposite film (a, b), AFM surface image of Ni-nanodiamond (c).

5. Nanocomposites for highly reliable applications

Micro and nanosystems are the completed devices that combine into one sensor, electronic, and mechanical parts. Mechanical interaction between nano-, micro-, and macro world is the limiting factor for such a complex system. Three dimensional moveable structures should be integrated in micro and nanosystems from design and technology perspective. Moreover, in general, reliability of the systems is determined by the reliability of a mechanical part.

Friction, wear and corrosion are the key problems for MEMS with real mechanically moveable elements. Codeposition processes allow getting nanocomposite elements with high operate reliability: wear resistance increased in 2-2.5 times, microhardness increased twice, coefficient of friction and corrosion current were reduced factor 1.5 and 1.6 respectively. Developed technologies were tested on prototypes of the electromagnetic and pneumatic micromotors (Fig. 6).

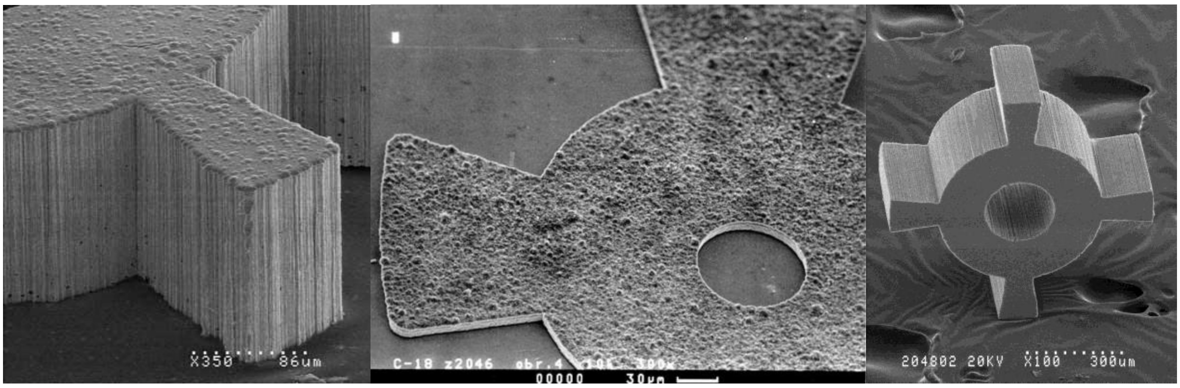
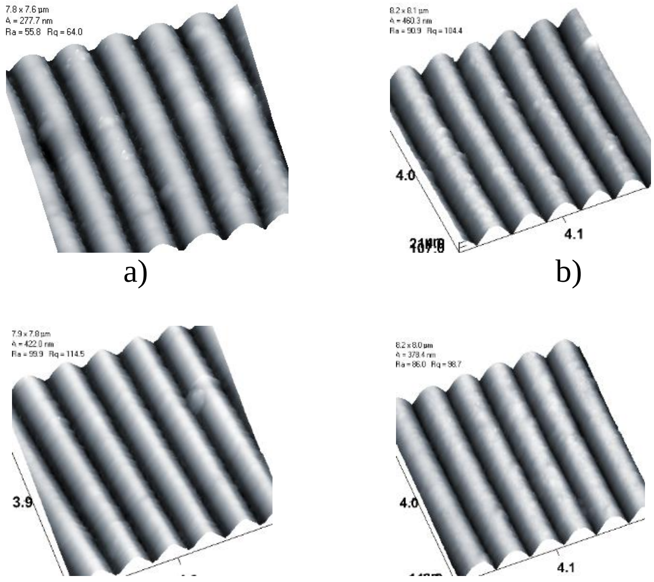


Fig. 6. Nanocomposite MEMS elements.

Codeposition of thin composite coatings to improve the tribological properties of the contacting surfaces during roll-to-roll processing and nanoimprint lithography (NIL) is one of the most effective ways to achieve higher performance characteristics of devices. Another way is fully composite electrochemical foils with the one-side matrix profile to enhance the runability of working holographic matrixes. Working nanocomposite nickel matrix was developed, as well as composite chromium protective coating deposited with nanodiamond particles on top of pure nickel matrix (Fig. 7). Test results show the increase of holographic matrixes runability on 60-400% with improved printed image quality.

Application of composite materials in NIL and roll-to-roll process is the appropriate solution to solve issues and improve reliability of templates and whole technology at all [5].



a) b)

c) d)

Fig. 7. AFM images of test nanocomposite samples of copies: a) pure Ni, b) Ni with Al_2O_3, c) Ni with diamond particles, d) Ni with aluminum monohydrate.

6. Conclusions

We have described positive consequences of introduction of the nanocomposites in the advanced technologies. Application of nanocomposites in MEMS, NEMS, NIL and roll-to-roll technologies makes it possible to improve quality and reliability of these processes and end products. Nanocomposite technology may be integrated in the systems technology by replacement of homogeneous pure materials by heterogeneous nanocomposites. This allows improving physical and mechanical properties, such as wear resistance, microhardness, corrosion resistance and friction coefficient. Nanocrystalline structure of nanocomposites enables to resolve sub-100 nm features in MEMS, NEMS, NIL, and other advanced applications.

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