Journal of Engineering Physics and Thermophysics, Vol. 80, No. 2, 2007

FORMATION OF COPPER LINES ON DIELECTRIC SUBSTRATES BY THE THERMOTENSOGRAPHY METHOD

B. A. Bezuglyi, M. M. Denisov,
and O. A. Tarasov

UDC 535.211,532.68

It has been shown that the thermotensographic process in the layer of a copper dibromide solution in ethanol followed by catalytic reduction of copper in a hydrogen current at 450°C can be used to obtain conducting lines. It has been established that in an open liquid layer lines of isolated small crystals of copper are formed, and in a layer of a closed volume lines of intergrown small crystals are formed due to the evaporation-convective intensification of the image. In the first case, the lines do not conduct electric current, and in the second one their specific resistance is $4 \cdot 10^3$ *times higher than in monolithic copper.*

Introduction. At the present time, to form a conducting pattern on printed circuit boards, one uses photolithography that was developed beginning in the 1950s [1, 2]. Despite the obvious advances,[1] it is still a multistage process that requires expensive equipment. If it is required to make nanoscale objects, e.g., integrated circuit elements, then photolithography has no alternative and its high cost is justified. However, costs of lines with a width of hundreds of micrometers are inexpedient. Photolithography also has other serious disadvantages:

1. It requires a whole number of substances (photoresists, solvents, acids), which increases production costs [4].

2. The expensive copper is used ineffectively. At the final stage of production of printed circuit boards, conductors and contact areas occupy more than 25–30% of the surface, and the remaining metal passes into etching solution [4]. In the case of a dielectric foiled on one side with a copper layer of thickness 50 μm, the metal loss is 0.45 kg from 1 m^2 of the surface. To reduce copper from the used-up etching solution, additional equipment and electric energy expenditures of about 2 kW·h per 1 kg of metal are required [5].

3. The photolithographic process is ecologically harmful. A large number of inorganic and organic substances, mainly oxides and hydroxides of metals, as well as chemical waste resulting from the removal of a photoresist get into waste waters [6]. Since the photoresist thickness (25–60 μm) is comparable to the thickness of the copper foil, the quantity of waste from its treatment is comparable to the quantity of copper etching waste [4]. In view of the current ecological requirements, complete reclamation of the above substances in purification works of enterprises is practically impossible [6]. And the operational cost of purification works per 1 m^2 of a printed circuit board approaches the total cost of 1 m^2 of the fabric-based laminate and reagents for its treatment [4].

The disadvantages of photolithography have stimulated the search for new techniques of printing conducting lines. Because of the existing tendency toward increasing the number of leads in integrated circuits (in 2010, production of microcircuits with more than 1200 leads is expected [4]), it will be essential to decrease the mesh width of printed-circuit boards, i.e., to decrease the line width. At the present time, the narrowest lines of width 50 μm are used to print integrated circuits in cases with ball grid arrays [7], and the alternative technology should provide printing of lines with a width of a few micrometers.

Cuk et al. [8] proposed a technological process in which lines from a solution of copper hexanoate in a volatile solvent are printed on a glass substrate by means of a capillary or a jet printer and transformed to copper ones by annealing. This process has a substantial disadvantage: upon evaporation of the solvent, the lines split under the action of the thermocapillary effect and become unsuitable for electronics.

---

[1] According to the development schedule approved by the semiconductor industry association, the design standards in 2008 and 2014 should be 0.07 and 0.35 μm, respectively [3].

Tyumen State University, 10 Semakov Str., Tyumen 625003, Russia; email: bezuglyi@utmn.ru. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 80, No. 2, pp. 186–192, March–April, 2007. Original article submitted November 11, 2005.

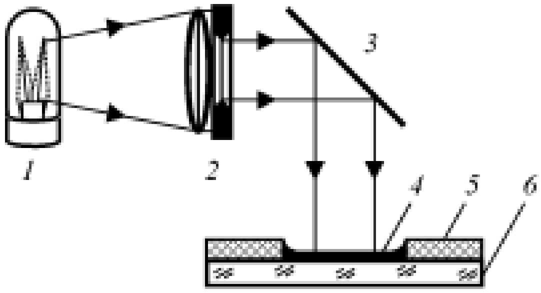

Fig. 1. Scheme of the facility for forming copper bromide lines in an open layer.

Lines were formed by imprinting a copper hexanoate film on a glass substrate by a silicon form (see [9]). The layer of the substance that remained between the lines was removed by etching in the forming-gas at 155°C. The material of the lines was transformed to copper or copper oxide by heating to 200°C in a vacuum chamber (1). Annealing in the forming-gas at 200°C completely reduced the copper. The advantage of the method of [9] is that it permits obtaining lines of width of the order of 1 μm, and its disadvantage is that the process is multistage and requires fabrication of printing plates by photolithography.

In [10], a method for fabricating multilayer printed circuit broads in which both the lines and the insulator are deposited by jet printing is described. The specimen of a 20-layer printed circuit board has lines of width 50 μm consisting of silver microparticles. This method has many advantages: exactly the required quantity of metal is used; no water pollution; no masks for photolithography are needed; it is easy to make multilayer printed circuit boards, since the interlayer insulator is deposited in the course of a continuous process. Unfortunately, only air-nonoxidizing noble metals can be used as a material of conductor particles.

In the present paper, we propose a radically new approach to the formation of conducting lines on dielectric substrates that is free of the above disadvantages and is based on thermotensography — the liquid-layer technique of forming images proposed and developed by B. A. Bezuglyi in the 1980s [11, 12]. Its essence is as follows. A layer of a solution of a tensoactive material (i.e., a material with whose increasing concentration the surface tension of the solution increases) in a volatile solvent is deposited on the substrate and a subject image is projected. Because of the heating, on illuminated parts of the layer the evaporation rate of the solution increases, which leads to an increase in the concentration of the tensoactive material and, as a consequence, to the appearance of shear stresses directed to the center of these parts. They cause the appearance of liquid flows that carry the tensoactive substance from the dark parts to the lighted ones and form a negative image of the subject. Upon complete evaporation of the solution the image becomes fixed.

Experimental Results and Discussion. ***Open liquid layer.*** The facility for forming lines from a copper compound is schematically represented in Fig. 1. The radiation from the incandescent lamp 1 with an M-shaped spiral of power 100 W was collected by a Helios-44-M lens 2 and directed by a mirror 3 onto the liquid layer 4 on a glass plate 6 of thickness 1.3 mm. The layer was confined within an area of 2×2 cm^2 by strips of Scotch tape 5. The lamp–lens and lens–layer distances were equal and measured 11 cm. As a liquid, we used a copper dibromide solution in ethanol with a concentration of 200 g/liter. Copper dibromide was chosen due to its high solubility in ethanol and the possibility of reducing it to copper in a hydrogen atmosphere.[2]

Lines were formed in the following way. A portion of the solution of volume 5 μliter was micropipetted onto the area. Because of the wetting of the sides, part of the solution formed a meniscus, but at the center of the area the layer was practically uniform in thickness (about 50 μm) (Fig. 2a). The lamp, the image of whose spiral was focused on the layer, was switched on (Fig. 1). At the initial instant of time, under the action of the thermocapillary mechanism of flow the liquid flew out of the irradiated portions (Fig. 2b). When the temperature of these portions became

---

[2] It should be noted that for this purpose amorphous copper-organic compounds are the most suitable. Unfortunately, attempts to synthesize these compounds were unsuccessful. Therefore, the investigations were carried out with a crystalline inorganic matter, which had a negative effect on the electrical and mechanical properties of copper lines.

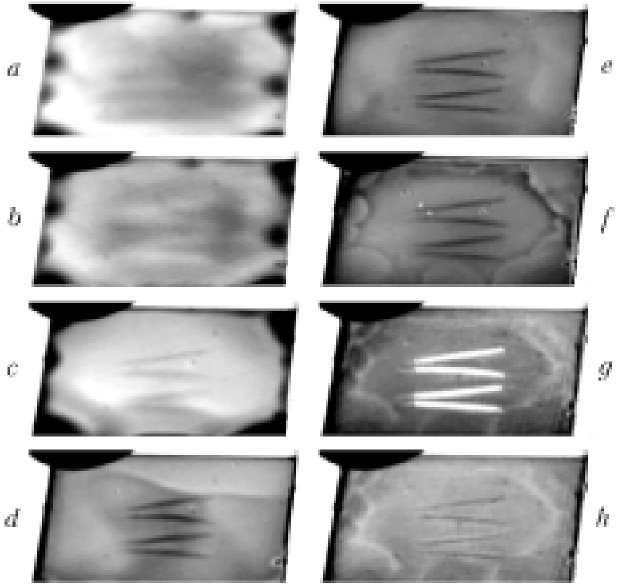

Fig. 2. Video frames of forming lines from $CuBr_2$ solution in ethanol. Camera angle of 25°. Area dimensions of 2×2 cm^2.

sufficient for intensive evaporation of the solvent, the concentration-capillary mechanism was initiated and the direction of the liquid flow was reversed. The liquid streamed into the irradiated regions, forming lines (Fig. 2c). Because of the inhomogeneous evaporation of the liquid, spontaneous roller-like flows along the full length of the layer arose (Fig. 2d). The passage of a liquid roller led to an increase in the thickness of the layer and lines (Fig. 2e). Upon complete evaporation of ethanol, the water that was initially present in the layer remained in it. The lines formed were partially blurred under the action of the thermocapillary mechanism, and at the edge of the drying-out layer a cloud-like picture appeared (Fig. 2f). Upon complete evaporation of water, a negative image of the spiral from small $CuBr_2$ crystals diffusing the lamp light and a dense background remained on the substrate (Fig. 2g). The same lines in the daylight are shown in Figs. 2h and 3a. Observing the obtained images with a microscope, we have found that the background and the lines consist of small $CuBr_2$ crystals, the concentration of crystals in a line being twice as high (Fig. 3b). The sizes of the small crystals of the background and the lines were equal ($\sim$10 μm), but in the former case they were separated from one another and in the latter case they formed separate chains of length 50–200 μm. Upon reduction, such chains are not conducting, which was confirmed subsequently.

Changes in the concentration of the solution, in its layer thickness, and in the lamp power do not lead to the formation of a continuous structure of the lines due to the fact that the major portion of $CuBr_2$ upon drying of the layer forms the background, and only a small portion forms a line in the time of solvent evaporation.

Liquid layer in a closed volume. To obtain continuous lines and eliminate the background, we used the effect of evaporation-convective intensification of the thermotensographic image discovered in 1983 [13]. It was first used to concentrate into a light beam impurities from solvents used for cleaning electronic devices [14]. Since, under such concentration, a single impurity drop grew, from the point of view of thermotensography intensification of one point of the image took place. So far, the possibility of intensifying extended images of the type of the lamp spiral has not been explored.

The intensification effect is observed when the liquid layer is inside a closed volume (Fig. 4a). Under nonuniform illumination of the layer, the solvent evaporates from the heating regions and condenses on cooler portions of the substrate. Since the surface tension of the pure solvent is smaller than that of its solution with a tensoactive substrate (in the given case, the tensoactive substances are water and $CuBr_2$), flows directed from the dark portions of the layer to the illuminated ones arise. These flows are stronger[3] than for the open layer, since the surface-tension drop between the portions with the tensoactive substance solution and with the condensing pure solvent is much higher than the drop

---

[3] At the same evaporation rate.

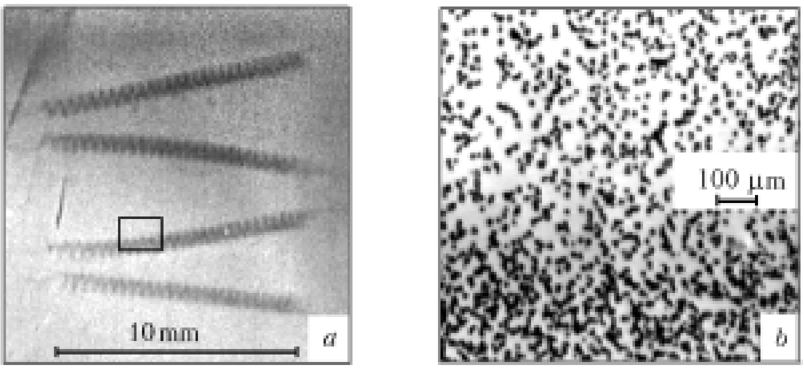

Fig. 3. Negative image of the incandescent lamp spiral — $CuBr_2$ lines (a) and enlarged (×12) image of the singled-out region (b). A dense background is characteristic of the image obtained without evaporation-convective intensifica-

between the portions of the solution with a different concentration of the tensoactive substance. After some time, as a result of the solvent circulation, practically the whole of the active substance is carried to the lighted portions. Thus, the evaporation-convective intensification makes it possible to simultaneously increase the thickness of the lines and eliminate the background surrounding them.

To perform experiments with evaporation-convective intensification, we used the same facility (see Fig. 1), but the liquid layer was situated not on an open glass plate but on the flat bottom of a quartz cell (internal diameter 50 mm, height 30 mm, neck diameter 10 mm). The solution was micropipetted into the cell and its neck was corked. For the solvent vapors to condense only on the bottom of the cell, it was cooled by an air flow, and the upper wall of the cell was heated by the radiation from a lamp of power 20 W. Since, in the closed cell, the vapors of ethanol are more saturated, its evaporation rate decreases and the concentration-convective effect noticeably weakens compared to the open layer. To maintain the same mass-transfer intensity, the lamp inducing this effect was replaced by a more powerful lamp (150 W) with an erect spiral. The layer thickness optimum for forming lines turned out to be smaller (30 μm) than for the open layer, since in a thin layer it is easier to provide the same concentration drop of the surface tension than in a thick one.

Once inside the sealed cell lines have been formed, to fix them, one has to remove the solvent. We have investigated four regimes of solvent evaporation with the inducing lamp on:

1. In the *passive* regime, the solvent diffuses through the open neck of the cell. Because of the long duration of the process (about an hour), other regimes were proposed.

2. In the *thermal* regime, the whole of the cell is heated by the light from an additional lamp, which reduces the evaporation time by a factor of 2–3.

3. In the *active* regime, a weak air stream is fed into the cell neck or the solvent vapors are evacuated from the cell volume. This regime also reduces the evaporation time by several times but requires uniform air feed or vapor evacuation so as not to excite in the layer concentration-capillary flows destroying the lines.

4. The *combined* regime combines the thermal and active regimes, which reduces the process time to 10 min. Therefore, the experiments were performed in this regime.

The investigations have shown that in printing lines, it is essential to control not only the evaporation rate of the solvent but also the power of the inducing lamp. As a line is formed, its optical density increases. Therefore, there is also an increase in its temperature and hence in the evaporation rate of the solvent, increasing the concentration drop of the surface tension. Here negative feedback takes place, due to which the concentration-capillary effect continuously intensifies and the supply of liquid into the lines increases. This process proceeds as long as a wetting film exists on the substrate. At some instant of time, the volume of evaporated solvent begins to exceed the volume of the solvent that arrives through this film, which causes disruption of the film and drying of the lines. The time interval between the switchingon of the lamp and the disruption of the film is inversely proportional to the value of the luminous power. By giving a different lamp power, one can vary the thickness of the lines obtained.

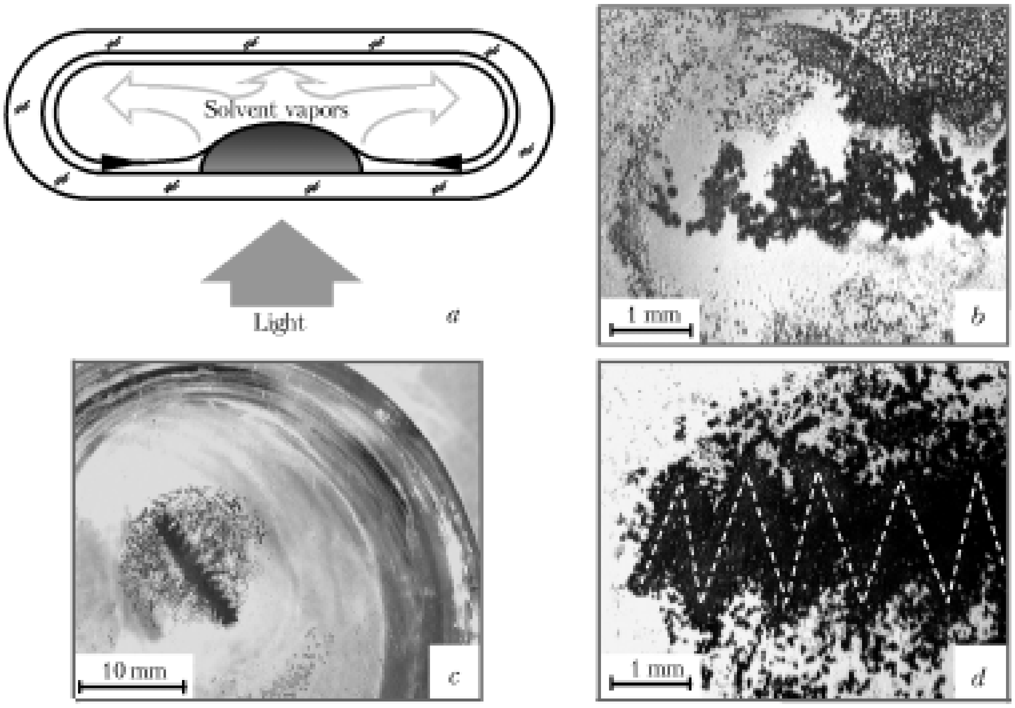

Fig. 4. Evaporation-convective intensification with the example of a Gaussian beam (a); $CuBr_2$ lines printed with evaporation-convective intensification on the quartz cell bottom at a constant power of the inducing lamp (b) and with its stepwise lowering (c, d). The broken dashed line shows the profile of the lamp spiral.

Despite its simplicity, the method of forming lines with a constant power of the light source has one drawback. Disruption of the wetting film occurs before the whole of the copper dibromide passes from the volume into the line. Therefore, upon complete evaporation of the solvent, a marked background from small $CuBr_2$ crystals remains around the lines (Fig. 4b), and it should be stripped after the lines reduce to copper. Part of the solution that has left the heating region upon the thermocapillary disruption of the wetting film forms a clearly marked arc. If the formation time of lines is short, then even the evaporation-convective intensification does not permit obtaining their continuous structure (Fig. 4b).

A better result is obtained by controlling the light-source power in the process of thinning of the wetting film to prevent its premature disruption. In this case, practically the whole of the copper compound goes into the lines (Fig. 4c), and their thickness is determined by its initial concentration in the solution, the layer thickness, and the substrate area occupied by the lines. In the final experiments, we used stepwise lowering of the beam power in both forming lines and in the subsequent combined regime of solvent evaporation.

The lines obtained under the conditions of evaporation-convective intensification in combination with stepwise lowering of the beam power consisted of intergrown small $CuBr_2$ crystals and had a thickness of a few hundred micrometers (Fig. 4c and d). At a distance from the line the background is absent. The aggregation of small crystals near the line (Fig. 4c) appeared because of the thermocapillary spread of the part of the solution forming the line at the stage of water evaporation. Thermocapillary spread can be avoided by using a single-component volatile solvent instead of the two-component one (ethanol and water).

In order that the quartz cell not be destroyed by the reduction of lines, we made, instead of it, demountable cylindrical cells of diameter 40 mm and height 20 mm from two glass plates of thickness 1.3 mm and a plastic ring cemented together by an "Epoxy-titan" adhesive. The solution was poured into the demountable cell through the ring hole, which was then closed. Having formed a line, we opened the hole and evaporated the solvent using the com-

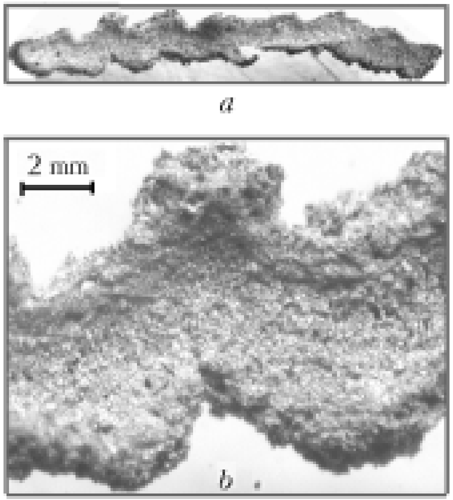

Fig. 5. Photograph of a line of length 12 mm upon reduction (a) and its enlarged (×6) portion (b).

bined regime. The cell bottom with the line was carefully separated from the plastic ring and placed into the facility for reduction.

Reduction of Lines. A glass substrate with the lines was placed into a quartz tube connected by a hose to a GV-4 hydrogen generator. When the tube was filled with hydrogen, the wire heater applied on it was switched on and the substrate temperature was increased to 450 ± 10^{o}C. The lines were reduced in a hydrogen current for three hours and then, without switching on the hydrogen generator, cooled to room temperature.

The lines obtained consisted of ~5-μm copper crystals adjoining one another (Fig. 5). The resistance of the lines was measured in the air as soon as they were removed from the tube. The specific resistance of their material was measured to be 6 mΩ·cm, which is $4 \cdot 10^{3}$ times higher than the specific resistance of monolithic copper [15]. The low conduction of the lines is due to the fact that the small copper crystals do not form a solid body but contact one another only by edges. The loose structure of the line is well seen in Fig. 5b. Indirect evidence of the weak contact of the copper crystals is the brittleness of the lines. They failed under a slight effort, e.g., under the pressure of the multimeter probe.

To obtain a more monolithic structure of the lines, they were reduced at 480^{o} — a temperature close to the melting temperature of copper dibromide (498^{o}C [16]). The thus-obtained lines were more rigid indeed (they feature some flexibility), but because of the sharp intensification of sublimation about one-half of the copper dibromide settled on the substrate surface and formed, upon reduction, a thin copper film. To use the lines obtained in practice, one will have to strip this film, which will lead to a further thinning of the lines. Thus, the method of reducing lines at the melting temperature of copper salt is unsuitable for practice because of the copper loss and the thinning of the lines.

To obtain a solid structure of lines, it is necessary to use amorphous copper-organic compounds rather than the crystalline inorganic compound that we used because of their absence. The best suited compound to this end is copper hexanoate which was used successfully by the authors of [8, 9]. Despite the fact that in these works the reduction of lines to copper ones led to a decrease in their size and granulation of the structure, the lines had a specific resistance of about 10 μΩ·cm, which is only 6.5 times higher than the tabular value for copper.

Conclusions. It has been established experimentally that thermotensography with evaporation-convective intensification can serve as the basis for a new technique of fabricating printed circuit boards. The proposed technique has many advantages. The process of printing lines consists of two stages — forming of lines from a copper compound and their reduction to copper ones as opposed to the multistage technique of [1]. The realization of the proposed method requires inexpensive equipment: an incandescent lamp, a condenser, a transparency with a negative image of lines, a lens, and a hydrogen generator. Practically the whole of the copper from the solution of its compound in an organic solvent is expended in forming lines, i.e., the process of printing lines is waste-free as opposed to the technique of [1], where 70–75% of the copper passes into the etching solution, from which it has to be reduced. The proposed technique is ecologically clean, since it requires no additional substances (photoresists, solvents, acids), which upon completion of the process turn to toxic liquid wastes. Another advantage of the technique is the fact that copper lines printed on smooth dielectric plates (e.g., glass) are easy to transfer onto flexible substrates (e.g., lavsan) by thermal stamping. In this manner, it is possible to fabricate the flexible printed circuit boards increasingly required by the electronics industry [17].

Due to the high resolution of thermotensography (over 600 lines/mm) [11–13], it seems possible to print lines of width less than 1 μm. To this end, instead of crystalline inorganic compounds it is necessary to use amorphous copper compounds. In this case, it may be expected that the lines will have a specific resistance close to the tabular value of copper. To improve this technique, experiments with copper-organic compounds are planned.

The authors wish to thank N. Yu. Tret'yakov (Chemical Department of the Tyumen State University) for helpful consultations on copper reduction and for supplying the facility for the investigations.

REFERENCES

1. V. P. Lavrishchev (Ed.), *Introduction to Photolithography* [in Russian], Énergiya, Moscow (1977).
2. F. P. Galetskii, Characterization of the present-day technologies of printed-circuit boards. http://www.fpgaletsky.ru/fpg/statji_g/ops_galt.htm.
3. A. Borzenko, EUV-lithography: At the limit of what is possible. http://www.computer-museum.ru/technlgy/euv.htm.
4. V. Khamaev and N. Samartsev, Ecologically clean technology of printed-circuit boards and large hybrid ISs. http://www.chipnews.ru/html.cgi/arhiv/99_07/stat_29.htm.
5. S. Blutshtein, Process of etching of printed-circuit boards and regeneration of the ELO-CHEM etching solution http://www.compitech.ru/html.cgi/arhiv/02_02/stat_124.htm.
6. Z. V. Koryakova, S. V. Kazimirchuk, and L. K. Nikerova, Technological process of complex reclamation of copper-containing etching solutions used in production of printed-circuit boards. http://www.rezonit.ru/pcb/articles/technology/05.
7. F. P. Galetskii, Printed-circuit boards with microtransitions. http://www.rezonit.ru/pcb/articles//technology/09.
8. T. Cuk, S. M. Troian, C. M. Hong, and S. Wagner, Using convective flow splitting for the direct printing of fine copper lines, *Appl. Phys. Lett.*, **77**, No. 13, 2063–2065 (2000).
9. C. M. Hong, X. Sun, S. Wagner, and S. Y. Chou, High resolution copper lines by direct imprinting, *Materials Development for Direct Write Technologies*, in: *Proc. Material Research Society Symp.*, **624**, 219–223 (2000).
10. *News Release*, Epson Inkjet Technology Used to Fabricate the World's First Ultra-Thin Multilayer Circuit Board, Tokyo, Japan, 2004. http://www.epson.co.jp/e/newsroom/news_2004_11_01.htm.
11. B. A. Bezuglyi, *Capillary Convection Controlled by the Thermal Action of Light and Its Application in Information Recording Techniques*, Candidate's Dissertation (Physics and Mathematics), Moscow (1983).
12. B. A. Bezuglyi and E. A. Galashin, Thermotensography — A New Imaging Technique, *Zh. Nauch. Prikl. Fotogr. Kinematogr.*, **27**, Issue 1, 69–71 (1982).
13. B. A. Bezuglyi, Image intensification in liquid films, *Zh. Tekh. Fiz.*, **53**, Issue 5, 927–929 (1983).
14. B. A. Bezuglyi, A. E. Golub, A. A. Efremov, V. Z. Krasil'shchik, D. P. Krindach, V. S. Maiorov, and M. S. Chupakhin, A method for determining the mass of a dissolved substance and a device for its implementation, USSR Inventor's Certificate No. 753270, *Byull. Izobr.*, No. 40 (1985).
15. I. S. Grigor'ev and E. Z. Mikhailov (Eds.), *Physical Quantities: Handbook* [in Russian], Énergoatomizdat, Moscow (1991).
16. *Chemist's Handbook* [in Russian], Vol. 5, Gos. Nauch.-Tekhn. Izd. Khim. Lit., Moscow–Leningrad (1968).
17. F. P. Galetskii, Purpose and properties of flexible and flexible-inflexible printed-circuit boards. http://www.rezonit.ru/pcb/articles/technology/10.